

Charge Reduction in a Vermiculite by Acid and Hydrothermal Methods: A Comparative Study

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Received: December 7, 2004; In Final Form: August 10, 2005

A comparative study on acid and hydrothermal methods as ways to reduce interlamellar charge has been carried out on a vermiculite. This study showed that the application of the hydrothermal treatment as a previous step to pillaring the vermiculites, reported here for the first time, is a new route to obtain the porous material with a particular interest as heterogeneous catalysts, starting from mineral clays with a high density of charge. Modified clays have been characterized by atomic absorption, emission spectrograph, X-ray diffraction, cation-exchange capacity, total acidity, infrared spectroscopy (DRIFT), and nitrogen adsorption. The results have shown that all solids have been structurally modified. However, acid and hydrothermal methods showed different behavior. For the vermiculite, the hydrothermal treatment did not produce major differences in terms of the crystalline structure, whereas the acid method caused severe structural damage. The catalytic properties have been tested over Pt-impregnated samples (1%) using the hydroisomerization of heptane. Important catalytic activity was established for all solids with high selectivity regarding the isomer products.

Introduction

For the last two decades, the study of clays has focused on the molecular modification of their structure to give origin to very resistant porous materials. The sheet structure of expandable clays (Type 2:1) allows for the insertion of polyhydroxy cations of great size in the spacing between the sheets, generating a two-dimensional channel system with micropores similar to the zeolitic structures, aiming for (i) accessibility to the numerous acid sites present in the spacing between sheets of the clay, and (ii) the prevention of the collapse between sheets when a natural clay is submitted to high temperatures. This allows for the use of these solids as catalysts or catalytic supports in absorption processes, gas separation, ceramic materials, water treatments, and so forth. These aspects have been reviewed on several occasions.^{1–4}

The development of pillared clays for processes that require high temperatures and strong reaction conditions (coke formations, presence of water vapor, etc.) can be focused on clay minerals as micas and vermiculites. Indeed, vermiculites possess higher structural thermal stability than the smectites, as a result of the type of distribution of Si/Al in the tetrahedral sheets.^{5,6} Unfortunately, contrary to the smectites, vermiculites cannot be easily altered by pillars due to the elevated charge between sheets. Vermiculites possess an elevated number of isomorphic substitutions in the tetrahedral layers, higher than in beidellites and saponites.^{5,6} The substitution of Al^{3+} by Si^{4+} is imposed in all the structures generating an excess negative charge coming from the AlO_4^- groups in the tetrahedral layers of the clay,^{7–10} an indication of potentially acid sites to which we would have access if pillaring was carried out.^{5,6} The previously mentioned fact has importance, due to the fact that a clear relation between the amount of tetrahedral substitutions and catalytic performances exists.¹⁰

The degree of difficulty generated by the elevated density charge¹¹ is reflected in the limited number of trials to pillar vermiculites reported in the literature^{12–16} with the absence of pillaring or low levels of pillaring. Dealumination using $(\text{NH}_4)_2\text{SiF}_6$ solutions and subsequent aluminum intercalation using a solution of Al hydroxyl polymer (Al_{13}) was carried out over a vermiculite, giving material with d spacings of about 14 Å.¹² Nevertheless, recently reported studies^{5,6} have opened the way for obtaining micas and Al-pillared vermiculites with d spacings of 18 Å, whose textural characteristics are identical to the rest of the pillared clays but with the particularity of being stable at high temperatures (around 850 °C) and possessing catalytic activity similar to that of the zeolites. In general, the methodology reported is based on an acid treatment in clays with high charge between layers, which brings about an important decrease in the global negative charge, through the extraction of aluminum in the tetrahedral layers. This process produces a material which is easily modifiable later through the usual pillaring process. Subsequent research has reported the partial pillaring of vermiculites and phlogopites¹⁵ and the incipient pillaring of Colombian vermiculites.¹⁶ Nevertheless, the application of this methodology in the last case shows the effect of the genesis of the clay. In fact, a previous acid treatment followed by calcinations at 400 or 600 °C as a charge reduction method is not enough to achieve the pillaring in this clay and, although it facilitates the process better at 400 than 600 °C, the pillaring obtained takes place readily at the two temperatures.¹⁶ This generates the need to implement studies related with the optimization of the method to reduce the charge and through its understanding provide tools that will allow for the improvement of modeling designs for its properties. In this way, the challenge arises to look for new alternatives in which the extrapolation of the known hydrothermal treatment (HTT), commonly used in the dealumination of zeolites,^{17–22} can be used as a new way to reduce charge in vermiculites, as a previous step to the subsequent pillaring processes.

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Several effects originated by this treatment have been proposed for the zeolites. First, there is a decrease in the amount of aluminum from the network, by means of which they are more isolated and more acid.²² Second, the extraframework Al species generated can be a catalytically active site and in addition interact with aluminums in the network to stabilize the charge density of close Brønsted acid sites causing an increase in the acid strength of these.²³ In addition, the formation of the different species depends on the quantity of water molecules present during the process. Third, there are changes in the porous characteristics of the solids, and the lifetime of the catalyst is increased, especially in reactions that involve the formation of coke. In the same way, more thermally stable bonds are generated, and, in addition, there is a decrease in the negative global charge.¹⁹

In the context described, the hypothesis for the HTT application in vermiculite assumes that at least part of the effects caused by the HTT in zeolites could occur in the vermiculite, taking into account the following. (i) Some chemical and physical similarities can be established between the zeolites and the vermiculites. In this way, the zeolites as well as the clays belong to the aluminosilicate family and, although their structural organization is different, in both units of Si-oxygen tetrahedra and Al-oxygen octahedra are found; (ii) the origin of the high density of the charge in vermiculites is due to the presence of aluminum in the positions normally occupied by silicon in the tetrahedral layer. If HTT allows us to change the Si/Al ratio of the tetrahedral units in the zeolites through the extraction of aluminum, it is then possible to predict a similar effect of the HTT in the vermiculite. (iii) The difficulty in obtaining vermiculites with spacing of 18 Å or above could decrease, changing the (Si/Al)^{iv} ratio toward values close to 7.7 (as in beidellites).¹³

On the other hand, additional reasons for focusing efforts on the search of extraction methods of Al from the tetrahedral units of the vermiculite are based on a recent theoretical study²⁴ in which different cell units in the structure of a vermiculite are compared energetically, and it becomes clear that the increase in the Si/Al ratio of the tetrahedral layers favors structural stability due to the polarization of the hydrogen bonds of the O_T...O—H bond by Si⁴⁺ cations.

This work shows a parallel between the effect of the acid and hydrothermal methods as a previous stage to pillaring a Colombian vermiculite, with particular emphasis on the last method. To the author's knowledge, this is the first report on the application of HTT as an effective way to decrease the charge density in a vermiculite. Investigation of the mechanism through which the charge reduction takes place in a vermiculite through hydrothermal treatment is currently in progress.

Experimental Section

Starting Material. The vermiculite used in this study corresponds to a commercial claylike mineral (FUMITORO LTDA), which comes from the region of Santa Marta, Colombia, and whose structural formula corresponds to (Mg_{0.23}Ca_{0.04}Na_{0.005}K_{0.02})(Mg_{2.00}Al_{0.22}Fe_{0.52})(Al_{1.18}Si_{2.82}O₁₀)(OH)₂, which was determined from the chemical analysis applying the methodology reported in ref 11. This vermiculite, in particular, corresponds to the product of the dehydration of mica—biotite—magnesite, therefore having magnesium as the principal inter-change cation.²⁵ Its XRD pattern shows that we are dealing with a vermiculite with a high degree of purity (Figure 1).

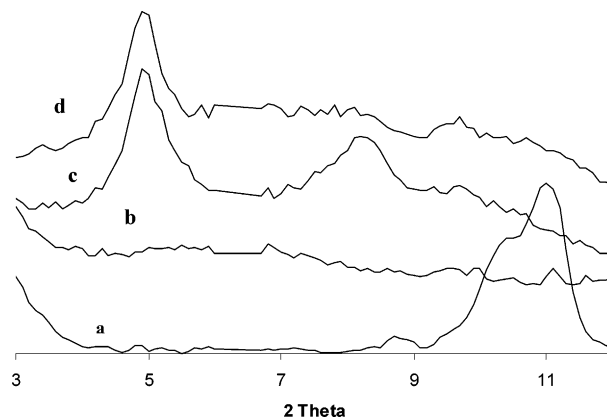


Figure 1. XRD of (a) VA600Al (ref 16), (b) VA2.0Al, (c) VH200Al, and (d) VH400Al.

The modifications were carried out on a fraction of crude vermiculite, with a particle size of 180 μm. The cation-exchange capacity (CEC) in the starting clay was of 116.9 mequiv/100 g.

Two methods were used for the charge reduction of the vermiculite—the acid and the hydrothermal treatments. The former treatment is presented mainly for comparison purposes following the method proposed by del Rey;⁵ in the second treatment, the effect of the temperature was explored keeping vapor pressure conditions constant. The solids obtained by the two methods were modified by pillaring with Al and Al—Zr species.

(a) Acid Treatment. Nitric acid (0.8 and 2.0 M) was used, carrying out the following protocol.^{5,6,16} The starting vermiculite was leached with nitric acid (10 mL acid/g of vermiculite) at 95 °C for 4 h under stirring. The solid was washed and dried at 60 °C. Subsequently, the solid was calcined at 400 °C for 4 h, at a heating rate of 15 °C/min, followed by washing with oxalic acid (0.12 M) at 80 °C for 1 h under continuous stirring, with the aim of removing the extraframework species. The mineral was washed by centrifugation and dried at 60 °C.

The solid obtained was exchanged, for which 2.5 g/100 mL suspension was prepared in a 3 M NaCl solution at 92 °C under continuous stirring. The NaCl solution was replaced 5 times during the entire exchange process. Finally, washing and drying were carried out as above.

This same procedure was carried out in the natural vermiculite using concentrations of nitric acid (0.8 and 2.0 M) and calcining at 400 °C after the acid treatment.

(b) Hydrothermal Treatment. The conditions used for the HTT were based in previous works of dealumination of zeolites. In this way, the solid was treated with a pressure of water vapor at 50% in nitrogen, at 2.0 L h⁻¹, for 6 h at 200 and 400 °C. The solids obtained were washed with diluted nitric acid (10 mL HNO₃ 0.5 M/g) kept at 80 °C for 1 h under continuous stirring, with the purpose of removing the extraframework species retained.¹⁸ The solids were washed by centrifugation and dried at 60 °C.

Finally, the samples were exchanged as above.

(c) Pillaring Procedures. The solids obtained by the two methods described were modified using conditions essentially similar to those reported elsewhere.^{5,6,9,10,26}

Modification with Al. To an AlCl₃ 0.4 M solution, under continuous stirring, an adequate volume of 0.4 M NaOH solution was slowly added to reach an OH/Al molar ratio of 2.4. The temperature was maintained at 80 °C during the preparation, and it was aged at room temperature for 24 h. The final pH value of this solution was 4.35.

The necessary volume of pillaring solution was added to a solid suspension in demineralized water (2 wt %) in order to supply 12 mmol of Al per gram of vermiculite at 80 °C, stirring during the whole process. The final dispersion was maintained at 80 °C for 4 h. Finally, the solids were washed and dried at 60 °C and calcined at 400 °C for 2 h.

Modification with Al–Zr. To a solution of 0.1 M AlCl_3 a solution of 0.1 M ZrOCl_2 was added slowly, under stirring at room temperature to reach 9 mmol Al/1 mmol Zr per gram of solid. Subsequently the temperature was raised to 60 °C, and a solution of 0.2 M NaOH was added dropwise in order to reach an OH/Al molar ratio of 2.0. The final solution was heated for 2 h at 60 °C under stirring. Finally the solution was aged for 24 h at room temperature. The final pH of this solution was 4.09.

The solids obtained are differentiated according to the method used in the charge reduction with its corresponding variable. In this way, for example, VA0.8Al corresponds to the vermiculite treated with 0.8 M nitric acid, calcined at 400 °C, and modified with Al; VH400Al corresponds to the vermiculite treated by hydrothermal treatment at 400 °C and subsequently modified with Al. Likewise, for comparative purposes, both the starting vermiculite (Vi) and vermiculite after HTT at 400 °C with (VH400WA) and without (VH400) subsequent washing with nitric acid were used in this work.

Characterization. The solids obtained by acid treatment are only used for comparison purposes with respect to their effect on the pillaring process. Therefore, for these samples we report here only the results of the chemical analysis (Si/Al ratio), CEC and XRD.

The chemical analysis by atomic absorption was carried out in Perkin-Elmer 3110 equipment. Such an analysis was carried out also on the starting vermiculite (Vi) and after it was submitted to hydrothermal treatment (VH400). The content of Zr was determined semiquantitatively by spectrographic analysis.

The initial and residual cation-exchange capacities (CEC) were determined by the micro-Kjeldahl method, using a previously standardized technique.²⁶

The diffractograms of the samples were obtained by the powder method in Bruker AXS D5005 equipment with $\text{Cu K}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation.

The superficial area of the solids modified was obtained from the adsorption–desorption of nitrogen isotherms in a range of relative pressures between 0.05 and 0.25 at the temperature of liquid nitrogen with Micromeritics ASAP 2010 equipment.

The total acidity contents were determined from the amounts of ammonia adsorbed at 250 °C followed by temperature-programmed desorption between 150 and 400 °C with a plateau of 16 h at 400 °C. The ammonia content was obtained by back-titration with 0.005 M sulfuric acid.²⁷ In the determination of the total acidity, it is assumed that for each mmol of NH_3 absorbed (or desorbed) there is a mmol of protons.

Ammonia was used as a probe molecule to characterize the acidity of the solids modified. DRIFT spectra were recorded with a Nicolet 510P FT-IR spectrometer over power samples as follows: (i) the first spectrum, the sample was treated at 400 °C under flowing N_2 (7 mL min^{-1}) for 1 h; (ii) a second spectrum was recorded over this same sample but after the ammonia adsorption (7.5 mL min^{-1}) at room temperature for 1 h; and (iii) subsequently, the spectra were recorded after outgassing in flowing N_2 (7 mL min^{-1}) at room temperature and then stepwise heating for 1 h, at temperature intervals of 100 °C, between 100 and 400 °C and cooling.

TABLE 1: Chemical Composition and Cation-Exchange Capacity

sample	Si/Al ratio	Na_2O (%)	ZrO_2 (%)	CEC (mequiv/100 g)	residual CEC (%)
V(i) ^a	2.33	0.04		116.9	
VH400 ^b	3.02	2.01		62.5	
VH400WA ^c				75.6	
VA0.8Al	2.61	0.13	0.01	26.8	77.1
VA2.0Al	4.80	0.05	0.01	43.8	62.6
VA0.8Al–Zr	2.94	0.11	0.03	30.2	74.1
VA2.0Al–Zr	4.71	0.04	0.40	40.1	65.7
VH200Al	1.63	0.39	0.01	36.9	68.5
VH400Al	1.76	0.23	0.01	34.2	70.8
VH200Al–Zr	1.72	0.08	0.40	38.2	67.3
VH400Al–Zr	1.86	0.05	0.27	34.4	70.5

^a V(i) starting vermiculite. ^b VH400 after HTT at 400 °C. ^c VH400WA after HTT at 400 °C and subsequent washing with nitric acid.

Catalytic Evaluation. The hydroisomerization–hydrocracking of heptane, a reaction requiring both protonic and metal functions, was used as a test reaction and evaluated over samples previously impregnated with $5 \times 10^{-3} \text{ M}$ tetrammineplatinum(II) chloride solution in order to load the solid with 1 wt % Pt. The catalytic test was carried out in a unit which operates with a fixed-bed microreactor at atmospheric pressure connected in line to a gas chromatographer. The pretreatment and reaction conditions were similar to those detailed elsewhere.^{26–28} The catalyst (200 mg) was activated in-situ in flowing air at 400 °C for 2 h, followed by helium purge, and reduction of the metal in flowing H_2 at 400 °C for 2 h. The reactor was then cooled to 150 °C and stabilized at this temperature. Heptane steam was generated by flowing hydrogen through a glass thermostated at 27 °C. The WHSV was of $1.2 \text{ g-heptane g-catalyst}^{-1} \text{ h}^{-1}$. The reaction was carried out from 150 up to 400 °C, using a ramp of $8 \text{ }^\circ\text{C min}^{-1}$. Analysis of on-line gas phase was done in a Hewlett-Packard 5890 gas chromatograph with a capillary column HP-1 (methyl silicone) of $5 \text{ m} \times 0.53 \text{ mm} \times 2.65 \text{ }\mu\text{m}$ and a FID detector.

Results

Chemical Analysis. The results of the chemical analysis of the natural vermiculite and of all the solids modified (Table 1) shows the change in the chemical composition of the latter ones with respect to the starting material, indicating a first effect of the treatments applied in the modification of the clay structure.

In the case of acid treatment, our purpose was to look for the viability of the application of this method to the Colombian vermiculite to facilitate the later process of pillaring; for this reason, the chemical analysis was carried out only in the initial samples at the end of all the process. The results obtained allow us to establish that independently from the pillaring solution, an increase in the Si/Al is shown as the acid concentration increases, suggesting a direct influence of the acid concentration in the dealumination.

When the hydrothermal treatment is carried out at 400 °C on the vermiculite (VH400), a solid is generated with a considerable increase of the Si/Al ratio, suggesting that the charge reduction on the vermiculite was effective by this method.

The solids treated by the hydrothermal method and subsequent washing with acid and modified with Al show an increase of the aluminum content between 50 and 70% with respect to the hydrothermally treated vermiculite (VH400) and a considerable decrease of the Na content in the modified solids, confirming the effectiveness of the exchange of the species of the pillaring solution caused by the compensation cation.

TABLE 2: Basal Spacing, Areas BET and Total Acidity^a

solid	basal spacing <i>d</i> (Å)	width at half-maximum peak (2θ)	<i>S</i> _{BET} (m ² /g)	total acidity (mequiv H ⁺ / 100 g)
V(i)	14.40		4	17.5
VA600Al ^b	9.40	0.60		
VA0.8Al	ND	ND	114	41.8
VA2.0Al	16.05	2.00	270	57.7
VA0.8Al–Zr	ND	ND	127	49.2
VA2.0Al–Zr	15.77	1.38		82.9
VH200Al	18.02	0.67	124	61.5
VH400Al	18.02	0.53	111	51.8
VH200Al–Zr	17.31	0.79	79	43.3
VH400Al–Zr	17.66	0.97	67	47.0

^a ND = not detected. ^b From ref 16 (vermiculite obtained by acid treatment followed by calcinations at 600 °C for 4 h and subsequently pillared by contact with base-hydrolyzed Al solution).

In the samples modified with Al–Zr (with both treatments), the insertion of zirconium in the solids can be effectively established, despite the fact that the analysis through which this measuring was carried out (emission spectrometry) corresponds to a semiquantitative technique.

Residual Cation-Exchange Capacities. The residual CEC provides an estimate on the fraction of the layer charge which is not compensated by cationic pillaring species. The CEC values obtained in this work are reported in Table 1. The CEC for the natural vermiculite used in the present work (116.9 mequiv/100 g) is found within the range reported in the literature (between 100 and 150 mequiv/100 g).⁵ In all cases, the modified vermiculite shows values of CEC less than those of the natural vermiculite. For the case of the solids submitted to the acid treatment, the results obtained do not allow us to establish if there exists a relation between the fraction of the charge compensated by the aluminum interchanged and the concentration of the acid used in the charge reduction of the natural clay.

The solids obtained by hydrothermal treatment show a significant decrease in exchange capacity on both Al and Al–Zr pillaring samples, which in principle could suggest that the solids present effective structural modifications after hydrothermal treatment, which leads to a greater facility in the subsequent modification with pillaring species.

With the aim of making the effect of the hydrothermal method in the decrease of the charge density more explicit, the CEC were determined for a sample after the hydrothermal process (VH400) was carried out and for the same sample but with subsequent washing with nitric acid (VH400WA). The CEC results of such solids show a significant decrease in charge and provide initial support to the hypothesis on the effectiveness of the hydrothermal process in the extraction of aluminum as a way to decrease the charge of the vermiculite structure.

X-ray Diffraction Data. In this analysis, both the basal spacing (*d*₀₀₁) and the width at half-maximum peak were taken into account for all the solids. The results are compiled in Table 2, and Figure 1 shows the XRD of some samples. In the case of acid-treated solids, the Al and Al–Zr pillaring procedures resulted in an increase of the 001 basal spacing only for the high acid concentration (16.05 Å for VA2.0Al and 15.77 Å for VA2.0Al–Zr). Nevertheless, both the width and the low intensity of this signal suggest an incipient formation of the pillar. The solids treated with less concentrated acids do not present reflections of pillar formation.

On the other hand, in the series of solids pretreated by the hydrothermal process, all of them clearly exhibited a pillar formation with spacings between 17.3 and 18.0 Å. This last result is consistent with the one reported in the literature for

the case of smectites²⁶ where it is shown that the value *d*₀₀₁ depends strongly on the metallic precursor in solution. For the case of Al–Zr, the intrinsic acidity of the Zr causes deformation in the structure of the pillar, which partly explains the slight fall of the basal spacing with respect to the solids where only Al species exist.

The width at half-maximum peak for the solids in which pillars were generated (Table 2) can be employed to estimate the quality and distribution of these.^{9,29,30} In this sense, the results indicate a marked difference between the two methods employed in the decrease in charge of the vermiculite. This performance suggests that the hydrothermal process provided materials with pillars that have a better order in the direction *c*, probably as a consequence of a much more homogeneous distribution of charge than the one obtained in solids pretreated with acid.

Surface Area. The superficial area of the solids, calculated by the BET method, is reported in Table 2. The solids modified by acid treatment present a marked increase in their area as the concentration of nitric acid increases. Only the sample treated with 2.0 M acid presented an incipient pillar formation, suggesting that the high superficial area in the solids is due mainly to the partial delamination of the structure, which exhibited an evident increase of external superficial area.

The natural vermiculite treated with the HTT showed in all cases a significant increase in the BET areas. Such increase contains an important component derived from the existence of the pillars, as discussed previously (see XRD), and most likely due particularly to the presence of micropores.^{5,6,26}

Acidity. To determine the total acidity of the solids, the saturation method was used, followed by the desorption of ammonia. The results obtained for the natural vermiculite and the material modified are compiled in Table 2, in which a significant increase of the acidity of all the solids with respect to the original vermiculite is evident. In the case of the solids modified with nitric acid, a greater acid content is observed for those in which pillaring solution of Al–Zr was used than in the ones with pillaring solution with only Al. This result was to be expected, given the acid nature of the zirconium.

Regarding the effect of the hydrothermal method over the acidity, as mentioned above, it is noticeable. In all cases, an increase of acidity between 150 and 250% with respect to the starting vermiculite is exhibited. Nevertheless, in this series, contrary to what occurs in the acid method, the solids modified with Al–Zr present less acidity than the ones modified with only Al. This could have an explanation in the types of species of Al, Zr, and Al–Zr that could have been formed. In the case of the series of the acid method, some Zr species predominate and part of the structure is in amorphous form as indicated by the XRD. In this case, possibly the Zr is deposited in the external parts of the sheets, while in the case of the solids obtained by hydrothermal treatment it is possible that the zirconium is less available, given the conditions of pillar formation.

The characterization of the solids suggests that there is no marked effect of the temperature of the hydrothermal process in the range studied (200–400 °C) on the claylike structure before the pillaring process. A study in progress on the mechanism of decreased charge caused by the hydrothermal process seems to support this affirmation.

The DRIFT technique was used in the present work to determine the type of acid sites (Brønsted and Lewis), the proportion of these, and their relative strength, using ammonia as a probe molecule and working a temperature range between 25 and 400 °C. The protonated form of the ammonia NH₄⁺ indicates the interaction with Brønsted acid sites and presents

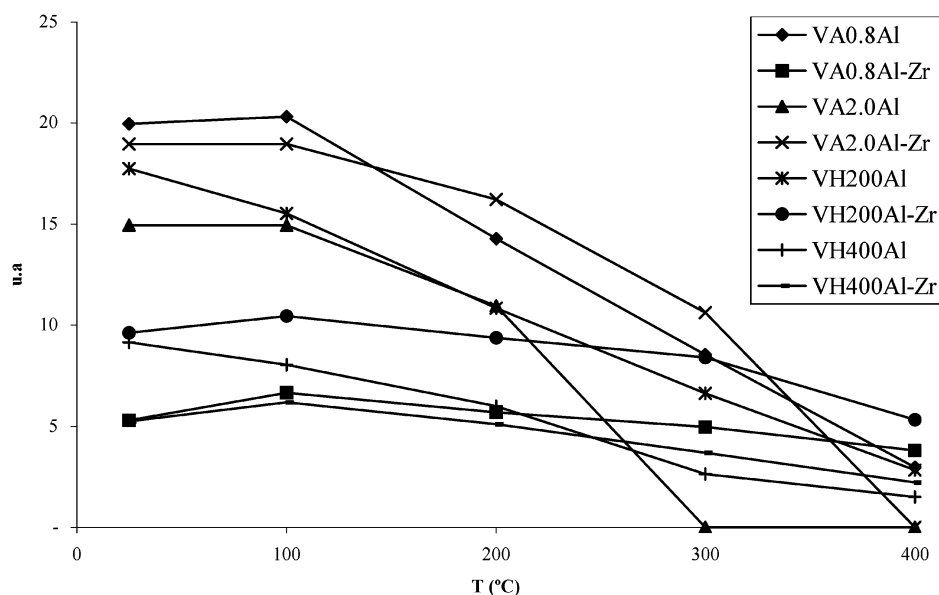


Figure 2. Areas of the NH_4^+ -Brønsted (1450 cm^{-1}) bands vs outgassing temperature.

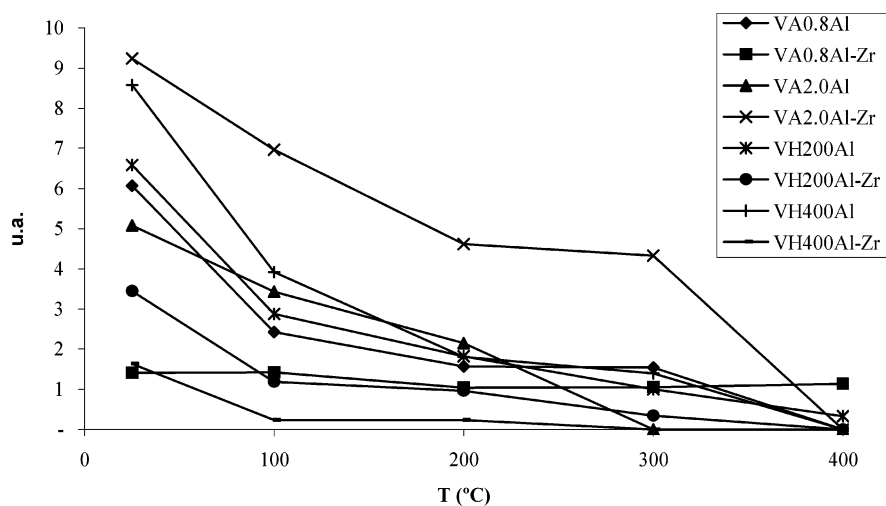


Figure 3. Areas of the NH_4^+ -Lewis (1630 cm^{-1}) bands vs outgassing temperature.

bands close to 1450 and 3130 cm^{-1} . The ammonia coordinated to Lewis acid sites exhibited vibration frequencies close to 1250 , 1630 , and 3330 cm^{-1} .³¹ To carry out the semiquantitative study, the integrated areas (Kubelka MunK units) of the bands at 1450 cm^{-1} (Brønsted acid sites) and 1630 cm^{-1} (Lewis acid sites) were provided by the Mathematics 4.0 software after baseline optimization. It was found that the values obtained were reproducible with $\pm 10\%$.

The natural vermiculite does not absorb ammonia, which means that under working conditions, the starting clay does not interact with the ammonia and does not place in evidence its acid sites. The results indicate that all the solids modified present an important increase in their acidity with respect to the natural clay, which agrees with the total acidity reported in Table 2. This indicates that the modification procedures applied to natural clay were effective in increasing the acidity. The variations of the relative intensity of the NH_4^+ -Brønsted and NH_4^+ -Lewis band versus the outgassing temperature are shown in Figures 2 and 3.

The strength of the Brønsted acid sites of the solids obtained by acid treatment decreases with an increase of the temperature (Figure 2). The samples VA2.0Al and VA2.0Al-Zr lose their

acid strength completely at 300 and $400\text{ }^\circ\text{C}$, respectively. The sample VA0.8Al-Zr present the most acid strength, although despite this it does not present a very high acid value at low temperatures, but maintains its acid value almost constant with the increase in temperature. These results suggest that the introduction of zirconium in the structure of the solids improves Brønsted-type acid strength in the temperature range studied. The strength of the solids obtained by hydrothermal treatment also depends on the Zr introduced in the structure, due to the fact that the acid sites type Brønsted of the solids modified with Al-Zr are kept at a more constant temperature than the samples with only Al species.

The strength of Lewis acid sites in the samples obtained by acid treatment exhibited a decrease in the acidity with the increase in temperature (Figure 3). It is interesting to observe that the solids to which zirconium was introduced show greater Lewis acid strength sites than the equivalent samples modified only with aluminum. The results of Lewis acidity of the samples obtained by hydrothermal treatment show that the solids modified with aluminum have a greater acid strength than the solids-modified aluminum-zirconium. Nevertheless, the last solids have more strength, as indicated by the less-pronounced declination, than in the former case.

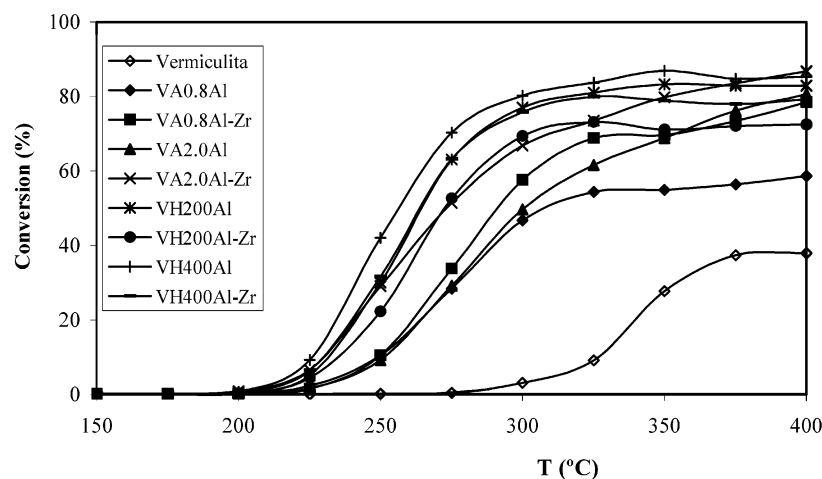


Figure 4. Variation of total conversion of heptanes vs reaction temperature.

TABLE 3: Catalytic Evaluation Parameters

solid	$T_{10\text{ISO}}$ (°C)	T_{max} (°C)	conv. t (%)	Y_{ISO} (%)	Y_{CR} (%)	sel_{ISO} (%)
V(i)	302	375	37.4	35.6	1.4	95.0
VA0.8Al	249	325	54.4	49.7	3.6	91.3
VA2.0Al	252	325	68.8	55.5	7.8	80.7
VA0.8Al-Zr	249	325	68.8	59.9	6.8	87.1
VA2.0Al-Zr	230	300	66.8	60.9	4.4	91.1
VH400Al	225	275	70.2	68.1	2.1	97.0
VH200Al	232	300	77.0	70.0	6.5	90.9
VH400Al-Zr	230	300	75.7	67.7	7.6	89.4
VH200Al-Zr	235	300	69.4	64.8	4.2	93.4

Catalytic Activity. The balancing of the two catalytic functions and the reaction mechanisms of skeletal isomerization and hydrocracking of alkanes in the presence and absence of molecular shape selectivity are well understood.³² Indeed, isomerization and hydrocracking of alkanes on bifunctional catalysts require a cooperation of noble metal particles and Brønsted acid sites. The noble metal catalyzes hydrogenation–dehydrogenation reactions, while isomerization and cleavage of the hydrocarbon skeleton occurs over the Brønsted acid sites. When the two functions are well balanced, the rearrangement of the alkenes on Brønsted acid sites is the rate-limiting step of the conversion.¹⁰ On the basis of previous studies²⁶ with respect to the ideal metal content (Pt) for this reaction, in this work a charge of 1% in metal mass is used on the clays. In fact, differences in platinum dispersion according to the nature of the pillar can probably be excluded.²⁶

Figure 4 shows the variation of the total conversion of heptane versus reaction temperature obtained over all solids modified, which exhibited a significantly higher activity than the natural vermiculite. The solids obtained by HTT show an increase in activity similar to the ones obtained with the solid pretreated with acid (between 100 and 130%), with respect to the natural clay. The increase of the conversion percentage begins at 225 °C, a temperature which is 75 °C below the one registered in the natural vermiculite (300 °C).

Characteristic values taken from the experimental results have been compiled in Table 3, where $T_{10\text{ISO}}$ is the temperature at which yield of heptane isomers reaches 10%. The values in the following columns were taken at maximum isomerization conversion, namely, the temperature (T_{max}), the conversion of heptane (conv. %), the yield of isomers (Y_{iso} %), the yield of cracking products (Y_{cr} %), and the selectivities to C_7 isomers (S %).

The modified solids show an important decrease in $T_{10\text{ISO}}$ with respect to the natural vermiculite (302 °C). It is observed that the materials pretreated at 200 and 400 °C have $T_{10\text{ISO}}$ values very similar among them, which are inferior to the solid obtained by acid pretreatment.¹⁶ The T_{max} values show equally that the solid VH400Al is the most outstanding catalyst, because it presents the lower temperatures in the isomer production of the alkane (25 °C below the other solids and 100 °C below the natural vermiculite).

The total conversion values that fluctuate between 69 and 77% and the Y_{ISO} (55–70%) and sel_{ISO} (81–97%) values suggest significant differences among the solids of the series pretreated hydrothermally and the pillared material after an acid pretreatment. Such results indicate a better catalytic behavior with the samples obtained by Al pillaring pretreated hydrothermally at 400 °C.

The presence of zirconium in the solids modified with acid generates greater conversion percentages at lower temperatures than in the equivalent solids modified with aluminum, in the temperature range studied. This situation is not found in the samples modified with hydrothermal treatment; so, despite the fact that the conversion percentages are increased at a temperature similar to 225 °C, the samples with Zr show the lowest conversion percentages with respect to equivalents pillared with aluminum.

Discussion

The results obtained in the physicochemical changes of the solids modified with respect to the natural vermiculite are clear. The two treatments applied to the clay provided the function of decreasing the charge between layers. Nevertheless, such treatments do not produce the same effect on the structure of the vermiculite.

In the acid method, the influence of the concentration of the nitric acid used is observed, since the higher acid concentration favors both dealumination (increasing Si/Al ratio) and the exchange of the interlayer cations by polyhydroxy cations of great size. Nevertheless, the crystallinities were somewhat poorer, which suggests a large amount of clay delamination; this is consistent with the high superficial area obtained.

Similar observations were reported by del Rey et al.⁵ for Al-pillared vermiculite. In fact, these authors have shown that the use of nitric acid solution with higher concentration than 0.8 M had a negative global effect because, in addition to the exchange of the interlayer cations, the excess protons caused appreciable structural damage.

The lower acid concentrations are not as efficient in the dealumination procedure, which does not mean that the structure remains intact. On the contrary, the analysis carried out showed significant changes with respect to the starting clay (variations in the cation quantity present in the structure, decrease in the CEC, increase in both the superficial area and acidity, and loss of crystallinities), which possibly indicates formation of a metallic cluster on the surface.

Likewise, the nitric acid activates acid sites in the clay, generating a significant increase in the acidity, possibly by proton migration within the sheets, which in turn increases the Brønsted acid type sites. The semiquantitative analysis of DRIFT showed the increase of the thermal stability in the acid sites with the application of the pillaring procedure, especially with the zirconium. Indeed, despite the apparent failure of effective pillaring, these solids present a high catalytic activity in the hydroconversion reaction of the heptanes.

The vermiculites submitted to hydrothermal treatment showed better pillaring than the ones submitted to the acid method. Indeed, the HTT causes greater efficiency in the dealumination process and no longer appeared to influence the structure of the clay (there is no significant loss of crystallinities). Besides, at the temperatures used (200 and 400 °C), the final solids exhibited similar properties, which indicates that, at this temperature range, the process is equally efficient. The XRD analysis showed important differences between the solids modified with Al and those modified with Al–Zr. The degree of pillaring of the former was better than in the last ones, which can be explained by the probable coexistence of the three types of polyhydroxy cations in the pillaring solution (Al, Al–Zr, and Zr species). It can be noticed that, with the analysis carried out, it is difficult to be sure where the zirconium is located in these solids, which leads us to consider three possibilities: (i) that the big polyhydroxy cations of only zirconium have formed independent pillars from the aluminum, (ii) that the polyhydroxy cations of Zr of smaller size will deposit themselves on the clay surface and on some aluminum pillars as simple decoration oxides, and (iii) that mixed Al–Zr pillars have been formed. At any rate, in the scientific field, there are still many discussions in this sense and the debate is still open.

The XRD of the solids submitted to HTT suggest a more homogeneous distribution of the pillars, which indicates that the charge between layers in the structure was possibly decreased homogeneously, contrary to what happens with the solids obtained by acid treatment. This suggests that a more specific knowledge of the HTT effect in the charge of the vermiculite is presented as a very promising way to be able to establish controlled parameters to fashion specific structures.

The acidity values also increase with respect to the natural vermiculite and are higher than those reported for pillared mica (29 meq/100 g).⁶ Although in the hydrothermal method nitric acid was used, the process is not strong, because a diluted acid was used and it was located in contact with the clay only for 1 h at 80 °C, while in the acid method the treatment was with concentrated solutions for 4 h at 95 °C. Despite the fact that initially the use of nitric acid in the hydrothermal treatment had the purpose of washing extra structural species, we cannot ignore the influence that this treatment could have brought about in the increase of acidity.

This study was mainly focused mainly on a new route to obtain pillared vermiculite. Hydroconversion of heptane on platinum-loaded samples was used, first, only as a way to explore the catalytic potential of the pillared materials. More studies to investigate the influence of each step of the HTT

and the nature of the pillars on the catalytic properties as well as their comparison with the other materials under the same reaction conditions are in progress and will be treated separately. However, some preliminary comments will be made.

The catalytic potential of the solids modified indicates a very clear difference in the catalytic properties with respect to the starting vermiculite. The results of high conversion and the distribution of the products obtained are not surprising because, as mentioned, all the solids modified increased their acidity and their superficial area, generating a substantial catalytic activity in all cases.

At present, to the author's knowledge, the catalytic properties of the Al-pillared vermiculite were reported only for the hydroisomerization of octane,³³ whereas those for Al–Zr-pillared vermiculite were not reported. In the former case, the catalytic results were compared with reference to zeolites (H– β and H–ZSM-22). Obviously, the zeolite was more active than the pillared materials. However, higher yields and selectivities for the C8 isomers were achieved on the pillared vermiculite. Indeed, at maximum isomerization conversion, the yields of C8 isomers represented 80% of the reaction products, compared with 70% for the zeolite, namely, selectivities of 90% vs 82% for the zeolite. In comparison, Pt/H–ZSM-22 (the most active zeolite) gave, at maximum isomerization (at 229 °C), a yield of C8 isomers of 79% (sel. 92%).

Bearing in mind the differences between octane and heptane, the results obtained in this study for the Al-pillared vermiculite will be compared and are consistent with the analogous studies reported.³³ Indeed, at maximum isomerization conversion, the yields of C7 isomers represented 68 and 70% of the reaction products and selectivities of 97 and 91% for VH400Al and VH200Al, respectively (Table 3), compared with 80 and 79% of the yields of C8 isomers and selectivities of 90 and 92% for Al-vermiculite and Pt/H–ZSM-22 reported for the cited authors.

Likewise, Patriceon et al.³⁴ have studied four types of zeolites (Y, β , EU-1, ZSM-22) and a pillared beidellite, loaded with 1 wt % of Pt, in heptane isomerization. They reported, at the maximum yield of isomers, the conversion between 82 and 87% (with the maximum conversion for the pillared beidellite) and the yields of C7 isomers between 59 and 78% (with the maximum for the H–ZSM-22) which correspond to selectivities between 72 and 93%. Unfortunately, for the comparison proposed, the reaction conditions used by these authors are different from the ones used in the present work (namely, the contact time, which was varied for a fixed temperature reaction, and the molar ratio H₂/hydrocarbon). Bearing this in mind, this study has shown, as mentioned above, that the better pillared vermiculites (VH200Al, VH400Al, and VH400Al–Zr) are less active than some zeolites (for instance H–ZSM-22) but with similar yields of C7 isomers and higher in selectivity.

Therefore, despite the “nonsteady” conditions under which the catalysts were evaluated, the results have a meaningful comparative value. Clearly, this study has shown that the better pillared vermiculites (VH200Al, VH400Al, and VH400Al–Zr) obtained by HTT present selectivities similar to those of their analogous Al-pillared vermiculites³³ and, although less active than some zeolites (for instance H–ZSM-22), their selectivities are also higher than the former ones.^{33–34}

On the other hand, Patriceon et al.³⁴ inferred from their results three behaviors in heptane hydroisomerization, and these differences seem to be strongly related to the porous structure of the solids. The open-structure solids lead to a low cracking yield; the more-restricted-structure solid gives more cracking. Low cracking yield observed in this study for all solids shows

that they are clearly secondary products of the reaction and may indicate the existence of open structure in all solids obtained.

Conclusions

Chemically modified vermiculites with Al and Al–Zr are obtained, which are very active catalysts in the hydroisomerization of heptanes. Such activity is related to the quantity of acid sites generated by each one of the treatments.

The hydrothermal treatment at 200 and 400 °C turned out to be very efficient in the permanent reduction of the layer charge density of the vermiculite without causing drastic changes in the crystalline structure. This method permitted us to obtain solids with a better distribution of pillars in the layers in between than those treated by the acid method, through which it is possible to sense that the charge reduction occurs in a more homogeneous way in the HTT. It may also be further improved.

This study has shown that the application of the hydrothermal treatment as a previous step to pillaring of the vermiculites, reported here for the first time, is a new route to obtain the porous material with a particular interest as heterogeneous catalysts, starting with mineral clays with a high density of charge.

Acknowledgment. The authors offer their gratitude to the SENA-COLCIENCIAS-UNIVERSIDAD NACIONAL DE COLOMBIA, for the financial support of the Project No. 1101-05-12412 (CT 00410 de 2002).

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