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Synthesis of camphene from α-pinene using SO_3^{2-} functionalized MCM-41 as catalyst

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Abstract

MCM-41 and Aerosil-200 functionalized with different quantity of SO_3^- groups were used as catalysts for the heterogeneous synthesis of camphene from α-pinene. The characterization of the catalysts was made by thermodesorption of NH_3 and physisorption of nitrogen. Three types of acid sites were found on the functionalized MCM-41, whereas on Aerosil-200 mainly strong acid sites were found. The conversion of α-pinene increased with the quantity of medium strength acid sites. The highest conversion was 100% with yield to camphene of 39.3% for catalyst with the higher content of SO_3^-. The highest yield to camphene was 42.2% with a conversion of 95% and was reached for moderate acid treatment of catalyst. The Aerosil-200 based catalyst did not show conversion of α-pinene. Other terpenes as limonene, terpinolene and δ-terpinene were obtained as by products.

Keywords: MCM-41; Sulfonic acid; Pinene; Camphene

1. Introduction

α-Pinene is obtained as byproduct from cellulose pulp industry as sulfated turpentine, being its main application as solvent and precursor of chemicals of higher commercial value. Camphene is one of those chemicals, which is attractive by its uses on pharmaceutical and cosmetic applications. By the 1950s, camphene was obtained from pinene by a two-step path; first bornyl chloride was obtained by treating pinene with hydrochloric acid, then a metallic salt of carboxylic acid was used to transform bornyl chloride to camphene [1]. Many efforts had been made in order to obtain camphene from α-pinene by a simple one-step process. One of the best results on the isomerization of α-pinene was reported by Findik and Gündüz [2] who obtained a yield to camphene of 43% using clinoptilolite as catalyst. In a previous work (Chimal-Valencia et al. [3]), we used ion exchange resins with surface sulfonic groups as catalysts for the same reaction, nevertheless the use of Amberlyst is limited, since its low thermal stability, limits the reaction temperature to a maximum of 140 °C. The yield to camphene reached using this commercial catalyst was near to 40% with reaction temperatures lower than those reported by Findik, with equivalent reaction times. Other terpenes are obtained during the syntheses of camphene [3]. Main byproducts obtained with the acidic isomerization of α-pinene are terpinolene and limonene (Fig. 1).

Considering that silica based mesoporous materials as MCM-41 have excellent properties as support for catalyst due to high surface area, narrow pore size distribution, and pore diameter which let the access of different molecules inside of the channels, many attempts have been made to modify the surface or the structure of MCM-41 in order to obtain different catalytic properties. A path for the activation of the surface of MCM-41 is the modification of surface to change the inert surface nature to acidic. Rác et al. [4] treated the surface of MCM-41 to obtain Brönsted type acid sites by means of anchoring sulfonic groups on the surface of the silica. The availability of such acid sites should be equivalent to the structure of the sulfonic resin with the advantage of having better mechanical properties and chemical stability to the solvents, favoring with this the recycling of the catalyst.

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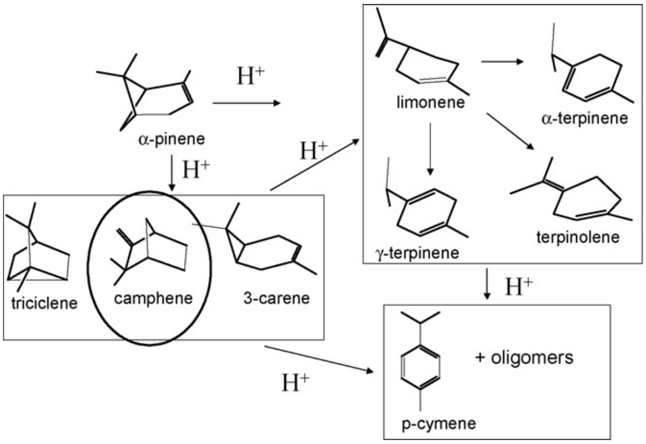

Fig. 1. Scheme of the α-pinene isomerization in acidic media.

On the present work MCM-41 and Aerosil-200 were modified to anchor sulfonic groups on the surface and provide the silica base material with Brönsted acid properties. The obtained catalysts were tested for the isomerization of α-pinene to camphene.

2. Experimental

Ammonium hydroxide 28–30% and hydrogen peroxide 30% were provided by Fagalab S.A., cetyl trimethyl ammonium bromide (CTAB) and 3-mercaptopropyltrimetoxy silane (MPTS) were from Sigma–Aldrich Co., Tetra ethyl ortho silicate (TEOS) was from Alfa Aesar, sulfuric acid was J.T. Baker, and Aerosil 200 was provided by Degussa, α-pinene was 93% pure and was supplied by COPAMEX S.A. de C.V. The substances were used as provided with no other purification.

2.1. Synthesis and functionalization of MCM-41

The MCM-41 was prepared according with the next method. A mixture containing 720 mL of NH_4OH, 1080 mL of distilled water and 8 g of CTAB was kept under magnetic stirring for 30 min, then 40 mL of TEOS were added drop by drop in to the previously prepared mixture maintaining the stirring. The thus obtained gel was kept at ambient conditions during 48 h. Afterwards, the solids were filtered, dried overnight at room temperature and calcined to 550 °C for 3 h in air.

MCM-41 and Aerosil-200 were modified following the method reported by Van Rhijn et al. [5]. Two grams of the silica base material were suspended in 125 mL of toluene in presence of different amount of MPTS as shown on Table 1. The suspension was magnetically stirred and maintained under reflux by 4 h. The solid obtained was filtered, washed with chloroform and dried. Each solid was treated for 8 h with a solution containing 10 mL of hydrogen peroxide 30% and 30 mL of methanol, filtered, washed with distilled water and dried overnight at room temperature. Finally, each solid was suspended 4 h in 50 mL of H_2SO_4 0.1 M, filtered, washed with distilled water and dried at 100 °C for overnight. Each catalyst was labeled depending on the silica material and the quantity of MPTS used as shown on Table 1 and stored on a sealed vial until its use.

Table 1
Quantity of 3-mercaptopropyltrimethoxysilane (MPTS) used for the acid-functionalization of silica support

Name	Support	Type of acid treatment	Quantity of MPTS used (g/g of support)
MCM41-T1	MCM-41	Low	0.53
MCM41-T2	MCM-41	Medium	1.06
MCM41-T3	MCM-41	High	1.59
A200Ac	Aerosil-200	–	0.18

2.2. Catalysts characterization

The acid sites per gram of each catalyst were quantified by thermal desorption of NH_3 in a Micromeritics Autochem 2910 analyzer. The catalysts were saturated for 2 h with 50 mL/min of a mix 17% NH_3–He at room temperature. The physisorbed material was cleaned using helium at 50 mL/min at ambient temperature. The chemisorbed NH_3 was desorbed using helium as carrier gas at 50 mL/min and heating rate of 10 °C/min, from ambient temperature to 210 °C. The surface area and diameter pore distribution were measured by nitrogen absorption using BET and BJH methods, respectively, in a Quantachrome Autosorb 1c equipment. Chemical analysis was performed by Energy dispersive spectroscopy (EDS) in a Jeol JSM-5800LV scanning electron microscopy equipped with a EDAX DX Prime EDS detector.

2.3. Isomerization of α-pinene

The isomerization reactions were made in a 250 mL glass reactor provided with magnetic stirrer, sampling port, heating mantle and condenser. A typical experiment was as follow: 50 g of α-pinene were loaded in to the reactor, stirred and heated up to the boiling point (145–150 °C). Once the desired temperature was reached, one gram of the catalyst was loaded into the reactor to start reaction. The reaction products were analyzed by gas chromatography taking samples at 5, 10, 30, 60, 120 and 240 min after adding the catalyst. Samples were cooled to halt the reaction and the compounds present in the samples were identified by analysis in a Thermofinigan GC Top 8000/ Voyager MS gas chromatograph/mass spectrometer system. The column used was an All Tech AT-5 capillary column with 30 m of length 0.25 mm of internal diameter. The temperatures of injector and transference line were maintained constant at 250 °C. The initial temperature of the furnace was maintained at 60 °C by 3 min, then it was increased at rate of 15 °C/min up to 150 °C, where stayed by 1 min. Finally, temperature was increased at a rate of 15 °C/min up to 250 °C and this temperature was maintained 1 min. Once identified, the total content of each specimen was quantified in a Perkin-Elmer Auto-System XL gas chromatograph, equipped with FID detector, and the same chromatographic method and column used for CG/MS study was used for quantitative analysis.