

Isomerization of 1-butene catalyzed by ion-exchanged, pillared and ion-exchanged/pillared clays

Alexander Moronta^{a,*}, Tania Oberto^a, Gabriela Carruyo^a, Roger Solano^a,
Jorge Sánchez^a, Eduardo González^a, Lenin Huerta^b

^a*Instituto de Superficies y Catálisis, Facultad de Ingeniería, Universidad del Zulia, Maracaibo 4003, Venezuela*

^b*Laboratorio de Espectroscopia Molecular y Atómica, Facultad Experimental de Ciencias, Universidad del Zulia, Maracaibo 4003, Venezuela*

Received 29 June 2007; received in revised form 27 September 2007; accepted 29 September 2007

Available online 5 October 2007

Abstract

A natural smectite clay (STx-1, USA) was ion-exchanged with Al, Fe or pillared with polyoxocations of the same metals. Samples were also prepared by combining these two treatments. The prepared solids were characterized by X-ray fluorescence (XRF), X-ray diffraction (XRD), thermogravimetric analysis (TGA), TPD of ammonia and N₂ adsorption. The catalytic activity was evaluated by using the isomerization of 1-butene at 300 °C. XRF results showed an increase in the content of Al or Fe thus giving evidence that these metals were effectively exchanged or deposited over the starting material. Al- and Fe-pillared clays showed a significant increase of the surface area. Ion-exchanged clays showed similar surface areas to that of the starting clay. From XRD patterns only the Al-pillared clay gave an increase of the *d*-spacing. The synthesized pillared clays were superior catalysts for the isomerization of 1-butene than the ion-exchanged clays; the ion-exchanged/pillared clays showed a similar catalytic behavior as that of the parent pillared clays. The Al-pillared clay was the best catalyst for the reaction and its efficiency was related to the high acidity and high surface area.

© 2007 Elsevier B.V. All rights reserved.

Keywords: 1-Butene; Clays; Ion-exchanged clays; Isomerization; Pillared clays

1. Introduction

Clay minerals represent a convenient source to prepare potential catalysts because of their environmental compatibility, low cost, high selectivity and reusability. Natural occurring clay minerals have a poor ability to catalyze organic reactions. Nevertheless, the surface properties of these solids can be modified by different activation methods to produce catalysts of improved surface area, porosity, acidity and thermal stability. The most frequent used modification techniques include acid activation, cation exchange and pillaring among others.

The cations in the interlaminal region of natural clays are hydrated cations of Na⁺, Ca²⁺ and occasionally K⁺. These cations can be exchanged with other ions when the clay mineral

is brought into contact with its salt solutions. The most frequent used metal cations in the preparation of cation-exchanged clays of catalytic interest are Al³⁺, Fe³⁺, Cr³⁺ [1–3], Zn²⁺, Mg²⁺, Ni²⁺, Cu²⁺ and Co²⁺ [4–6]. They are known to be good catalysts because of the dissociation of water molecules by generating Brønsted acidity. However, these catalysts dehydrate and undergo layer collapse at high temperatures. A way of overcoming this disadvantage is to incorporate large polyoxocation species into the interlayer region of expandable clay minerals followed by calcination; this process is known as pillaring. In addition to the high thermal stability, high surface area and structural integrity, the pillars themselves may be catalytically active. A variety of inorganic metal oxides: Al₂O₃ [7], ZrO₂ [8], TiO₂ [9], Cr₂O₃ [10] and Ga₂O₃ [11], and mixed metal oxides: Al₂O₃–Ga₂O₃ [12] and Al₂O₃–SiO₂ [13,14] have been successfully pillared in smectites.

Skeletal isomerization of linear butanes to isobutylene is an interesting reaction from industrial point of view, since the product is used in the production of octane enhancing fuel additives. Zeolites and microporous molecular sieves, such as

* Corresponding author. Tel.: +58 261 7598791; fax: +58 261 7598697.

E-mail addresses: amoronta@cantv.net, amoronta@luz.edu.ve (A. Moronta).

ZSM-22 and SAPO-11, are good catalysts for the selective skeletal isomerization of *n*-butanes [15]. This is due to the sufficient Brønsted acid function and shape selective pore structure. The products distribution of the catalytic 1-butene isomerization is widely utilized to evaluate the acidity of heterogeneous catalysts. The products distribution is divided into the following groups: (a) double bond isomerization (*cis*-2-butene and *trans*-2-butene); (b) skeletal isomerization products (isobutene); (c) hydrogenated products (*n*-butane and isobutene); (d) cracking products (C4-) (methane, ethane, ethylene, propane and propene); (e) surface carbon residues and higher molecular weight compounds. Moronta et al. [16] have reported that 1-butene gives good yield to *cis*- and *trans*-2-butene over acid-activated organoclays when they are first exchanged with the tetramethylammonium (TMA⁺) and then acid activated (maximum conversions of 70%), whereas a reduction in the catalytic activity was observed by employing the inverse procedure (maximum conversions of 51%). This behavior was due to the fact that the organocation content was higher than the proton population in the lamellar region. In a more recent study, Moronta et al. [17] carried out the isomerization of *cis*-2-butene and *trans*-2-butene over two commercial acid-activated clays exchanged with different cations (Al³⁺, Cr³⁺, Fe³⁺ and Ni²⁺). The order of activity for acid- and the different exchanged forms was H⁺ > Al³⁺ ≈ Ni²⁺ > Cr³⁺ > Fe³⁺ with a maximum yield of 75% for isomerization of *cis*-2-butene and 53% for isomerization of *trans*-2-butene. However, there is not literature report on the isomerization of 1-butene over ion-exchanged/pillared clays. Therefore, the objective of this work was to study the effect of the ion-exchange activation with Al³⁺ and Fe³⁺, the pillaring with oxides of these metals and the combination of these two treatments in a natural clay to obtain potential acid catalysts for the isomerization of 1-butene. This should improve the surface acid properties without affecting the laminar structure of the starting material.

2. Experimental

2.1. Materials

A Ca-montmorillonite (STx-1, dioctahedral bentonite of low iron content and referred to hereafter as ST, Texas, USA) obtained from The Clay Mineral Repository of the Clay Minerals Society was used as received. The cation exchange capacity of STx-1 is 0.84 mequiv./g. For comparison purposes, two zeolites Z-443 (Si/Al = 38.7) and Z-427 (Si/Al = 3.5) supplied by the French Petroleum Institute and a high-purity γ -alumina (Rhône-Poulenc G.F.S.C) were used.

2.2. Catalyst preparation

The aluminum complex was prepared by employing the procedure described by Bradley et al. [18], while the iron complex was obtained according to the method reported in Starke [19], and modified as followed:

A 250 g portion of Fe(NO₃)₃·9H₂O (Merck, 99%) was mixed with 150 ml of ethanol, then 450 ml of acetic anhydride were

added drop-wise in constant stirring. The mixture was heated gently at 65 °C to initiate the reaction and placed in an ice bath afterwards. The resulting precipitate was left to stand for 17 h, separated by filtration and washed five times with acetic acid and three times with petroleum ether. Finally, the complex was dried in air flow at room temperature.

ST was washed three times with 30 ml of a 0.5 M aqueous solution of the desired metal cation [AlCl₃·6H₂O (Aldrich, 98%) or Fe(NO₃)₃·9H₂O] to convert them into 100% Mⁿ⁺-clays. The clay suspensions were stirred overnight at room temperature, then centrifuged and the resulting ion-exchanged clays were washed thoroughly with de-ionized water until a low conductivity was detected (<30 μS). Finally, the ion-exchanged clays were dried in an oven at 110 °C overnight, ground and stored in sample vials. Samples obtained by this procedure are designated as ST-Al and ST-Fe.

The pillared clay (STpAl and STpFe) forms were obtained by ion-exchange as follows: a solution containing the metal complex was added drop-wise to 1 wt.% clay suspension in constant stirring at room temperature for 2 h. The stirring was maintained for two additional hours and then stopped for 1 h to allow sedimentation. The solids were filtered, washed with de-ionized water, dried at 120 °C for 1 h and finally calcined at 400 °C for 3 h.

Ion-exchanged/pillared clays were prepared by combining the two experimental procedures described above. Firstly the pillared forms were obtained and then exchanged with the corresponding metal solution. These samples are identified as: Al/STpFe and Fe/STpAl.

2.3. Characterization techniques

The surface area and porosity of the starting ST clay and the catalysts prepared were measured by nitrogen adsorption isotherms at 77 K, conducted on a Micromeritics Gemini 2375 porosimeter. Samples were outgassed at 300 °C and 0.13 Pa for 2 h before the measurements. The surface area (S_{BET}) was calculated using BET method. The total pore volume (V_t) was estimated from the amount of adsorption at a relative pressure close to unity. The micropore surface area (S_{micro}) was determined by the *t*-plot method. The mesopore surface area (S_{meso}) was calculated by subtracting the S_{micro} value from that of S_{BET} .

The bulk chemical composition was measured by XRF utilizing a Shimadzu EDX-700 HS. XRD patterns of the clays were obtained in a Philips PW 1120 diffractometer, operating at 40 kV and 20 mA at a scan rate of 2°/min, using Co K α radiation.

The acidity was estimated by exposing the samples (previously dried a 120 °C overnight) to cyclohexylamine (Reagent grade) for periods in excess of 48 h. A Mettler TG50 thermobalance equipped with a TC11 processor was used to determine the weight loss between 240 and 350 °C and then to monitor the acidity in terms of mmol of cyclohexylamine desorbed, on the assumption that one molecule of this base interacts with one protonic center [6]. For this determination, a 10–15 mg portion of sample was weighed into a ceramic crucible and heated from 35 to 800 °C at 20 °C/min under a

Download English Version:

<https://daneshyari.com/en/article/43205>

Download Persian Version:

<https://daneshyari.com/article/43205>

[Daneshyari.com](https://daneshyari.com)