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α-Pinene isomerization to camphene
Effect of thermal treatment on sulfated zirconia

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Abstract

The isomerization reaction of α-pinene produces bicyclic and monocyclic compounds and other products. The purpose of this study is to investigate the influence of the pre-treatment temperature of the catalyst on the concentration of Lewis and Brönsted acid sites and the activity and selectivity of the catalyst. Catalyzed reactions in heterogeneous and homogeneous phases were performed. In heterogeneous reaction, sulfated zirconia (SZ) and pre-treated SZ catalyst at several temperatures were used. The thermal treatment affects the ratio between Brönsted and Lewis sites. Results were contrasted with those obtained with SZ catalyst without thermal treatment. In homogeneous reaction the catalyst is sulfuric acid, and in the reaction medium Brönsted sites are only present coming from the H^+ of the acid. The ratio between bi/monocyclic compounds for H_2SO_4, SZ catalyst and pre-treated catalyst at several temperatures, SZ250, SZ350 and SZ500, varies between 0.4 and 4.3. It can be observed that there exists an optimal thermal treatment where the ratio is higher. FT-IR spectra of adsorbed pyridine on catalysts pre-treated thermally show the presence of Lewis and Brönsted acid sites. The amount of acid sites was determined by TPD of adsorbed pyridine.

Keywords: α-Pinene isomerization; Sulfated zirconia; Camphene

1. Introduction

The α-pinene isomerization in presence of acid catalysts occurs by a mechanism in parallel, where, on one hand bicyclic compounds are obtained as camphene, tricyclene, bornylene through a cycle rearrangement, and on the other hand monocyclic compounds as limonene, terpinolene, α- and γ-terpinene are obtained by means of the rupture of one of the rings (Scheme 1). The isomerization reaction is developed in presence of strong acid catalysts, where the catalyst acidity has a strong effect on the activity and the camphene yield. Camphene is used in the manufacture of camphor and its related compounds.

Zeolites, clays, and different oxides have been used in this reaction [1–14]. Our group reported previously the α-pinene isomerization on catalysts of sulfated zirconia and sulfated zirconia modified with the addition of Fe and Mn, zirconia with molybdate and zirconia with wolframate, kaolinitic and bentonitic clays [15–18].

In the isomerization of α-pinene the activity is associated with the catalyst acidity while the type of active sites (Brönsted or Lewis) and their strength affect the selectivity to bicyclic and monocyclic products.

Severino et al. [2] studied the α-pinene isomerization reaction catalyzed with zeolites, and they state that Lewis acid sites (weaker than Brönsted sites) are beneficial for the formation of bicyclic compounds, while Brönsted sites are the responsible for the formation of monocyclic compounds.

Yadav et al. [13] studied the reaction catalyzed by a montmorillonite pre-treated with sulfuric acid. They reported α-pinene conversions of 96% with selectivity for camphene ranging from 39 to 49%. The production of monoterpenes is related with the concentration of sulfuric acid, thus, concentrations between 1 and 4N produce principally limonene, while concentrations between 5 and 9N produce α-terpinene. The highest conversions and selectivities in camphene were obtained at 150 °C.

De Stefanis et al. [1] compared the α-pinene isomerization in mesoporous solids and found that the reaction is influenced by the solid acidity more than by the accessibility of reagents to the pores.

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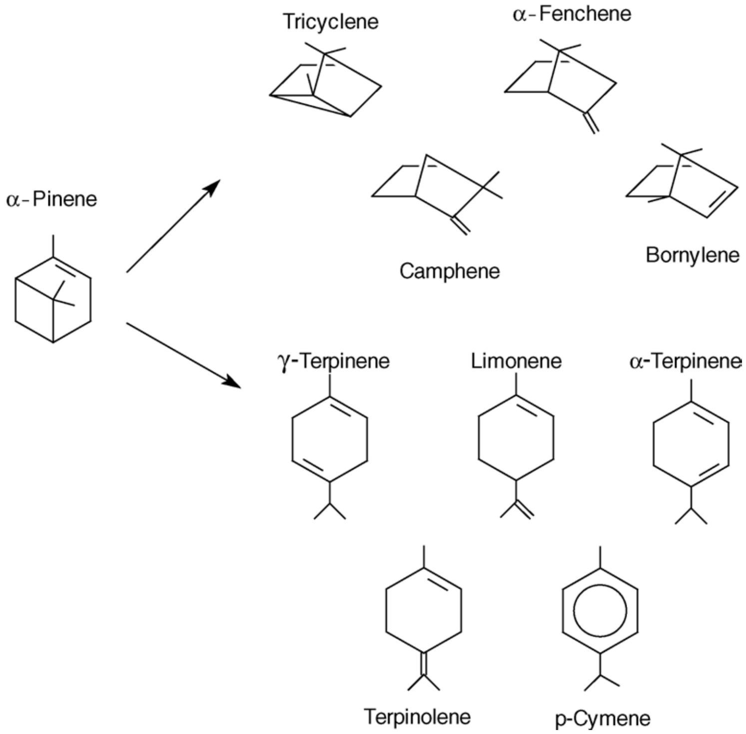

Scheme 1. Involved compounds in the α-pinene isomerization.

Encormier et al. [11] studied the catalyzed reaction by sulfated zirconia and found that at low S loads, weak acid sites are formed favoring the camphene formation while that at high loads, strong acid sites are formed favoring the limonene formation.

Although it is clear that weak acid sites direct the reaction toward the camphene obtention and strong acid sites direct the reaction toward the limonene formation, there exists controversy about the site type that influences on the catalyst activity. Sulfated zirconia has been widely studied since it is able to catalyze the isomerization of alkenes of short lineal chain at temperatures relatively low. The sulfated zirconia is very sensitive to preparation conditions and to the activation process used before reaction. The activation temperature plays a very important role in the acidity determination of the catalyst due to its hygroscopic properties and influences on the reaction selectivity.

Studies performed by different authors Hammache and Goodwin Jr. [19], Gonzalez et al. [20] show that the Brönsted/Lewis acid site ratio (B/L) decreased with the increase in drying temperature as the Brönsted acid sites were converted to Lewis acid sites upon dehydration.

Although several works using sulfated zirconia in different reactions have been published, the role of active sites is not even clear. Several intents have been carried out in order to try to establish models that explain the behavior of these catalysts.

The model of Morterra et al. [21] describes the formation of Lewis sites produced by the highly covalent character of the sulfate ion and the formation of the Brönsted acidity as consequence of the interaction of water molecules with these sulfates.

Arata and Hino [22] propose a structure where the sulfate is bonded to two zirconium atoms and suppose that the Brönsted acidity is produced by the attack of water molecules that behave as weak base on Lewis acid sites.

Clearfield et al. [23] propose a model (Scheme 2) based on the supposition that the dominant species is the bisulfate ion when the catalyst is prepared with sulfuric acid, thus forming the species I. The bisulfate ion can react by heating with an adjacent hydroxyl group generating Lewis acid sites, species II, or the water is freed from two neighbor hydroxyl groups maintaining intact the bisulfate ion structure, species III, and then generating Brönsted acidity. This acidity is produced by the fact that Lewis sites neighbor to the S–O–H group strongly attract electrons, weakening the union and facilitating the loss of a H^+ (Scheme 3).

Babou et al. [24] suppose the existence of three types of sites, L_1 assigned to Zr^{4+} atoms of zirconia support, L_2 and B that are related with the adsorbed sulfate species on the surface. By means of outgasing at increasing temperatures, they find that L_1 and B sites decrease with the temperature increase, while L_2 suffer little variation with respect to the same treatment, thus concluding that these last ones are the strongest ones. These authors propose that there exist different sulfate species adsorbed on the surface, generating different types of sites, thus (SO_3)ads generates L_2 sites while (H_2SO_4)ads, $(-HSO_4)$ads and (H_3O^+)ads generate Brönsted sites. The two first Brönsted sites are converted into Lewis L_2 sites by means of the thermal treatment. Hammache and Goodwin Jr. [19], Comelli et al. [25] found that sulfated zirconia presents a maximum activity in the *n*-butane isomerization reaction when it is pre-treated between 500 and 520 °C.