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Relationship between hydrothermal treatment parameters as a strategy to reduce layer charge in vermiculite, and its catalytic behavior

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Abstract

The effect of two parameters involved in the application of the hydrothermal treatment (HTT) as strategy for reducing layer charge in Colombian vermiculite, preceding a conventional pillaring process has been evaluated. The selected parameters in HTT were the time of contact of the water vapour and the particle size of the starting mineral. The effect of these parameters has been evaluated by means of the detection of the structural changes determined by X-ray diffraction and the catalytic behavior using the hydroconversion of heptane of Al-pillared vermiculites from the solids obtained after the treatment. The results showed that the time of contact of water vapour during the treatment has a significant effect in the catalysts structure, while the particle size does not seem to have considerable effects. Pt/Al-vermiculites exhibit interesting catalytic properties in the hydroconversion of heptane and a marked selectivity toward isomer products.

Keywords: Vermiculite; Charge reduction; Hydrothermal treatment

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1. Introduction

Vermiculite is a natural clay make up intermediate minerals in the natural weathering sequence between micas and smectites. Consequently, many samples are pseudo-phases of the trioctahedral type or a mixture of vermiculite, interstratified vermiculite–mica, and mica [1]. Its genesis has been related with weathering, hydrothermal action, or a combination of both.

From a catalytic point of view, vermiculite is a very attractive material due to its high thermal resistance [2] and the high number of tetrahedral substitutions, which is an indicative of potentially acid sites of the Brønsted type [3]. These substitutions are generally absent from other types of smectites and bentonites. This set of characteristics offers considerable interest for obtaining pillared clays (PILCs), which involve the introduction of voluminous clusters of inorganic or organic type within the interlamellar region during their synthesis [4].

However, pillaring vermiculite with $Al_{13}{}^{7+}$ suspensions through the conventional methodology produces materials with basal spacings of 1.4 nm [5,6], whereas they generally reach about 1.8 nm in pillared smectites [7]. In fact, when the Si^{4+} substitutes an Al^{3+} ion, every unit develops an excess negative charge, which is frequently compensated by Mg^{2+} or Ca^{2+}, which have replaced K^+ ions in the original mica, conceding limited swelling properties. Due to these substitutions, the high global negative charge of the structure located on the tetrahedral layer, is the determining factor for the high layer stacking in the vermiculite structure [8], thus generating an obstacle for further cation exchange processes due to the cations available are being strongly retained.

This has led to different methodologies had being proposed in the past few years in order to achieve pillaring of vermiculites, including previous intercalation with ornithine [9], acid treatment [10] and more recently, ultrasound in the liquid phase with H_2O_2 [11,12] and the application of hydrothermal treatment (HTT) [13]. The latter, highly used in zeolites [14–16], has produced an effective reduction in the global negative charge, without considerable structural damage to the starting material, through a mechanism involving the

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extraction of aluminium from the tetrahedral layer [13], as in zeolites [14]. This would suggest that the extrapolation of this process from zeolites to vermiculites would generate some similar effect(s) such as the modification in acidity (Si/Al ratio), catalytic activity, and thermal stability. However, since there are similarities but rather differences between these two structures, it is necessary to carry out studies to explain in more detail the mechanism related to this methodology applied to vermiculites. In this sense, this work was focused on the effect of two essential parameters involved in the application of HTT in Colombian vermiculite prior a conventional pillaring process with aluminium: (i) water vapour flow and (ii) particle size in the starting material. The effect of these parameters was determined in solids pillared with Al after HTT, which were characterized by X-ray diffraction and their catalytic behavior was evaluated by heptane hydroconversion.

2. Experimental

2.1. Starting material

The starting vermiculite selected for this work is labelled V, and it corresponds to a commercialized mineral (Fumitoro Ltd.), from the Santa Marta region, in Colombia. The modifications were performed on the fraction with a particle size smaller than 180 μm, separated by seaving from raw vermiculite without prior purification treatment. Its characteristics are reported in Table 1.

The structural formula for the Colombian mineral, obtained through elemental analysis through X-ray fluorescence [17] corresponds to:

$$[(\mathrm{Si}_{3.04}\mathrm{Al}_{0.92}\mathrm{Ti}_{0.04})(\mathrm{Al}_{0.11}\mathrm{Fe}_{0.35}{}^{3+}\mathrm{Fe}_{0.07}{}^{2+}\mathrm{Mg}_{2.41}\mathrm{Mn}_{0.003})\,\mathrm{O}_{10}(\mathrm{OH})_2]\mathrm{Ca}_{0.21}\mathrm{K}_{0.05}\mathrm{Na}_{0.10}$$

3. Methodology

3.1. Hydrothermal treatment [13]

The starting material underwent thermal treatment in the presence of water vapour for a period of 6 h at 400 °C. The solid was loaded into a fixed bed reactor (15 g of clay) and taken to the desired temperature at a heating rate of 5 °C min^{-1}. Then, the nitrogen flow saturated with water vapour was generated through a thermostated saturator containing distilled water at the temperature needed to obtain a water vapour partial pressure of 50% in nitrogen. The total nitrogen–water flow was modified in order to obtain different WHSV (weight hourly space velocity) through the reactor, within a range of 20 and 180 $\mathrm{g(H_2O)\ g(clay)^{-1}\ h^{-1}}$. The particle sizes for the raw vermiculite were selected between 45 and 180 μm with different sieves. In order to remove the extra-red species generated after HTT, the sample was washed with nitric acid solution 0.25 M (10 ml/g(clay)) at 80 °C for 1 h under permanent stirring. The solids were finally washed and dried. After the treatment previously described, the samples were exchanged four times with NaCl 3 M solution under permanent stirring at 80 °C, followed by washing and drying at 60 °C.

Table 1
Cationic exchange capacity (CIC), surface area (S_{BET}), micropore volume (V_μ) and particle size for Colombian vermiculite

CIC (mequiv.($\mathrm{NH_4^+}$) $\mathrm{g(clay)^{-1}}$)	1.10
S_{BET} ($\mathrm{m^2\ g^{-1}}$)	7.4
V_μ ($\mathrm{cm^3\ g^{-1}}$)	0.0008
Particle size (μm)	<180

3.2. Pillaring

The aluminium polymeric solutions were prepared to provide 12 mol of Al per gram of clay [10], by means of the drop by drop addition of 0.4 M NaOH solution to $\mathrm{AlCl_3}$ 0.4 M solution, while the temperature was increased to reach 80 °C using the volume needed to reach an OH/Al molar ratio of 2.

The pillaring solution was slowly added to a suspension of clay (2 wt% in water prepared 24 h before the exchange) after it was aged for 36 h at room temperature under vigorous stirring. The temperature during the exchange was 80 °C and it was kept for 4 h after the addition. The final clay suspension was later aged for 12 h. The salt excess was eliminated through washing with distilled water until conductivity was reduced to a value approaching that of distilled water. Finally the clays were dried at 60 °C and calcined at 400 °C for 2 h, with heating rate of 5 °C min^{-1}.

4. Characterization

X-ray diffraction spectra were recorded a scanning rate of 0.02θ with 2 s for step time with a Philips PW1710 instrument using Cu Kα radiation, on powder samples after hydrothermal treatment and pillared process.

4.1. Catalytic evaluation

The catalytic behavior of the different solids was examined in the hydroconversion of heptane over samples previously impregnated with tetraamineplatinum(II) chloride solution, in order to achieve solids with 1wt% of metal. The activation of the solid and the catalytic test was carried out in a fixed bed reactor at atmospheric pressure. The catalyst was taken at a temperature of 400 °C at a heating rate of 10 °C min^{-1} in flowing air for 2 h, followed by nitrogen purge for 15 min, the reduction of metal by hydrogen was carried out at the same temperature for 2 h. Then the reactor was cooled down to 150 °C and stabilized at this temperature. Heptane steam was generated by flowing hydrogen through a saturator at 27 °C. The total flow of hydrogen/heptane was 10 ml min^{-1} and the WHSV was 1.2 $\mathrm{g(heptane)\ g(catalyst)^{-1}\ h^{-1}}$. The reaction was followed at a temperature range of 150 and 400 °C at a heating rate of 0.9 °C min^{-1}. The analysis of the products was done in line with a Shimadzu GC-17 gas chromatograph, with a capillary HP-1 (5 m × 0.53 mm × 2.65 μm) column and FID detector.

The methodology adopted for the treatment of the results was the one described by Moreno et al. [18].

5. Results and discussion

The systematic study of the parameters involved in HTT process [13] is necessary in order to optimize conditions of charge reduction on vermiculite to know their consequences in the structural and catalytic properties on pillared clay.

The characteristic reflections for vermiculite [19] are clearly identified in the XRD pattern of the natural Colombian mineral (Fig. 1). The high layer stacking of its structure is verified by the presence of reflections 0 2 *l*, 1 1 *l* and by the narrowing second order reflection located at 1.43 nm typical for this mineral. The reflections of 6th, 8th and 10th order, located at 0.480, 0.360 and 0.288 nm, respectively, show a progressive series which is classic in vermiculites, besides the absence of interstratifying phases or other minerals, which would be present if the sequence were by different [12].

Regarding reflection 060 located at 0.154 nm, we can affirm that the clay structure is trioctahedral, which is usually formed by the weathering of mica–biotite [20]. In fact, mica is present as an impurity, manifest through the series of reflections at 0.932, 0.468 and 0.312 nm [1].

In relation to the structural formula, some of the tetrahedral sites are occupied by aluminium and titanium cations, and most of the aluminium found occupies tetrahedral positions, which results in an excess charge of $-0.92\mathrm{e/O_{10}(OH)_2}$. This charge is mainly compensated by $\mathrm{Ca^{2+}}$, $\mathrm{Na^+}$ and $\mathrm{K^+}$. The octahedral unit has a positive charge of 0.35, originating a total negative charge of $-0.57\mathrm{e/O_{10}(OH)_2}$ [17]. According to the international nomenclature for clays, respect to their CIC and charge per formula unit [21], this mineral corresponds to trioctahedral vermiculite.

Fig. 2 records the variation in the catalytic activity of Al-vermiculites as a function of the total flow of nitrogen–water

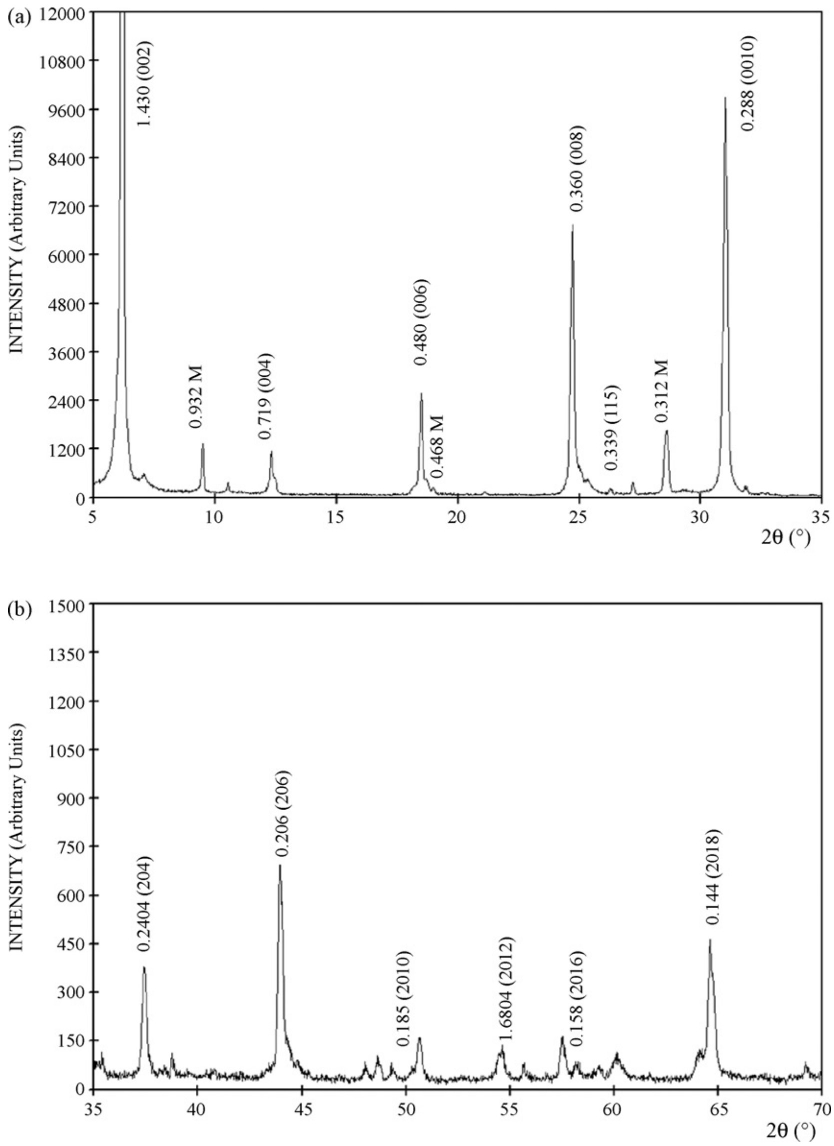

Fig. 1. XRD pattern of Colombian vermiculite: 5–35° (a) and 35–70° 2θ (b) regions, respectively. M, Mica.

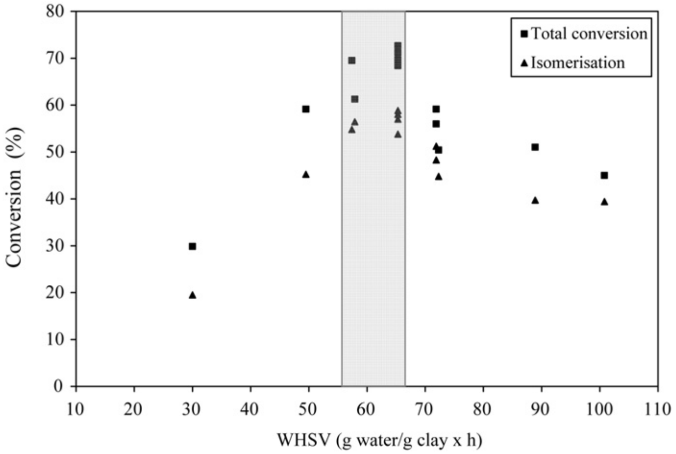

Fig. 2. Variation of the total heptane conversion on pillared vermiculites with aluminium vs. WHSV used in HTT.

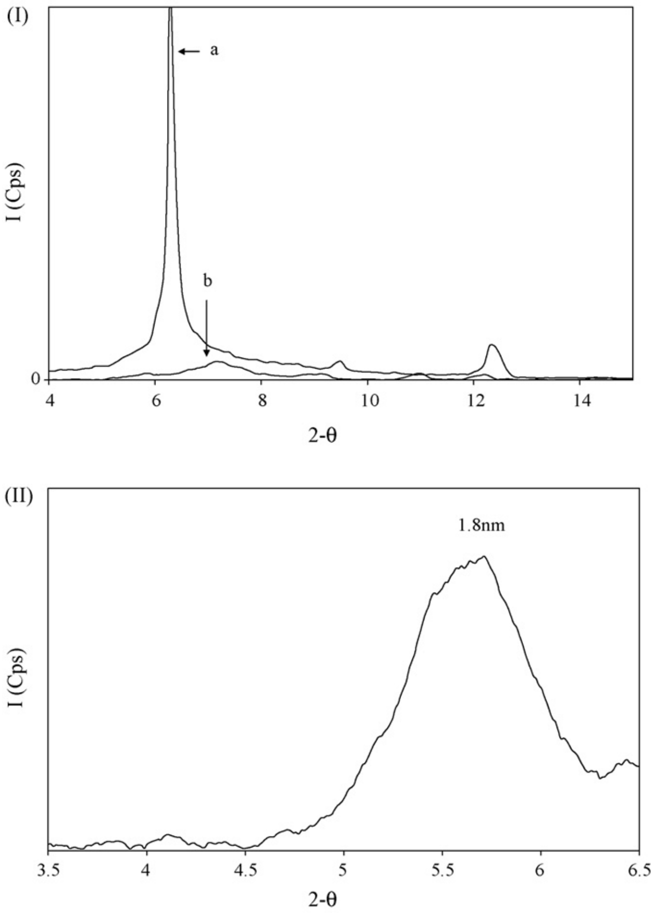

Fig. 4. Influence of WHSV of HTT in XRD patterns of Al-vermiculites: (Ia) 25 $g(H_2O)\,g(clay)^{-1}\,h^{-1}$, (Ib) 170 $g(H_2O)\,g(clay)^{-1}\,h^{-1}$ and (II) 65 $g(H_2O)\,g(clay)^{-1}\,h^{-1}$.

(expressed as WSHV) used during the HTT. Clearly, their catalytic behavior is influenced by the water vapour flow during treatment, indicating a maximum activity corresponding to a range between 55 and 65 $g(H_2O)\,g(clay)^{-1}\,h^{-1}$. Besides the number of active acid sites, the diffusion determined by the textural characteristics has an influence on the catalytic behavior. In pillared clays, these characteristics are a consequence of several parameters, one of them the structure of the starting clay. Previous studies [18] have revealed that clays with tetrahedral substitutions such as saponites, generate catalysts which are significantly more active than clays with octahedral substitutions, due to the fact that the Si/Al distribution in tetrahedral layer results in negative charge excess and a greater number of active sites ideal for acid-catalyzed reactions. In the pillared clay an increase in acidity, thermal stability and porosity are expected with respect to the starting material [22].

The pillaring process depends mainly on the nature of the clay. For this reason, if the charge reduction was successful in raw vermiculite, the subsequent cation exchange is possible, and this will then be reflected in the catalytic behavior of the pillared clay. Fig. 3 shows more evidence on this effect, due to the notable evolution in the total conversion of heptane through this process, from the starting material to Al-pillared catalysts.

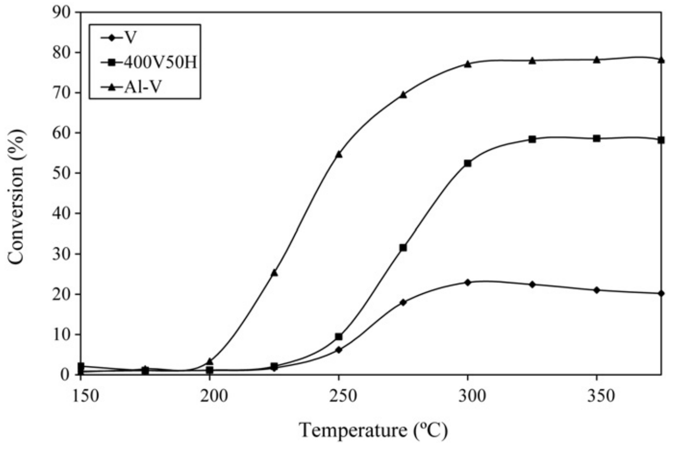

Fig. 3. Heptane conversion vs. reaction temperature, on (V) starting material (400V50H) after charge reduction process and (Al-V) pillared Al-vermiculite.

When the WHSV used during treatment is smaller or larger than the one mentioned in the central region highlighted in Fig. 2, a significant reduction was found in the catalytic activity. In the first section the modification was incipient, since no change was observed in the basal spacing with respect to the starting mineral (Fig. 4I). In the central section, solids show a basal spacing of 1.8 nm (Fig. 4II), distinctive of pillared clays. On the other hand, when the values are superior, the reduction in the catalytic activity was related with the structural damage caused, which is revealed by the dramatic reduction in XRD reflections of the mineral, as shown by signal ‘b’ in Fig. 4I.

In this way, Al-vermiculites submitted to HTT before pillaring process on a range between 55 and 65 $g(H_2O)\,g(clay)^{-1}\,h^{-1}$ show the most conclusive signals for pillared clays on XRD, and the best catalytic activity in heptane hydroconversion. This is also observed in Table 2, which shows the characteristic parameters for catalytic activity [18]. At the region mentioned, besides an increase in catalytic activity, solids exhibit a reduction in the maximum isomerisation temperature T_{MAX} and the T_{10ISO} factor corresponding to

Table 2
Comparative data for hydroconversion of heptane on Al-vermiculites

WHSV (g(H$_2$O) g(clay)$^{-1}$ h^{-1})	T_{10ISO}[a] (°C)	T_{MAX}[b] (°C)	Conv[c] (%)	Y_{ISO}[c] (%)	Y_{CRA}[c] (%)	Sel_{ISO}[c] (%)
30	252	350	29.9	19.5	10.4	65.2
50	230	300	59.1	45.2	13.7	76.5
57	215	275	69.5	54.8	14.5	78.8
57	220	275	61.3	56.4	4.7	92.0
65	225	300	72.7	58.0	14.7	83.3
65	225	300	68.4	57.0	14.1	83.3
65	225	300	69.7	53.8	16.4	77.2
65	225	300	71.2	58.8	14.5	82.6
71	230	300	59.1	51.2	7.7	86.6
71	230	300	56.0	48.3	7.5	86.2
72	230	300	50.4	44.8	5.4	88.9
89	230	300	51.0	39.7	11.1	77.8
101	265	325	45.0	39.4	5.0	88.1
165	245	300	45.1	36.3	4.8	90.7

[a] The temperature at which the catalyst reaches 10% isomerisation.

[b] The maximum isomerisation temperature.

[c] Total conversion Conv, isomer yield Y_{ISO}, cracking yield Y_{CRA} and the selectivity to heptane isomers Sel_{ISO} at T_{MAX}.

the temperature at which 10% of the conversion involves heptane isomers. In this zone, cracking reactions are minimal and they do not mask the acid activity of solids.

In order to determine the effect of the particle size at the starting material on Al-vermiculite catalysts, the reaction was carried out on pillared clays obtained from different fractions of the raw mineral separated only by seave before the charge reduction process. As can be observed in Fig. 5, there was no considerable difference in Al-vermiculites obtained from the selected fractions.

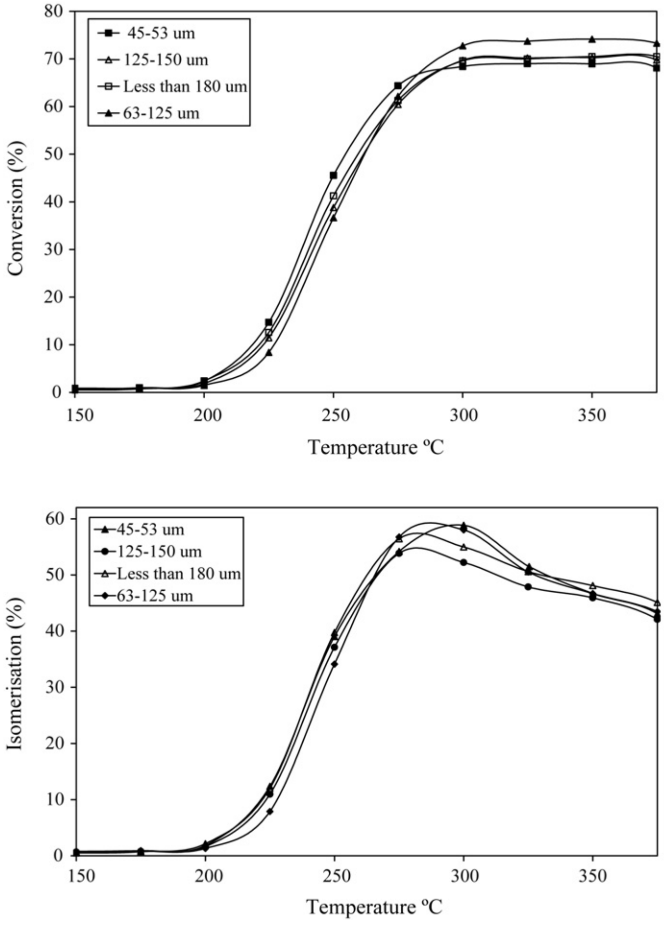

Fig. 5. Influence of particle size of starting mineral in heptane conversion and isomerisation yield on Pt/Al-V catalysts.

The total heptane conversion and its selectivity to isomerisation products do not reveal significant differences, and consequently this process seems to be independent from this parameter in the range assessed for this mineral.

On the other hand, the catalytic potential of modified solids is clearly superior to the starting material and provides evidence on the beneficial effect of HTT on it. These results and the isomerisation selectivity confirm textural modifications and the increase in acidity expected from the application of this methodology. In parallel, these results are consistent with those previously obtained in the same reaction [13] and comparable to the performance of recognized acid catalysts [23]. In fact, in the best Al-pillared vermiculites, heptane isomers represent between 80 and 90% of the conversion products at the maximal isomerisation temperature (Table 2). Besides, they exhibit a similar conversion with higher isomerisation selectivity than the catalysts referenced, although their maximal conversion temperature is higher. This fact supports the initial hypothesis about the potential activity of vermiculite in the synthesis of pillared clays to be later used in acid-catalyzed reactions and thus the importance of a detailed study on this methodology.

6. Conclusion

The effect of the contact time of water vapour and the particle size of vermiculite mineral have been evaluated during the hydrothermal treatment which was applied as a strategy in the reduction of negative charge density in the clays subsequently modified with aluminium. Regarding first parameter, an interval has been established in which the charge reduction process is more efficient, favouring the pillaring process, and thus, originating pillared clays with the best catalytic qualities. With respect to the second parameter, its influence was not significant for the range assessed, and therefore has no direct effect in the process.

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