

Production of Camphene by Isomerization Reaction on Sulfated ZrO₂

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Abstract The kinetics of camphene production in liquid phase from α -pinene was experimentally determined in an isothermal batch reactor. To this end, a sulfated ZrO₂ catalyst was used and the reaction studied in the temperature range of 370–403 K. By analyzing the experimental data, second reaction order for α -pinene was found. A kinetic model is presented which includes term for the catalyst load used. The specific rate constant at 393 K was $2.19 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}\cdot\text{min}^{-1}$, the activation energy being $93 \text{ kJ}\cdot\text{mol}^{-1}$. Both values are within the range of literature results.

Keywords camphene, kinetics, α -pinene, zirconium oxide, superacid catalyst

1 INTRODUCTION

Camphene is used as raw material to produce isobornyl acetate and insecticides. It can be obtained by α -pinene isomerization using acid catalysts.

While the technology of this process is known, few data have been reported on its reaction kinetics. A known fact, however, is that isomerization reactions take place on superacid catalysts. Literature reports have shown that the zirconium dioxide treated with sulfuric acid exhibits a strong acidity and that it is able to catalyze *n*-butane isomerization to isobutane at room temperature^[1]. The strong acidity of sulfated zirconium oxide makes it attractive for use as catalyst in isomerization processes. Numerous workers^[2–4] have prepared these catalysts, characterized their physicochemical properties and tested the catalytic yield in various chemical reactions but no reports were given to date on their use in the α -pinene isomerization to camphene.

The results of a previous work^[5] have shown that sulfation of the pure zirconium oxide is required for the catalyst to present isomerization activity. In these catalysts, the selectivity to camphene is about 70% under appropriate operating conditions, and this value is above those obtained in previous studies in sulfated TiO₂.

In the present work, experiments were carried out to study α -pinene isomerization onto zirconium dioxide impregnated with 10% sulfuric acid, particularly in what respects to influence the reaction kinetics.

2 EXPERIMENTAL

2.1 Catalyst

Hydrous zirconium dioxide was obtained by hydrolysis of ZrCl₄ (Fluka) with ammonium hydroxide (Tetrahedron, 28%) until the pH reached a value of 8.3. The hydrous oxide was then filtered, carefully washed and finally dried at 473 K for 24 h.

An aqueous solution formed by a mixture of 4 ml H₂SO₄ (Merck, 0.5 mol·L⁻¹) and 25 ml methanol (Betsil) was prepared to impregnate 2 g the hydrous zirconium, which was subsequently dried and calcined at 873 K for 4 h to give the sulfated zirconia (SZ10) catalysts.

2.2 Characterization

The catalyst was characterized by X-ray diffraction (XRD), BET and acidic properties (FT-IR). XRD patterns of sulfated zirconia (SZ10) were recorded on a Rigaku D-Max III C instrument using CuK α radiation (wavelength, 1.5378 nm; voltage 40 kV; current intensity, 30 mA). The values 2θ were varied in the range of 10–70° with scanning rate of 60°·h⁻¹. FT-IR spectroscopy of ammonia adsorbed was used for characterizing the strength of acidic sites on the SZ10 catalyst. Ammonia was allowed to adsorb at room temperature, at 15 cm³·min⁻¹ for 30 min. SZ10 catalyst sample containing adsorbed ammonia was diluted with potassium bromide, and diagram for this process recorded using a Bruker IFS66 FTIR equipment. The results show the presence of sites Brönsted.

The surface area of the catalyst was determined

by the classical BET method (N₂ physisorption at T = -195°C) and was around 87 m²·g⁻¹. Tetragonal and monoclinic ZrO₂ mixtures were observed by X-ray diffraction.

2.3 Reaction system and experimental procedure

The isomerization experiment was carried out at laboratory scale in a magnetically stirred batch glass reactor, kept at constant temperature by means of a glycerin thermostatic bath. This 100 cm³ glass reactor has three emery inlets. Reflux refrigerant is introduced in one of them, where the more volatile vapors condense. The second inlet is used to place the system for measuring reaction medium temperature while the third inlet is employed to load the reactor and to take samples for subsequent analysis. A volume of 20 cm³ of α -pinene is fed through the last mouth, and the reaction starts with addition of the catalyst (0.25%, 0.5% and 1% catalyst mass in the reaction volume).

All experiments were done at atmospheric pressure for reaction temperatures ranging from 370 to 403 K, and for the reaction time of 3 h in all cases.

Samples were taken at regular intervals and analyzed in the gas chromatography (GC). Reactants and products were quantitatively analyzed in the GC using flame ionization detector (FID) after separation of the individual compounds in a 60 m capillary column (Fused silica, J&W DB-1). The oven was programmed from 348 to 493 K at 3°C·min⁻¹, being the injection volume of 0.1 μ l with a split ratio of 1 : 100.

The relative amounts of individual components are based on the peak areas obtained. Reaction products were identified by comparing their relative retention times with those of reference samples, and confirmed by mass spectroscopy in a Perkin-Elmer Q-Mass 910. GC separation was accomplished in a Supelco SPB-1 30 m × 0.32 mm fused capillary column using helium as carrier gas. Column temperatures were programmed as follows: 348 K (1 min), 348–493 K at 4°C·min⁻¹ and 493 K (8 min).

2.4 Materials

The following chemical compounds were used: ZrCl₄ (Fluka), NH₄OH (Tetrahedron), CH₃OH (BETSIL), H₂SO₄ (Merck), α -pinene (Palma, SA). Terpinolene, limonene, camphene, tricyclene, α -terpinene, γ -terpinene and mircene were kindly provided by Fritzsche SAICA company. The α -pinene used in the reaction was provided by Derivados San Luis SA.

3 RESULTS AND DISCUSSION

To select operating conditions ensuring the absence

of external control, we did the experiments at stirring speeds ranging from 600 to 900 r·min⁻¹. In all cases, stirring proved to be efficient since all the solid remained in suspension and well dispersed. Concerning the kinetics, we found that the reaction rate did not depend on stirring rate for the range covered thus certifying that the process is not controlled by the resistance placed outside the catalyst particle.

The diffusional resistance inside the particle was estimated by the criterion of Weisz and Prater^[6]. The parameters were calculated using the models proposed by Smith^[7], Bird *et al.*^[8] and Satterfield^[9]. The results show the absence of internal diffusional control.

The change in concentration of isomerized α -pinene and those of the isomerization reaction products were plotted in Fig. 1 for 1% load of the SZ10 catalyst. The graph shows the formation of camphene, tricyclene, limonene, terpinolene and 'others' (α -terpinene, γ -terpinene and mircene). Concerning our results, some conclusions can be directly taken from the curves of Fig. 1. One of them is that camphene and limonene-terpinolene are formed simultaneously from α -pinene, just as proposed by Booth^[10] in the literature. Another is that the rate of camphene formation is appreciably faster; for instance the limonene-terpinolene concentration is about a third of that of camphene after an hour of reaction, keeping constant from then on.

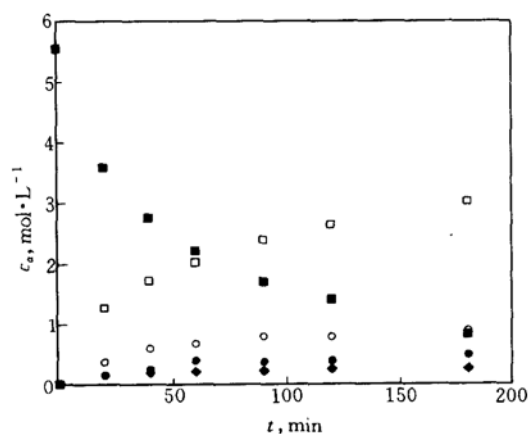


Figure 1 Concentration as the function of reaction time for the SZ10 catalyst ($T = 403$ K, Catalyst load: 10 g·L⁻¹)
 ■ α -pinene; □ camphene; ○ limonene-terpinolene;
 ◆ tricyclene; ● others

With the aim of evaluating the kinetic parameters, a series of experiments was conducted to analyze the influence of temperature and catalyst loading. The measurements taken between 370 and 403 K are shown in Fig. 2 as the reciprocal of α -pinene concentration *vs.* time.

As the graph shows a linear behavior of the data; we can conclude that the reaction is of second order with respect to α -pinene concentration under the conditions used here. Therefore, the reaction rate of α -pinene can be expressed as

$$\frac{dc_{\alpha}}{dt} = k_w c_{\alpha}^2 \quad (1)$$

The rate constant is estimated by fitting the integral form of the kinetic model to the experimental results of plotting the reciprocal of α -pinene concentration *vs.* time. The rate constant depends on temperature as indicated in Fig. 3, where it can be seen that the data follow the Arrhenius equation.

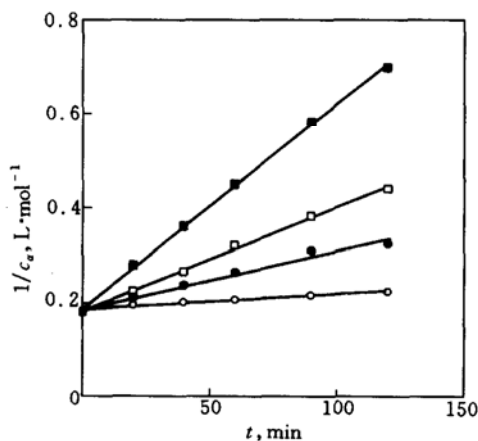


Figure 2 Test for the second order reaction at different temperatures
Catalyst load: $10 \text{ g}\cdot\text{L}^{-1}$;
T, K: ■ 403; □ 393; ● 385; ○ 370

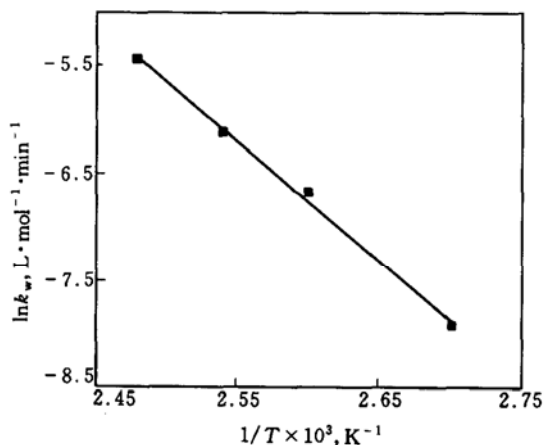


Figure 3 Arrhenius plot for α -pinene isomerization

The results of this fitting procedure are apparent activation energy, $93 \text{ kJ}\cdot\text{mol}^{-1}$, pre-exponential factor, $5.04 \times 10^9 \text{ L}\cdot\text{mol}^{-1}\cdot\text{min}^{-1}$. These values are in the order of those obtained in the work by Severino *et al.*^[11] from which a value of $110.9 \text{ kJ}\cdot\text{mol}^{-1}$ can be deduced for the reaction of α -pinene to camphene over TiO_2/SO_4 catalyst.

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Fig. 4 shows α -pinene concentration *vs.* time for different temperatures with symbols stand for experimental values and lines the prediction of the kinetic model.

On the other hand, to observe how reaction rates depend on catalyst loading, experiments were carried out for loads ranging from 0.25% to 1% (w/V) at constant reaction temperature. For these experiments, we plotted the initial reaction rates against loading in a log-log diagram (Fig. 5), and found a straight line with slope of being 2.

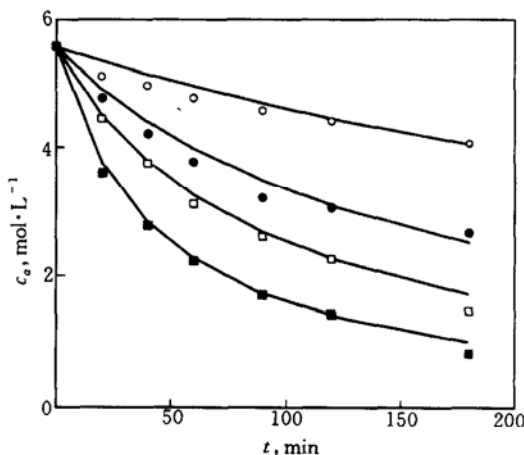


Figure 4 Kinetic model (lines) and experimental results (symbols) for different reaction temperatures
T, K: ■ 403 K; □ 393 K; ● 385 K; ○ 370 K

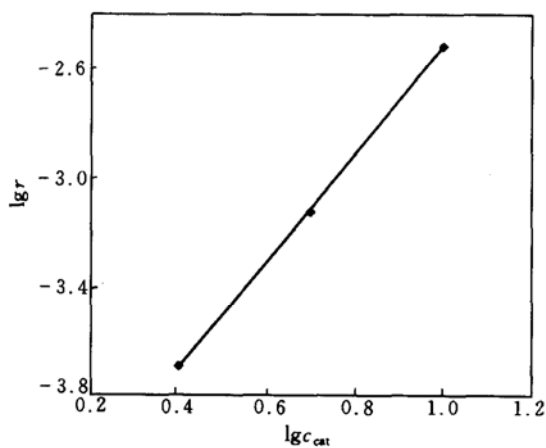


Figure 5 Effect of the catalyst concentration

4 CONCLUSIONS

The reaction studied presents a second order behavior with respect to α -pinene, with an activation energy of $93 \text{ kJ}\cdot\text{mol}^{-1}$ and a pre-exponential factor of $5.04 \times 10^9 \text{ L}\cdot\text{mol}^{-1}\cdot\text{min}^{-1}$. The reaction also shows a second order behavior with respect to catalyst loading.

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NOMENCLATURE

c_{cat}	catalyst concentration, g·L ⁻¹
c_{α}	α -pinene concentration, mol·L ⁻¹
k_w	specific rate constant, L·mol ⁻¹ ·min ⁻¹
r	reaction rate, mol·L ⁻¹ ·min ⁻¹
T	temperature, K
t	time, min

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