

Alkylation of benzene with olefins in the presence of zirconium-pillared clays

S.R. Guerra^a, L.M.O.C. Merat^{a,b}, R.A.S. San Gil^b, L.C. Dieguez^{a,*}

^aNUCAT/PEQ/COPPE, Universidade Federal do Rio de Janeiro, Caixa Postal 68502, CEP 21945-970, Rio de Janeiro, Brazil

^bInstituto de Química, Universidade Federal do Rio de Janeiro, Brazil

Available online 25 February 2008

Abstract

Purified Brazilian montmorillonite and Wyoming clays intercalated with zirconium acetate solutions with different Zr/clay ratios were pillared and characterized by X-ray fluorescence and diffraction (XRF, XRD), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), N₂ adsorption and temperature-programmed desorption (TPD) of NH₃. The intercalation time was followed by XRD analysis. The pillarization resulted in the displacement of the low-angle diffraction pattern, indicating structural modification of the samples. The Wyoming clay presented a significant increase of the surface area for the ratio of Zr/clay = 10 (from 29 to 217 m²/g). The Brazilian clay, under the same pillarization conditions as the Wyoming clay, showed an increase of the surface area from 108 to 206 m²/g. As a result of the thermogravimetric analysis, the Brazilian clay showed a smaller thermal stability than the Wyoming natural clay. The TPD of NH₃ analyses showed similar amounts of acid sites for K10 commercial acid clay, Brazilian and Wyoming-pillared clays with Zr/clay ratio of 10. The K10 commercial clay had greater activity and stability for the isomerization of 1-butene than the Brazilian and Wyoming-pillared clays. The alkylation reactions of benzene with 1-hexene, 1-octene and 1-dodecene showed greater selectivity for monoalkylated products for K10, and similar selectivities for the Brazilian and Wyoming-pillared clays, when using the olefin with longer hydrocarbon chain. As the hydrocarbon chain length was decreased, the selectivity for monoalkylated products was increased when using the Wyoming clay as compared to the Brazilian clay.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Zr-pillared clays; K10; 1-Butene isomerization; Alkylation; 1-Hexene; 1-Octene; 1-Dodecene

1. Introduction

The search for catalysts that present high activity, low deactivation and thermal stability have motivated the study of new materials using natural clays. In some cases the clays present activity in their raw form, but it is usually necessary to perform a chemical activation step, based upon their ionic exchange capacity. Among the predominantly used natural clays, the smectites are useful for producing active materials with interesting physico-chemical properties, due to their potential for modifying the interlayer distance through the exchange of compensating cations (Na⁺, Ca²⁺ and others) by hydroxonium ions (as in the case of K10 and other commercial acid clays), or cations and polyoxocations (intercalated and pillared clays).

Pillared clays are layered materials prepared by the exchange of compensating cations for oligomeric or polymeric hydroxymetals, followed by calcination. The calcination promotes the dehydration and dehydroxylation of the polycations, with the formation of metal oxides that act as pillars, maintaining the separation between the layers with the appearance of interlayer and interpillar spaces with molecular dimensions. Reviews on the subject have been published by several authors [1–4]. The literature describes the use of various cations as intercalation agents: Al, Ti, Zr, La and others. Zirconium compounds have been used to form stable pillars in smectite interlayers, resulting in an increase of the surface area, stability, acidity and shape selectivity comparable to zeolite structures [5–9]. Nickel catalysts supported on zirconium-pillared clays were tested in catalytic reforming reactions [10], while copper catalysts supported on those clays were employed for methanol dehydrogenation [11]. In addition, the alkylation of phenol with methanol using zirconium-pillared clays, by using clays doped with Ni²⁺ was studied [12].

* Corresponding author.

E-mail address: lidia@peq.coppe.ufrj.br (L.C. Dieguez).

The alkylation of aromatic hydrocarbons with olefins is an important industrial process for the production of ethylbenzene, cumene and linear alkylbenzenes (LABs). In a previous study, Guarino [13] indicated the importance of the zirconium cation in the intercalation of clays in order to obtain monoalkylated benzene products. However, when the results were compared to those obtained with aluminum, the catalytic performance with zirconium was lower. Furthermore, a dealumination was observed when zirconium chloride or zirconium oxychloride solutions were employed as the zirconium source. The low selectivity noticed for zirconium-intercalated clays was attributed to the microporosity, which may have hampered access of the olefin to the active sites [14].

The purpose of the present work is to prepare and characterize Brazilian and Wyoming zirconium-pillared clays, by using zirconium acetate as Zr precursor, in order to minimize dealumination of the clay structure. In addition, the work also intends to compare the properties of the active sites to the catalytic performance of these materials for the alkylation of benzene with olefins of different chain lengths, in order to evaluate the effect of microporosity on the activity and selectivity.

2. Experimental

2.1. Preparation

Two sodium montmorillonites were used: the Brazilian bentonite from Campina Grande, Paraíba (named F), with a cationic exchange capacity (CTC) of 106 mequiv./100 g of clay; and a clay from Wyoming (named W), USA (CTC = 76 mequiv./100 g and 4.3% Fe₂O₃). The Brazilian clay was fractionated by sedimentation (<2 μm), purified (named FAP) for the elimination of organic matter, and carbonates, and also for the reduction of iron structural content, which decreased from 14.2 to 12.7% Fe₂O₃. The aqueous suspensions with 1% solid content were treated with a solution of zirconium acetate (0.1 mol L⁻¹) at 298 K, where the Zr/clay ratio was varied: 1, 5 and 10 mmols of zirconium per gram of clay. The intercalation time was studied, for the Zr/clay ratio of 10, from 2 h to 6 days. After the intercalation period, the samples were dried at 333 K and pillared at 773 K for 2 h. The K10 commercial acid clay was used as a reference.

2.2. Characterization

The chemical analyses were determined by X-ray fluorescence (XRF) using a Rigaku RIX 3100 equipment.

The X-ray diffraction (XRD) was used to follow the d_{001} basal spacing after intercalation and pillarization. The analyses were performed on a Rigaku equipment, DMax and Miniflex (fix gap) models, equipped with a copper tube. The X-ray slides were prepared by oriented slide and powder methods. The oriented slide method is recommended when one intends to obtain rising values of the d_{001} main peak and d_{002} and d_{003} secondary peaks, and consists of preparing a varnish of the suspension in the slide. The powder method is the most

traditional used for the X-ray diffraction of solid samples, by which the material is macerated in a mortar and dispersed on a glass slide with the proper furrow.

The decomposition of the Zr polycation precursor inside the interlayer space of the clays and the thermal stability of the F and W raw samples were analyzed by TGA/DTG methods using a Rigaku Thermal Analysis Station TAS100 equipment. The samples were heated from 298 to 900 K (rate 10 K/min) under a 17% O₂/N₂ (60 cm³/min) mixture flow. A sample of γ-Al₂O₃ was used as reference.

The textural characterization was performed by an accelerated surface area and porosity (ASAP) equipment from Micromeritics (model 2000) for the determination of surface area (BET), microporous and the total porous volume. The samples were pre-treated in situ under vacuum at 373 K for 24 h. After the vacuum treatment the analysis was performed through adsorption and desorption isotherms of N₂ at 77 K.

X-ray photoelectron spectroscopy (XPS) of the Zr-pillared clays was performed with a PHI (model 1257) spectrometer using Al Kα (1486.6 eV). The pressure in the analysis chamber was kept at 10⁻⁹ Torr. A hemispheric analyzer PHI model 10-360 was used to select the energy of the electrons (46.95 eV). The binding energies of O 1s, Al 2p, Si 2p and Zr 3d were referred to the C 1s peak, established at 284.6 eV. The XPS atomic ratios (Zr/Si + Al) were calculated by using Zr 3d, Si 2p and Al 2p peak areas considering the sensitivity factors.

The NH₃ desorption analyses were performed with a Micromeritics equipment (model 2900), connected to a mass spectrometer with a Balzers quadrupole. The procedure consisted of drying the sample under helium at 453 K for 1 h. The NH₃ adsorption was performed in a flow of 4% NH₃/He at 423 K followed by He flow at the same temperature for 30 min. The NH₃ desorption was performed by heating the sample to 873 K (12 K/min) and following the mass signal of NH₃ (m/e) = 15 until complete desorption.

2.3. Catalytic tests

The pillared clays and the commercial acid were tested in the isomerization of 1-butene and also in the alkylation of benzene with 1-hexene, 1-octene and 1-dodecene. The experimental conditions of the reactions were adjusted to eliminate diffusional effects.

The isomerization of 1-butene was performed at 573 K, at atmospheric pressure, with a pre-treatment of 100 mg of catalyst at 623 K for 2 h under a flow of N₂. A mixture of 5.2% 1-butene/N₂ with a spatial velocity of 0.08 h⁻¹ was used. The activity and selectivity were evaluated for time of stream of reactant up to 20 h. The products were analyzed in line by an INTRALAB gas chromatograph (model 3300) equipped with a flame ionization detector and a capillary column of Al₂O₃/KCl (60 m length, 0.32 mm diameter).

The benzene alkylations with 1-hexene, 1-octene and 1-dodecene were performed in a glass batch-slurry reactor at 353 K, at atmosphere pressure, with magnetic stirring for a reaction time of 6 h. The reactions used 100 mg of catalyst previously dried for 22 h at 353 K and a mixture of 10 mL of

Download English Version:

<https://daneshyari.com/en/article/58270>

Download Persian Version:

<https://daneshyari.com/article/58270>

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