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α-Pinene conversion by modified-kaolinitic clay

C. Volzone [a,*], O. Masini [b], N.A. Comelli [b], L.M. Grzona [b],
E.N. Ponzi [c], M.I. Ponzi [b]

[a] *CETMIC-Centro de Tecnología de Recursos Minerales y Cerámica-(CONICET-CIC), C.C. 49, Cno. Centenario y 506, (1897) M.B. Gonnet, Prov., Buenos Aires, Argentina*
[b] *INTEQUI (CONICET-UNSL), Facultad de Ingeniería y Ciencias Económico Sociales, 25 de Mayo 384, V. Mercedes, Prov., San Luis, Argentina*
[c] *CINDECA (CONICET-UNLP) calle 47 No. 257, (1900) La Plata, Prov., Buenos Aires, Argentina*

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Abstract

The isomerization of α-pinene using natural kaolinitic clay before and after different treatments was studied in this work. The kaolinite is a clay material constituted by phyllosilicate 1:1 layer (one sheet of tetrahedral silicon and one sheet of octahedral alumina). The clay was treated at different times using 6.0 N solution of sulfuric acid previous heating to 500 or 700 K. The materials were characterized by X-ray diffraction, by chemical analyses and acidity measurements. The catalytic reactions were carried out at 373 K in a reactor batch with condenser and stirrer. Samples were taken at regular intervals, and reactants and products were quantitatively analyzed with a gas chromatograph after separation of the individual compounds. Conversions of alpha pinene between 67 and 94%, and selectivities in camphene and in limonene of 65 and 23%, respectively, were obtained with the clay treated at different conditions. The structural and textural changes of the clay by the treatments influenced on catalytic reactions.

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Keywords: α-Pinene; Kaolinite; Clay materials; Camphene; Limonene; Conversion; X-ray diffraction; Acidity

1. Introduction

Recent studies about isomerization of α-pinene by super acid catalysts were reported by Severino et al. [1], Findik and Gündüz [2], Masini et al. [3], Allahverdiev et al. [4], López et al. [5], E. Ponzi et al. [6], M. Ponzi et al. [7], Comelli et al. [8,9], Grzona et al. [10]. Whereas, Rhodes and Brown [11], De Stefanis et al. [12], Moronta and Breen [13], Breen [14] and Volzone et al. [15] studied transformation reactions of terpenes using treated clay materials (acid clays, acid-treated polycation-exchanged clays and pillared clays). Acid montmorillonite is the smectite clay frequently used in studies for acid catalysis and it is not common to find papers about the use of acid kaolinitic clay. The main reason is that the montmorillonite shows different physicochemical characteristics respect to the kaolinite, where the first one is higher swelling, higher exchange capacity, higher surface area, etc. than kaolinite. Nevertheless, it is possible to obtain modified-kaolinitic after special treatments and then it is suitable for different applications similar to modified montmorillonite uses, e.g., gas retentions [16–19].

The kaolinite is a clay material constituted by phyllosilicate 1:1 layer with one octahedral sheet containing Al^{3+} ions and one tetrahedral Si^{4+} sheet. Generally, Al^{3+} replaces Si^{4+} in tetrahedral sheet, and Mg^{2+}, Fe^{3+} and/or Fe^{2+} replace Al^{3+} in octahedral sheet. These isomorphic substitutions result in a charge deficit in the octahedral and tetrahedral sheets and are balanced by adsorbed cations such as Na^+, K^+ and Ca^{2+} situated in interlayer position [20].

The aim of this work is to evaluate the influence of some characteristics of the treated kaolinitic clays on the catalytic α-pinene reactions.

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[*] Corresponding author. Tel.: +54 221 4840247/4840167; fax: +54 221 4710075.
E-mail address: volzcris@netverk.com.ar (C. Volzone).

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2. Experimental

2.1. Materials and methods

The kaolinitic clay material (kaolin) came from Chubut province, Argentina, and it was supplied by Piedra Grande S.A.M.I.C.A. y F. Kaolinite with small amount of illite, and quartz as impurity were the mineralogical composition of the kaolin (A). The illite, a clay mineral, is phyllosilicate 2:1 layer formed by one octahedral sheet between two tetrahedral sheets. The clay has been processed to <5 μm size fraction mainly to reduce associated quartz. The size distribution was confirmed by Sedigraph 5000 equipment.

The acid treatment on the clay was carried out with a 6.0 N solution of sulfuric acid at boiling temperature during 60 min. Afterwards, the solid was separated and washed with distilled water. The acid clay was dried in air, and then at 373 K before use. The samples used were called: A, A5-60 and A7-60, where the numbers 5 and 7 correspond to heated clay at 500 and 700 K, respectively, previous acid treatment.

The diffractograms of samples were obtained with an X'PERT system X-ray equipment using the PW3710 Electronic Control Unit with a Philips 3020 Goniometer, Cu Kα radiation at 40 kV and 20 mA and Ni filter. The chemical analyses of the samples were attained by inductively coupled plasma-emission spectrometry (ICP).

N_2 adsorption–desorption isotherms of samples were obtained at the liquid nitrogen temperature with a Micromeritics Accusorb instrument. The N_2 adsorption–desorption isotherms were performed at 77 K, on powder sample previously outgassed at 100 °C for 12 h.

The total acidity was determined from the amount of adsorbed ammonia using a thermobalance (Shimadzu model TGA 50). The samples were dried in a He flow (150 ml min^{-1}) by heating from room temperature up to 373 K at 20 degrees min^{-1} and then cooled in He flow to 328 K. For ammonia adsorption, the catalyst was exposed to an NH_3-He (3000 ppm) flow at 100 ml min^{-1}, until a constant weight was obtained.

FTIR spectra of the catalyst samples with adsorbed ammonia were used to determine the presence of Brönsted and Lewis acidities. The ammonia was adsorbed at room temperature by flowing pure ammonia at a rate of 15 $\text{cm}^3\,\text{min}^{-1}$ for 30 min over the sample placed in a cell. The sample containing the adsorbed ammonia was mixed with potassium bromide and the infrared spectrum was recorded using Brucker IFS66 FTIR equipment.

2.2. Reaction

The reaction was carried out in a glass reactor with three openings. In one of them, a coolant was placed for the steam condensation. The second one was used for withdrawal of samples by a micropipette. A thermocouple was placed in the third opening to measure the reaction temperature. The reactor was submerged in a thermostatic glycerin bath. The reaction mixture was stirred by a magnetic stirrer at a rate of 500 rpm. A 10 ml of α-pinene (98.7% purity of a racemic mixture provided by Derivados de San Luis company) was heated at 373 K and 100 mg of catalyst was added. A 100 μl of sample was extracted at different times (20, 40, 60, 120 and 180 min) for analysis.

The reaction products were analyzed by gas chromatography (Shimadzu model GC-17A) with a FID detector, using a J&W DB-1 60 m × 0.248 mm capillary column. N_2 was used as the carrier gas and the temperature was programmed from 348 to 473 K at a rate of 3 K min^{-1}.

3. Results and discussion

3.1. Characterization of acid clays

3.1.1. X-ray diffraction

Fig. 1 shows the diffractograms of the clay before and after treatment. Kaolinite and illite clays, and quartz as impurity constituted the kaolinitic clay. The intensity of the kaolinite peak corresponding to 0 0 1 reflection (basal spacing 7.16 Å (12.35°2θ)) decreased after treatments and was absent after 60 min acid treatment previous heating at 700 K (A7-60). In last sample also all reflections of kaolinite clay disappeared. The illitic clay component remained in both modified-kaolinitic materials (A560 and A760), however the 0 0 l reflection was smaller and it shifted from 9.97 Å (8.86°2θ) to 10.23 Å (8.84°2θ) (Fig. 1), indicating that the interlayer spacing was slightly expanded.

3.1.2. Chemical analysis

Table 1 shows the chemical composition of the original kaolin before and after acid treatments. The acid treatment on heated kaolin removed the interlayer cations of the kaolinite,

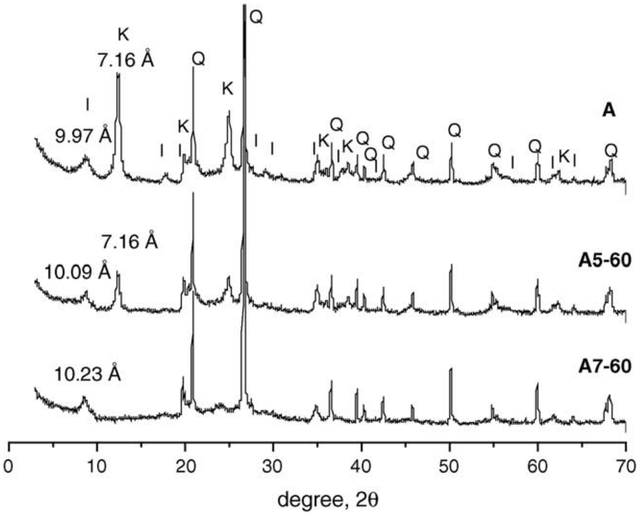

Fig. 1. X ray diffraction of the raw kaolinitic clay (A) and after thermal-acid modified-kaolinitic clays (A5-60 and A7-60). K, kaolinite; I, illite; Q, quartz.

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