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Decane hydroconversion with Al–Zr, Al–Hf, Al–Ce-pillared vermiculites

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ABSTRACT

A series of vermiculites pillared with mixed precursors of Al–Zr, Al–Hf and Al–Ce were obtained from natural vermiculite subjected to a process of negative charge reduction through hydrothermal treatment. The catalytic activity of the solids evaluated in the decane hydroconversion, was superior to that of recognized pillared clays and comparable to those of very active catalysts such as zeolites USY. The distributions of profiles of the reaction products suggest that the porosity/pore architecture of the pillared vermiculites should be similar to that of ultrastable Y zeolites.

1. Introduction

The particular catalytic properties of pillared clays are related to their intrinsic characteristics, due to better exposure of their active sites by the presence of metallic oxides or "pillars" in the interlayer spaces, thus increasing the superficial area and the microporous volume of the material. On the other hand, the oxides or pillars may be converted into active sites which have different levels of acidity depending on their nature. Their catalytic potential has already been evaluated for a wide range of reactions [1–4], especially those requiring medium acidity of the sites and moderate temperature conditions.

Similarly, and with the purpose of understanding and optimizing the catalytic behavior of these solids, detailed studies have been devoted to the parameters involved during the synthesis, showing that one of the most relevant factors is the nature of the starting mineral. Clays with substitutions in the tetrahedral layer, *viz*. beidelite, saponite, and vermiculite, lead to more efficient Brönsted acid catalysts [5,6]. This phenomenon is directly related to the presence of active acidic sites associated with the formation of Si–OH···Al bonds in the tetrahedral layers of the material. Vermiculites with a high degree of Al for Si substitution in the tetrahedral layers [7], turn out to be very attractive solid acids with superior thermal stability compared to other similar clays [8], yielding materials with high potential for processes that require extreme reaction conditions.

Prior to pillaring, the low expansion capability of vermiculites, due to the high degree of Al^{3+} for Si^{4+} substitution and the resulting high concentration of negative charges in tetrahedral layers [9], has to be improved by means of charge reduction treatments, as a stage prior to the conventional pillaring process. Although various reports show that this objective is difficult to achieve [10,11], del Rey-Perez-Caballero et al. [7,12] have presented a procedure for the synthesis of pillared vermiculites (PILV's) and micas with $d_{0\,0\,1}$ spacings of 1.8 nm, through a charge reduction by washing the material with acid before pillaring it. Recently, alternative processes have been proposed such as the treatment of clay with ultrasound radiation in the presence of H_2O_2 [13] and the dealumination by means of thermal treatment with water vapor [14]. The latter allows materials with interesting catalytic characteristics to be obtained, without producing considerable structural changes in the clay [14].

The hydroconversion reaction of *n*-alkanes on one hand is useful for the development of bifunctional catalysts and has practical implications for processes such as hydroisomerization, hydrocracking, and catalytic dewaxing, while on the other hand it can be used as a test reaction to characterize the pore architecture of such catalysts. It is well-known that for catalysts with well-balanced acid metal function a typical product selectivity of exclusively alkanes is observed, resulting from the rate-limiting conversion of carbocation intermediates. A perfectly balanced catalyst does not show any formation of C_1 and C_2 hydrocarbons, usually stemming from hydrogenolysis reactions in the metallic phase, in terms of turnover numbers present in excess of the Brönsted acidity. In contrast, the pore architecture of a bifunctional catalyst will affect the product distribution, at the level of the degree both of the branching and the position of the branchings in the hydrocarbon chain, and consequently in the selectivity of the hydrocracked products [15].

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The catalytic behavior of vermiculite is illustrated in very few documents. Natural vermiculite has been reported as an acid catalyst in reactions such as the dehydration of 1-butanol and the dealkylation of cumene on acid-activated vermiculite [16]. On the contrary, the perspectives of pillared or modified vermiculite as catalysts was shown to be promising in reactions such as the hydroisomerization of *n*-octane where the maximum isomerization yield amounts to almost 90%, compared to 82% for zeolite HBeta [5]. The conversion of heptane studied on Al-vermiculite [17], titanium and sulfate modified vermiculite [18] and Al–, Al–Zr-vermiculite reached 97% isomerization conversion [14]. Other reactions such as the selective reduction of NO by ammonia on Al-vermiculite modified with Cu and Fe have been evaluated as well [19]. Recently the hydroconversion of decane has been explored on Al–Ce–PILV [20].

In the present work, a series of vermiculites with mixed pillars of Al–Zr, Al–Hf and Al–Ce, were obtained from natural vermiculite previously submitted to a process of negative charge reduction through hydrothermal treatment [14]. The potential of these catalysts is evaluated in the isomerization and hydrocracking of *n*-decane. The effect on the acidity and the porosity of the PILVs is analyzed when a second metallic cation of acidic nature is added to the polymeric aluminum solution. Details of the synthesis and characterization of the catalysts will be publisher later.

2. Experimental

2.1. Materials

The starting vermiculite (V) is a commercial mineral, from the region of Santa Marta, Colombia. The modifications were made on a fraction with a particle size of less than 150 μm, separated from the raw vermiculite by sieving without any further purification treatment. The cation exchange capacity of the material was 1.10 meq g^{-1}.

The structural formula of the mineral, determined by means of X-ray fluorescence [21], corresponds to:

$$[(Si_{3.04}Al_{0.92}Ti_{0.04})(Al_{0.11}Fe^{3+}{}_{0.35}Fe^{2+}{}_{0.07}Mg_{2.41}Mn_{0.003})O_{10}(OH)_2]\ Ca_{0.21}K_{0.05}Na_{0.10}$$

2.2. Charge reduction treatment

The starting material was subjected to hydrothermal treatment in the presence of water vapor for a period of 6 h at 400 °C [14]. The solid was charged in a fixed bed reactor (15 g of clay) and taken to the target temperature with a heating rate of 5 °C min^{-1}. A flow of nitrogen saturated with water vapor was generated through a thermostated saturator, keeping distilled water at the temperature necessary for obtaining a partial water vapor pressure of 75% in nitrogen, the steam contact time being 60 g g^{-1} h^{-1} (g water. g^{-1}catalyst. h^{-1}) [22].

With the aim of removing the extra-structural species generated, the sample was washed with 0.25 M aqueous HNO_3 (10 mL g^{-1} clay) under stirring for 1 h at 80 °C. The washed and dried solids were exchanged 4 times at 80 °C with 3 M aqueous NaCl solution, and then washed and dried again; this sample is labeled as V–THT.

2.3. Modification with Al–Zr, Al–Hf and Al–Ce

Polymeric Al–Me solutions (with Me = Zr, Hf or Ce) were prepared in order to supply 12 mmol (Al + Me) g^{-1} clay [7]. A 0.1 M Me aqueous solution from $ZrOCl_2$ or $HfCl_4$, was slowly added at room temperature to a 0.1 M $AlCl_3$ aqueous solution or of 0.1 M aqueous $Ce(NO_3)_3$ to 0.1 M aqueous $Al(NO_3)_3$ under stirring. After increasing the temperature of the Al–Me solution to 60 °C, the 0.2 M NaOH solution was added dropwise under vigorous stirring, using the necessary volume to arrive at a OH/Al molar ratio of 2. After the addition, the solution remained for 2 h at the same temperature.

Table 1
Ratio Al–Me (Me = Zr, Hf or Ce) for synthesis of pillared vermiculites from natural vermiculite after hydrothermal process

Sample (Me = Zr, Hf or Ce)	Al–Me mmol g^{-1} clay
Me0.5	11.5–0.5
Me1	11.0–1.0
Me1.5	10.5–1.5
Me2	10.0–2.0
Me4	8.0–4.0

After standing the pillaring solution for 36 h at room temperature, it was slowly added to a 2% wt clay suspension under vigorous stirring. The exchange occurred at 80 °C for four additional hours. The final clay suspension was aged for 12 h at room temperature. Afterwards, the excess salt was removed by washing it with distilled water. Finally, the materials were dried at 60 °C and calcinated at 400 °C for 2 h using a heating rate of 5 °C min^{-1}.

The Al/Me ratios used were obtained taking into account the optimal value of 12 mmol of metal g^{-1} of clay for the pillaring of vermiculite with aluminum [7]. The concentration of the second metal to achieve its probable insertion in the aluminum Keggin structure was low, to avoid disturbing the optimal formation conditions of the aluminum polymer [23].

The materials notation was done by using the nature of the second metal and its quantity added to the polymeric aluminum solution (Table 1). In this way, the sample notation Zr0.5 corresponds to a PILV sample modified with an Al–Zr solution with 11.5 mmol of Al and 0.5 mmol of Zr g^{-1} clay.

2.4. Characterization of pillared clays

X-ray diffraction (XRD) spectra of powder samples were measured on a Phillips PW1710 spectrometer with copper anticathode.

The elementary analysis of samples was performed with X-ray fluorescence (XRF) using a Phillips FRX 2400 spectrometer. In addition, the analysis of Hf and Ce was carried out with ICP spectrometry.

The cation exchange capacity (CEC) was obtained from the nitrogen content of clays previously exchanged with ammonium acetate solution, as determined by the micro-Kjeldahl method [24].

Absorption–desorption isotherms of nitrogen at the temperature of liquid nitrogen were obtained from nitrogen adsorption isotherms established at liquid nitrogen temperature, using a Micrometrics Tristar 3000 instrument on samples previously degassed at 200 °C for 6 h. The micropore volume and the surface area were established in accordance with the methodology proposed by Remy et al. [25] for the analysis of adsorption isotherms in pillared clays.

2.5. Catalyst evaluation via high-throughput experimentations

The hydroconversion of *n*-decane requires bifunctional catalysts with a correctly balanced metal/acid ratio [26]. In a first step, the solids were treated with an ammonium chloride solution at