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Keggin-Al$_{13}$ Polycations: Influence of Synthesis and Intercalation Parameters on the Structural Properties of Al-Pillared Clays

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Abstract: Pillared clays are interesting materials with applications in catalysis and adsorption processes. To obtain these materials, several preparation procedures are necessary and must be optimized to tune the final properties of the resulting pillared clay. Therefore, this article reports the influence of synthesis parameters (temperature and concentration) of Keggin-Al$_{13}$ polycations and different intercalation times (0.5 up to 72 h) on the structural properties of Al-pillared clays. The natural clays are from Brazil, and they are composed mainly of montmorillonite. By XRD, N$_2$ sorption, XRF and ^{27}Al NMR results of the Al-PILCs, we verified that the pillaring solution could be prepared at room temperature with an aging time of 24 h. For the cation exchange process, a period of at least 2 h is necessary to ensure the formation of pillared materials. The concentration of the Keggin-Al$_{13}$ polycations was evaluated by using diluted pillaring solutions followed by applying re-pillaring procedures. After submitting the pillared clay to another pillaring process, the number of pillars in the interlamellar space increased; however, the micropore volume decreased concomitantly. Thus, by optimizing the synthesis conditions of the Keggin-Al$_{13}$ polycations, Al-PILCs could be obtained with good values of basal spacing and specific surface area.

Keywords: pillared clays; Al-PILC; Keggin-Al$_{13}$ polycations; synthesis parameters; temperature; intercalation time; pillar density

1. Introduction

Pillared interlayered clays (PILCs) are thermally stable porous materials obtained from the intercalation of inorganic polycations within the interlayer space of a natural clay. Typically, the clay mineral used is montmorillonite due to its high cation exchange capacity and swelling properties of the lamellae [1]. In general, a pillaring procedure is performed through the exchange of the hydrated cations, such as Na$^+$ and Ca^{2+}, present in the interlayer space of the clay mineral by large polycations, for example, Keggin-Al$_{13}$, which after calcination, act as pillars increasing the basal spacing and creating microporosity [2]. Due to the higher accessibility to the interlayer space, pillared clays can be applied in adsorption processes [3–5] and catalysis [6–8].

Keggin-Al$_{13}$ polycations ($[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$) are typically formed by base hydrolysis of Al^{3+} aqueous solutions (normally using NaOH and AlCl$_3$·6H$_2$O, respectively). In detail, as a general rule, the NaOH solution is added dropwise to the Al salt solution until a desired OH/Al ratio is reached [9]. However, other Al species can be formed depending on the pH solution [10]. Therefore, several synthesis parameters, such as OH/Al ratio, temperature, and time under stirring (aging), have been studied to improve the preparation of Keggin-Al$_{13}$ polycations to further use as a pillaring agent [10]. Additionally, the Keggin-

Al_{13} polycations can be mixed with other metals, such as Fe [11,12], Co [13] and Cu [14], to expand the applications of the resulting pillared clays.

To prepare a pillared clay, first, the pillaring solution is added to a diluted clay suspension, which after the cationic exchange, is vacuum filtered and thoroughly washed with distilled water. Afterward, the intercalated clay is dried and finally calcined to result in a pillared solid containing Al_2O_3 pillars increasing, besides from porosity and basal spacing, the acidity of the clay [15,16]. Nevertheless, the amount of liquids used in this traditional pillaring procedure is considerably high, hampering its industrial feasibility. Due to this, several studies have been conducted applying concentrated clay suspensions and pillaring solutions [12,17–22] to decrease the volume of liquids to scale up the pillaring procedure without compromising the properties of the PILCs (basal spacing and porosity). Other alternatives to improve the pillaring method are the utilization of microwaves [21,23] or even the reuse of the pillaring solution in sequential pillaring procedures [24].

The basal spacing of the resulting PILC depends on the nature of the pillaring agent, whereas the final porosity is a function of the number of pillars and the separation between them. Recently, Zhu et al. [25] reported a procedure using the Keggin-Al_{30} polycation as a pillaring agent to generate higher basal spacing and porosity in the resulting PILC. However, although the Al_{30} is considerably larger than the Al_{13}, the basal spacing calculated was similar for both PILCs, signing that the Al_{30} polycations accommodated horizontally within the clay layers. On the other hand, the porosity was greatly improved, probably due to the larger cation size and higher ion charge of Al_{30}.

The formation mechanism of Al_{13} and Al_{30} polycations has been recently reported by Wen et al. [26]. They highlighted that, with an OH/Al ratio = 2.4 and a final pH of 3.93, the Al_{13} formation is controlled by the temperature and aging process. If the synthesis of the pillaring agent is performed at room temperature, usually the solution is kept under stirring for six days [27]. When the temperature is increased up to 60 °C, an aging period of 24 h is sufficient to form Keggin-Al_{13} polycations [10,25]. Another critical parameter during the synthesis of the pillaring agent that affects the formation of Al species is the OH/Al molar ratio, which usually is in the range of 2.0–2.4 [10].

The basal spacing of a PILC pillared with Keggin-Al_{13} polycations is typically between 1.7–1.8 nm [6]. However, a straight comparison of basal spacing among PILCs reported in the literature can be hampered due to differences in the pristine clay (cationic exchange capacity, presence of impurities, among others).

Besides basal spacing, an increased porosity is another goal aimed with the pillaring process. In this sense, a lower quantity of pillars could lead to higher porosity, although an increased number of pillars could result in materials with greater thermal and mechanical stability [28]. Therefore, an optimum density of pillars should be used to achieve good textural properties and stability of the layered structure. Generally, a smectite clay with moderate cationic exchange capacity is preferred in pillaring procedures to ensure a proper balance between pillar density and porosity in the resulting PILC [10]. In addition, other strategies could be used to control the porosity of the pillared clays, such as re-pillaring procedures, by which a higher density of pillars could be inserted within the clay layers. However, to the best of our knowledge, such investigations have not been performed in the literature.

Considering the exposed above, in this work, we evaluated three key parameters to optimize the pillaring procedure: (i) the temperature of both dripping and aging steps during the preparation of the Keggin-Al_{13} polycations, (ii) the intercalation time through cationic exchange, and (iii) the pillar insertion within the clay layers by using diluted pillaring solutions, followed by re-pillaring procedures to control the porosity and density of pillars within clays.

2. Materials and Methods

2.1. Synthesis of the Pillaring Agent under Different Temperatures

The natural clay used in this study (CN-1) is from Campos Novos (PB, Brazil) and was kindly supplied by Centro de Tecnologia Mineral (CETEM). The chemical composition of the pristine clay is: 60.64% SiO_2, 20.76% Al_2O_3, 9.15% Fe_2O_3, 3.8% MgO, 1.8% Na_2O, 1.54% CaO, 1.24% TiO_2, 0.64% K_2O and 0.38% of others.

The pillaring agent was prepared through a slow dropwise addition of 500 mL (0.2 mol/L) of NaOH solution to 250 mL of a 0.2 mol/L $AlCl_3 \cdot H_2O$ solution under stirring at 60 °C. After completing the dropwise addition, the pillaring agent was kept under stirring at 60 °C for 24 h. Then, 3 g of CN-1 were stirred in 300 mL of distilled water for 2 h at ambient temperature to expand the lamellae. Subsequently, the pillaring agent was added to the clay suspension, and the mixture was maintained under stirring for 2 h at ambient temperature to allow the cationic exchange between the cations present in the interlayer space of the clay by the prepared Al_{13} polycations. Finally, the intercalated clay was vacuum filtered and washed thoroughly with distilled water until chloride tested free. The sample was dried at 60 °C for 24 h and subsequently calcined at 450 °C for 3 h. This pillaring procedure was labeled 60/60, i.e., the temperature was kept at 60 °C during the dropwise addition and at 60 °C during the aging stage (24 h under stirring).

Two other pillaring methodologies were applied: 60/25 and 25/25. In the former, the pillaring agent was kept at 60 °C during dropwise addition followed by aging at 25 °C. In procedure 25/25, the pillaring solution was prepared entirely at 25 °C. The subsequent pillaring procedures (clay suspension, cationic exchange, filtration, drying and calcination) were performed as explained above.

2.2. Evaluation of the Intercalation Time

Four pillaring experiments were performed using the pillaring solution 25/25 (explained above) differing in the intercalation times (cationic exchange procedure): 0.5, 1, 2 and 72 h. The remaining procedures were performed as described in the previous section and the natural clay used in this study was also CN-1. The resulting pillared clays were named accordingly with the period applied for the cationic exchange procedure, i.e., 0.5, 1, 2 and 72 h.

2.3. Diluted Pillaring Solutions and Re-Pillaring Procedures

To validate the results obtained using the pillaring agent synthesized by the 25/25 procedure, another clay from Campos Novos (PB, Brazil), named CN-2, which was also supplied by Centro de Tecnologia Mineral (CETEM), was used in this set of experiments. The chemical composition of the natural clay is: 58.57% SiO_2, 25.51% Al_2O_3, 5.72% Fe_2O_3, 4.2% MgO, 2.1% Na_2O, 1.0% CaO, 1.23% TiO_2, 1.19% K_2O and 0.47% of others.

The pillaring method was performed as described for the procedure 25/25 (Section 2.1). This experiment was named 100% because the pillaring solution was used as prepared, i.e., containing 100% of its original concentration. For other experiments, 10%, 25% and 50% of the volume of the pillaring agent were separated and diluted with distilled water to achieve 100% of its initial volume. Then, the diluted pillaring agents were applied in pillaring procedures as described in Section 2.1. The resulting pillared clays were named accordingly with the percentage of the volume of the original pillaring agent separated to be diluted (10%, 25% or 50%). Then, the calcined samples of 10%, 25% and 50% PILCs were submitted to a re-pillaring procedure, using the pillaring agent 100% concentrated to tentatively control the Al_{13} pillar insertion in the interlayer space of the pillared clays. These samples were labeled as RP-10%, RP-25% and RP-50%.

2.4. Characterization Techniques

The X-ray powder diffraction (XRD) patterns were measured on a Bruker D2 Phaser diffractometer using a Lynxeye detector (Bruker, Billerica, MA, USA) Cu-Kα radiation

(λ = 1.54 Å) with a Ni filter, a 0.01° step, 10 mA current, and 30 KV voltage. The basal spacings were calculated by Bragg's law (nλ = 2dsinθ).

Nitrogen sorption analyses were performed at −196 °C in a Micromeritics ASAP 2020 equipment (Micromeritcs, Atlanta, GA, USA). Prior to the analysis, the samples were degassed first at 60 °C for 2 h and subsequently at 200 °C under vacuum overnight. The values of specific surface area were calculated by Brunauer-Emmett-Teller (BET) method, micropore volumes were determined by the α-plot model (using an Al-PILC as standard), and total pore volumes were calculated by Gurvich's equation at a relative pressure of 0.99.

Chemical compositions were obtained by X-ray fluorescence (XRF) analysis using a Bruker S2 Ranger equipment (Bruker, Billerica, MA, USA) with Pd anode radiation and an XFlash® Silicon Drift Detector.

High Power Decoupling (HPDEC) MAS NMR spectra were measured for ^{27}Al in a Bruker Avance II+ 400 MHz (Bruker, Billerica, MA, USA), with a resonance frequency of 104.26 MHz, a pulse rotation angle of 90°, an acquisition time of 0.03 s, and an interval between pulses of 2 s. Aluminum hexahydrate was used as the reference.

3. Results and Discussion

3.1. Influence of Temperature in the Synthesis of the Pillaring Agent

The natural clay used in this study is from Campos Novos (PB, Brazil) and is denominated CN-1. The main clay mineral present in CN-1 is montmorillonite, although some quartz (as an impurity) could also be detected by XRD (Figure 1a). The basal spacing (d$_{001}$, calculated by the Bragg equation) of CN-1 is 1.57 nm (Table 1), indicating that Ca^{2+} is the predominant cation at the interlamellar space [29]. Figure 1a also presents the diffractograms of the pillared clays prepared with the three Al-pillaring agents synthesized under different temperatures (25/25, 60/60 and 60/25). The displacement of the first diffraction peak (d$_{001}$) of the PILCs to lower degrees (2θ), with respect to the natural clay, indicates the intercalation of Al$_{13}$ polycations in the interlamellar space of the PILCs. As a result, the d$_{001}$ increases due to the larger size of Al$_{13}$ polycations with respect to the original interlamellar cations (in this case, Ca^{2+}). Table 1 shows the calculated basal spacings for the pillared clays.
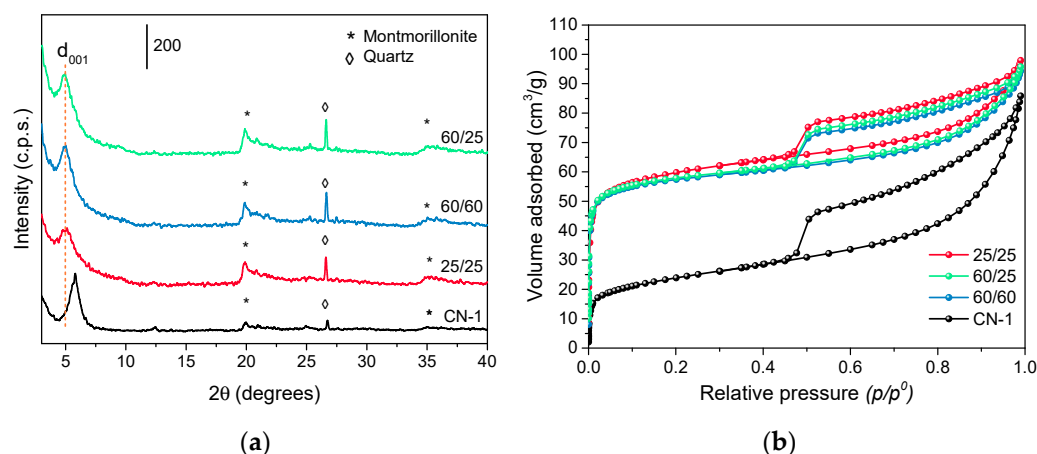

Figure 1. X-ray diffraction patterns (**a**) and N$_2$ adsorption-desorption isotherms (**b**) of the natural clay CN-1 and pillared clays prepared with the pillaring agents 25/25, 60/60 and 60/25.

After intercalation with the Al$_{13}$ polycations and calcination, the basal spacing of the pillared clays increased up to 1.75 nm (for 25/25 and 60/25 PILCs) and 1.71 nm (for 60/60 PILC), as shown in Table 1, compared to the basal spacing of 1.57 nm from the natural clay. The increase in the basal spacing is consistent with the insertion of Al$_{13}$-pillars, and it is in line with the basal spacings of Al-PILCs reported in the literature [21,22]. The calculated values of d$_{001}$ presented in Table 1 indicate, at first glance, that the three pillaring agents (25/25, 60/60 and 60/25) formed the same type of polycations, most likely Al$_{13}$.

Table 1. Basal spacings, textural properties and Si/Al molar ratios of the natural clay CN-1 and pillared clays prepared with the pillaring agents 25/25, 60/60 and 60/25.

Sample	d_{001} [1] (nm)	S_{BET} [2] (m²/g)	S_{ext} [3] (m²/g)	V_μ [4] (cm³/g)	TPV [5] (cm³/g)	Si/Al [6]
CN-1	1.57	90	42	0.03	0.13	2.48
25/25	1.75	226	95	0.07	0.15	1.77
60/60	1.71	224	79	0.07	0.15	1.77
60/25	1.75	224	79	0.07	0.15	1.77

[1] d_{001} = basal spacing; [2] S_{BET} = specific surface area; [3] S_{ext} = external surface area; [4] V_μ = micropore volume; [5] TPV = total pore volume; [6] Si/Al molar ratio.

Jalil et al. [30] also investigated the influence of temperature during the aging of an Al pillaring solution. They reported higher d_{001} spacings and specific surface areas for the PILC obtained from the pillaring agent prepared at 60 °C during dropwise addition of the base on the Al salt solution followed by aging under stirring during 12 h at 25 °C. Although they have not prepared an Al pillaring agent entirely at room temperature (i.e., as the 25/25 procedure described in this work), the authors reported that the aging step could be performed at 25 °C without compromising the properties of the resulting PILC.

Figure 1b presents the N_2 adsorption-desorption isotherms for the natural clay CN-1 and the pillared clays 25/25, 60/25 and 60/60. The N_2 isotherms can be classified as type IV(a), characteristic of mesoporous solids, which after the adsorption of the monolayer-multilayer, the capillary condensation takes place [31]. The hysteresis loops are similar to types H3-H4, consistent with slit-shaped pores. The textural properties of the natural clay and the prepared PILCs are gathered in Table 1. The pillared clays experienced an increase of approx. 2.5-fold in the specific surface area (from 90 m²/g to approx. 224 m²/g) due to the creation of micropores through the insertion of Al-pillars in their interlamellar space. The micropore volumes rise approx. 2.3-fold (from 0.03 to 0.07 cm³/g), and the total pore volumes increased from 0.12 up to 0.14 cm³/g for the pillared clays. Similarly, the external surface areas of the PILCs also increased with respect to the pristine clay. The three pillared clays presented alike textural properties, confirming, along with the XRD results, that the synthesis temperature of the pillaring agent prepared under 24 h does not exert a significant influence on the properties of the resulting PILCs.

The pillared clays were also analyzed by chemical analysis (XRF) to quantify the incorporation of Al as pillars. The CN-1 natural clay presented a Si/Al ratio of 2.48 (Table 1), and after pillaring procedures, the 25/25, 60/25 and 60/60 PILCs showed identical Si/Al = 1.77, indicating Al insertion at equal proportion in the three pillared clays. Besides, the Ca content (1.54% in CN-1) decreased below the detection limit of the equipment, confirming that Ca^{2+} was the main cation present in the interlamellar space of CN-1, as stated before by XRD analysis.

Therefore, according to XRD, N_2 adsorption-desorption isotherms and XRF results, the synthesis temperature of the Al pillaring agent at both dripping and aging procedures did not exert a significant influence in the formation of Al_{13} polycations. This is supported by the alike basal spacings, textural properties and amount of Al incorporated in the three studied pillared clays (25/25, 60/25 and 60/60). These results indicate that Al_{13} polycations can be synthesized entirely at room temperature and used as a pillaring agent resulting in a pillared clay with good values of d_{001} (1.75 nm) and specific surface area (226 m²/g). Therefore, the 25/25 pillaring agent was selected to conduct the investigations presented as follows.

3.2. Influence of the Intercalation Time

The intercalation times evaluated, i.e., the contact time between the clay suspension and the pillaring agent (25/25), were 0.5 h, 1 h, 2 h and 72 h. Figure 2a presents the X-ray diffraction patterns of the PILCs prepared under different intercalation times compared to the diffractogram of the CN-1 natural clay. The displacement of the d_{001} peak of the PILCs towards lower degrees (2θ), in comparison with the CN-1, indicates the intercalation of

Al_{13} polycations in the interlamellar space of the PILCs. However, a decreased intensity in the d_{001} reflection can be perceived for the 0.5 h and 1 h PILCs, which could sign for a lesser organized pillared structure. As a matter of fact, the basal spacing of the 0.5 h PILC (1.64 nm, Table 2) is lower than the d_{001} values calculated for the other PILCs (1.72–1.80 nm), signing that an intercalation time of 0.5 h is not suitable to produce pillared clays. The higher basal spacing calculated (1.80 nm) was obtained at 1 h of intercalation (Table 2). Increasing the intercalation time to 2 h and 72 h resulted in d_{001} values of 1.75 nm and 1.72 nm, respectively.
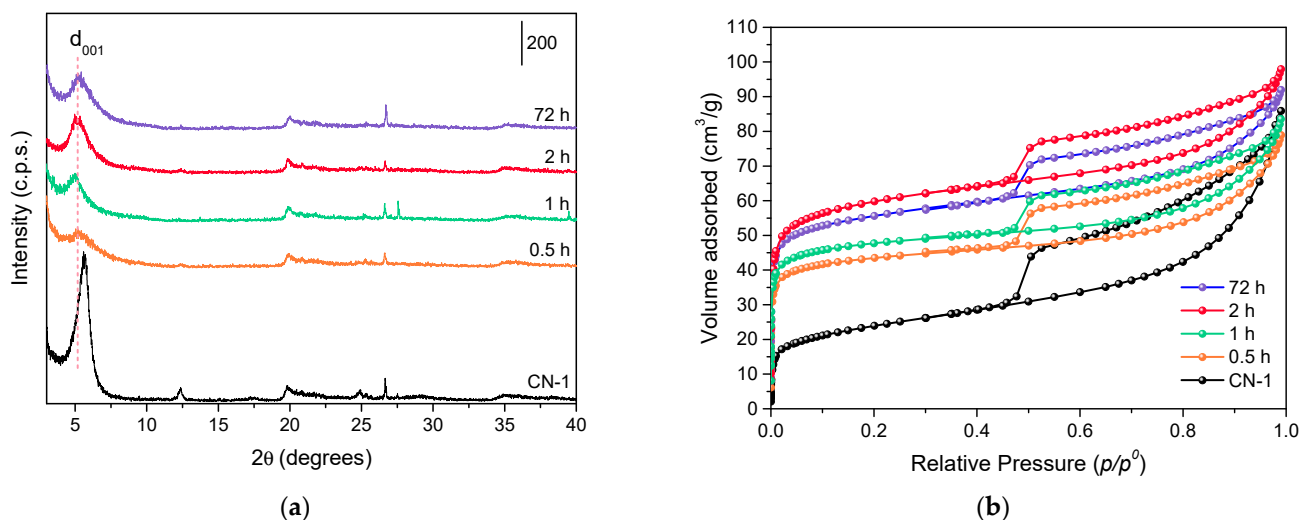

Figure 2. X-ray diffraction patterns (**a**) and N_2 adsorption-desorption isotherms (**b**) of the natural clay CN-1 and pillared clays prepared with intercalation times of 0.5 h, 1 h, 2 h and 72 h.

Table 2. Basal spacings, textural properties and Si/Al molar ratio of the natural clay CN-1 and pillared clays prepared with intercalation times of 0.5 h, 1 h, 2 h and 72 h.

Sample	d_{001} [1] (nm)	S_{BET} [2] (m²/g)	S_{ext} [3] (m²/g)	V_{μ} [4] (cm³/g)	TPV [5] (cm³/g)	Si/Al [6]
CN-1	1.57	90	42	0.03	0.13	2.48
0.5 h	1.64	168	46	0.06	0.12	1.76
1 h	1.80	213	65	0.07	0.13	1.74
2 h	1.75	226	95	0.07	0.15	1.77
72 h	1.72	184	52	0.06	0.14	1.74

[1] d_{001} = basal spacing; [2] S_{BET} = specific surface area; [3] S_{ext} = external surface area; [4] V_{μ} = micropore volume; [5] TPV = total pore volume; [6] Si/Al molar ratio.

The N_2 adsorption-desorption isotherms of the PILCs prepared with different intercalation times are presented in Figure 2b. The isotherms can be classified as type IV(a), characteristic of mesoporous materials, with hysteresis loops type H3-H4 typical of slit-shaped pores [31]. All PILCs presented higher N_2 uptakes than CN-1, although different volumes of N_2 adsorbed (at the same relative pressure) depending on the intercalation time, indicating distinct textural properties among PILCs (Table 2).

The specific surface areas (Table 2) increased along with the rise in the intercalation time up to a maximum of 226 m²/g for the 2 h PILC. Subsequently, extending the intercalation time to 72 h, the specific surface area dropped to 184 m²/g. The external areas and total pore volumes followed the same trend, with maximum values for the 2 h PILC (95 m²/g and 0.15 cm³/g, respectively). Similarly, the micropore volumes reached higher values (0.07 cm³/g) for samples intercalated during 1 h and 2 h. Therefore, despite the higher d_{001} displayed by the 1 h PILC (1.80 nm, Table 2), the textural properties reveal that improved specific surface area, total pore volume and external area were obtained with an intercalation time of 2 h.

In addition, the Si/Al ratios calculated from the XRF results (Table 2) show an increase in the Al content for all PILCs with a maximum of 1.77 (Si/Al) for the 2 h PILC. Interestingly, the 0.5 h PILC also presented a high Si/Al ratio (1.76), despite the lower basal spacing and textural properties compared to the 2 h PILC. This behavior could be explained by the rapid exchange of the natural cations present in the clay by the Al_{13} polycations ensuring a high Al amount in the 0.5 h PILC. Nevertheless, the 0.5 h of intercalation time seems insufficient to provide an organized pillared structure, with part of the Al species possibly being placed at the outer surface of the lamellae, accounting for the low external surface area measured for the 0.5 h PILC, as shown in Table 2. Notwithstanding, 72 h of intercalation time presented inferior results (Si/Al ratio, basal spacing and textural properties) compared to the 2 h PILC, pointing that longer periods of cationic exchange are detrimental to the pillaring procedure.

Thus, the intercalation time of 2 h resulted in a pillared clay with improved basal spacing, textural properties and Al content compared to the other contact times evaluated. Considering the results presented previously, the synthesis procedure 25/25 of the pillaring agent and the 2 h intercalation time were chosen to be used in the following investigation about the concentration of the pillaring agent and re-pillaring studies.

3.3. Control of Pillar Insertion

Re-pillaring procedures were performed to tentatively control the insertion of pillars in the interlamellar space, and consequently, the structural properties of the pillared clays. First, experiments using diluted pillaring solutions (10%, 25% and 50%) were applied to produce pillared clays with different densities of pillars. After calcination, the 10%, 25% and 50% PILCs were submitted to another pillaring process using a 100% concentrated pillaring solution (RP samples). Through this strategy, the main goal was to increase the density of pillars and, consequently, the textural properties of the PILCs.

In this study, another clay (CN-2) from Campos Novos (PB, Brazil) was used to test the reproducibility of the 25/25 pillaring procedure (Section 3.1). This clay is from the same natural deposit of the CN-1, and due to this, it can be used to validate the reproducibility of the results (basal space and surface area) obtained using the 25/25 pillaring solution. The diffraction pattern of the CN-2 natural clay (Figure 3a) showed characteristic peaks of montmorillonite as a clay mineral, besides the presence of quartz. Moreover, a peak at 12.5° can be perceived at the CN-2 diffractogram, which could be due to the (002) montmorillonite reflection. The d_{001} basal spacing calculated for CN-2 is 1.48 nm (Table 3), signing for the existence of Ca^{2+} cations in the interlamellar space [29].

Table 3. Structural and chemical properties of the natural clay CN-2 and pillared clays prepared with diluted pillaring solutions and re-pillared clays.

Sample	d_{001} [1] (nm)	S_{BET} [2] (m^2/g)	S_{ext} [3] (m^2/g)	S_μ [4] (m^2/g)	V_μ [5] (cm^3/g)	TPV [6] (cm^3/g)	Si/Al [7]	Al^{VI}/Al^{IV} [9]
CN-2	1.48	95	49	46	0.03	0.13	1.95	5.75
10%	1.70	179	35	144	0.06	0.14	n.d. [8]	6.39
25%	1.68	180	67	113	0.06	0.14	1.62	6.79
50%	1.70	175	51	124	0.06	0.13	1.65	7.74
100%	1.71	195	45	150	0.07	0.15	1.54	8.66
RP-10%	1.66	154	64	90	0.05	0.17	1.66	n.d. [8]
RP-25%	1.68	137	60	77	0.04	0.13	1.52	n.d. [8]
RP-50%	1.68	137	59	78	0.04	0.12	1.57	n.d. [8]

[1] d_{001} = basal spacing; [2] S_{BET} = specific surface area; [3] S_{ext} = external surface area; [4] S_μ = micropore surface area; [5] V_μ = micropore volume; [6] TPV = total pore volume; [7] Si/Al molar ratio; [8] n.d. = not determined; [9] Al^{VI}/Al^{IV} intensity ratio.
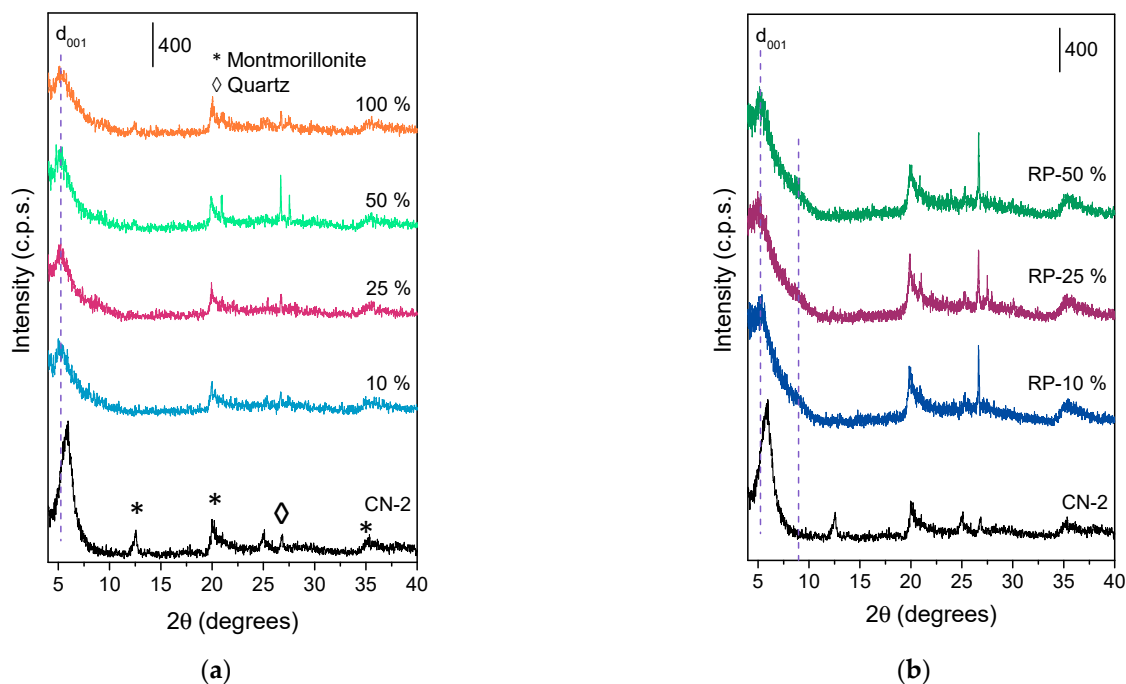
Figure 3. X-ray diffraction patterns of the natural clay CN-2 and pillared clays prepared with pillaring solutions of different concentrations (10%, 25%, 50% and 100%) (**a**) and re-pillared clays (RP-10%, RP-25% and RP-50%) (**b**).

Figure 3a also shows the diffraction patterns of samples prepared using diluted pillaring solutions (10% to 100%). Surprisingly, after calcination, all samples remained pillared, as indicated by the displacement of their first diffraction peak towards lower angles (2θ) compared to the corresponding peak from the CN-2 natural clay. The basal spacings calculated for the PILCs ranged from 1.68 nm up to 1.71 nm (Table 3), signing that even the pillaring solution only 10% concentrated was effective to produce a pillared clay. In fact, in our previous work [24], we demonstrated that the same pillaring agent could be reused up to four times in further pillaring procedures without any loss in the structural properties of the pillared clays. The reuse of the pillaring solution is possible due to the superior concentration of Keggin-Al_{13} polycations compared to the actual Al concentration incorporated within the clay through the pillaring process. Therefore, the diluted pillaring solutions used in this work contained a certain proportion of Keggin-Al_{13} polycations that was high enough to result in pillared clays.

Figure 3b presents the diffraction patterns of the PILCs submitted to a second pillaring procedure using the 100% concentrated Al_{13} polycations solution. The re-pillared clays showed displacement of the d_{001} diffraction peak compared to the natural clay, indicating that the samples remain pillared, although with a slight decrease in the d_{001} values (Table 3). However, a weak diffraction peak at approx. 9° of 2θ (marked with a dashed line, Figure 3b) can be visualized for the re-pillared clays, corresponding to a d_{001} distance of approx. 0.96 nm, relative to the thickness of a single lamella. Therefore, the re-pillaring procedure possibly results in the collapse of some lamellae without any cation in the interlamellar space.

The natural clay and PILCs prepared with diluted pillaring solutions were analyzed by ^{27}Al NMR (Figure 4), since this technique can indicate the presence of Al_{13} pillars in the structure of the pillared clays. The spectrum observed for the CN-2 clay shows a broad signal at 4.73 ppm assigned to octahedral Al, and a small signal at 57.33 ppm corresponding to tetrahedral Al substituting Si at the lamellae. Pillaring with Keggin-Al_{13} polycations usually results in a chemical shift between 60 ppm and 70 ppm, which is typically assigned to the tetrahedral Al in the Al_{13} pillar [32]. However, the pillared clays' spectra (Figure 4) showed the same signal positions as for the CN-2 clay and, therefore, the signal of Al^{IV} from Al_{13} pillars cannot be discriminated from the Al^{IV} of the clay structure. Nevertheless,

the intensity ratio of the Al signals (Al^{VI}/Al^{IV}, Table 3) can be used comparatively among samples to verify the Al incorporation in the pillared clays. The Al^{VI}/Al^{IV} intensity ratio progressively increased with the rise in the concentration of the pillaring solution, signing to a gradual insertion of Al$_{13}$ pillars as the concentration of Keggin-Al$_{13}$ polycations increased in the pillaring agent, reaching a maximum Al^{VI}/Al^{IV} ratio of 8.66 for the 100% PILC.
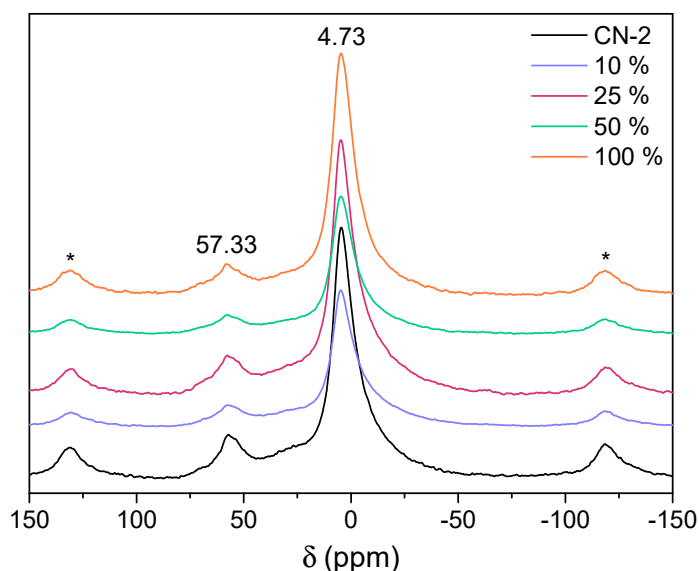

Figure 4. ^{27}Al NMR spectra of CN−2 natural clay and pillared clays prepared with diluted pillaring solutions (10%, 25%, 50% and 100%). Asterisks denote spinning sidebands.

The N$_2$ adsorption-desorption isotherms of pillared clays prepared with diluted pillaring agents are presented in Figure 5a and of re-pillared samples in Figure 5b. All PILCs presented isotherms of type IV(a) with hysteresis loops type H3-H4 [31], likewise as the pillared clays prepared from the CN-1 clay shown previously (Sections 3.1 and 3.2).

(**a**)

(**b**)
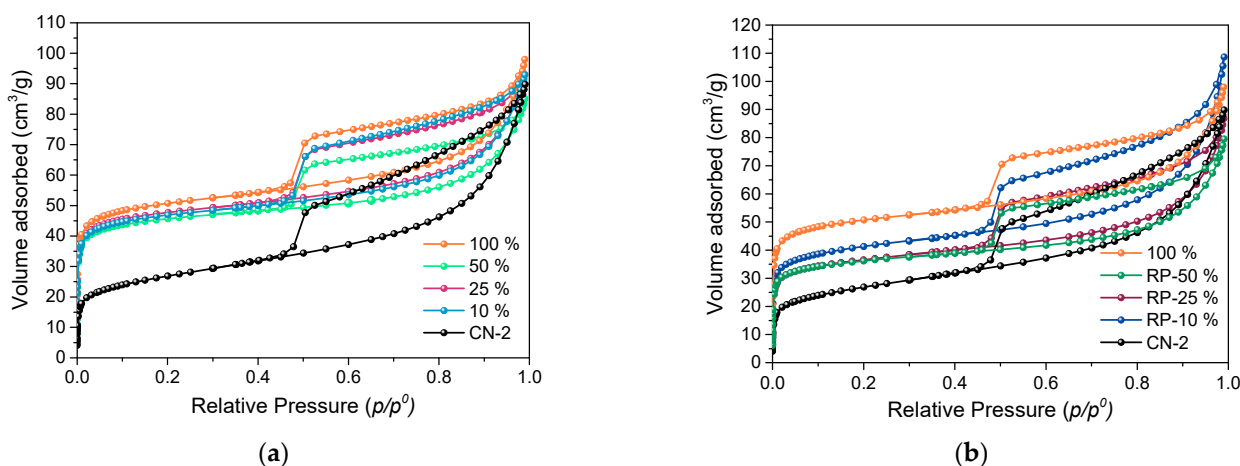
Figure 5. N$_2$ adsorption-desorption isotherms of the natural clay CN-2 and pillared clays prepared with pillaring solutions of different concentrations (10%, 25%, 50% and 100%) (**a**) and re-pillared clays (RP-10%, RP-25% and RP-50%) (**b**).

The specific surface areas (Table 3) were similar for the 10%, 25% and 50% PILCs (179 m^2/g, 180 m^2/g and 175 m^2/g, respectively), whereas the 100% pillared clay reached 195 m^2/g. The micropore volumes followed a similar trend observed for the specific surface areas, with identical values for the 10%, 25% and 50% PILCs (0.06 cm^3/g) and a maximum of 0.07 cm^3/g for the 100% PILC. For the micropore area and total pore volume

data, the 100% pillared clay also displayed the highest values (150 m^2/g and 0.15 cm^3/g, respectively). On the other hand, the external surface areas did not seem to follow any clear tendency. After the re-pillaring procedure, the re-pillared clays showed a decrease in the textural values, in which the major drop was observed for the micropore area (32% to 37%). Two possible reasons could be accounted for the decrease in porosity in the re-pillared clays: (i) the concentration of pillars in the interlamellar space is overly elevated, which prevented the access of N$_2$ molecules during physisorption analysis, or (ii) the second pillaring procedure reduced the lamellae ordering and caused the collapse of those lamellae still intercalated by natural cations.

To explain the decrease in porosity observed for the re-pillared clays, the PILCs prepared with diluted pillaring agents and the re-pillared samples were analyzed by chemical analysis, and the calculated Si/Al molar ratios are presented in Table 3. The PILCs prepared with diluted pillaring solutions (25% and 50%) showed similar Si/Al ratios (approx. 1.65), signing to the presence of a comparable amount of Al$_{13}$ pillars. The higher Al insertion was observed for the 100% PILC (Si/Al = 1.54). The Si/Al molar ratios of re-pillared samples slightly decreased (5% to 6%) compared to the starting PILCs prepared with diluted pillaring solutions, indicating a modest insertion of new Al$_{13}$ pillars in the re-pillared clays. Besides, with the re-pillaring procedure, the RP-PILCs reached a similar Si/Al molar ratio of the 100% pillared clay showing no further enhancement on the insertion of Al$_{13}$ pillars with the re-pillaring approach. This result could be due to the use of samples in their calcined state, in which the lamellae have been already stabilized (upon calcination) preventing an expressive swelling and subsequent cationic exchange for insertion of additional Al$_{13}$ pillars with the re-pillaring procedure.

Therefore, the decrease in the textural properties observed for the re-pillared samples (Table 3) is most likely a consequence of the loss in the structural ordering (as also pointed by the collapse of some lamellae in Figure 3b) due to the use of calcined materials. Further studies should be conducted using non-calcined samples in order to insert a higher amount of Al$_{13}$ pillars in the interlamellar space of the PILCs.

4. Conclusions

The synthesis temperature of Keggin-Al$_{13}$ polycations (25 °C or 60 °C) evaluated at both dropwise addition and aging steps showed no significant influence in the final properties of the resulting PILCs. Therefore, pillared clays with high basal spacing and surface area (1.75 nm and 226 m^2/g, respectively) can be prepared using pillaring solutions synthesized at room temperature for 24 h. Furthermore, this pillaring procedure was validated using the CN-2 natural clay, and similar results of basal spacing and surface area (1.71 nm and 195 m^2/g, respectively) were obtained.

Regarding the intercalation times evaluated (0.5 h, 1 h, 2 h and 72 h), 0.5 h demonstrated to be not suitable for preparing pillared clays due to the low values of basal spacing and surface area obtained. Increasing the intercalation time up to 2 h resulted in optimum values for basal spacing and surface area. However, more extended periods for cationic exchange (72 h) were detrimental to the textural properties of the resulting PILC.

Finally, the PILCs prepared with diluted pillaring solutions (10%, 25% and 50%) displayed good basal spacings (approx. 1.70 nm) and surface areas (approx. 180 m^2/g), although the chemical analysis and the Al^{VI}/Al^{IV} intensity ratio showed an inferior pillar density compared to the 100% PILC. After re-pillaring procedures, the number of Al$_{13}$ pillars increased, as revealed by chemical analysis, however, the values of basal spacing and surface area of RP-PILCs decreased. These drops can be due to a loss in the structural ordering of the lamellae, probably by the use of calcined PILCs in the re-pillaring procedures. Therefore, additional experiments are being developed using non-calcined intercalated clays to continue the study on controlling the pillar density.

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