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Isomerization of Alpha-Pinene Over Acid Treated Natural Zeolite

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In this study, isomerization of α-pinene was studied over several acid-treated natural zeolite catalysts rich in clinoptilolite. Zeolite samples were contacted with HCl at different concentrations at 30°C or at 60°C for 3 and 24 hours and tested in isomerization reaction of alpha-pinene. The catalysts prepared were characterized by XRD, nitrogen adsorption, and acidity studies. Acidity strength and the distribution of Lewis and Brønsted acid sites of the catalysts were determined, and their catalytic activities in α-pinene isomerization and selectivities to main reaction products, camphene and limonene, were investigated. Acid treatment improved the selectivity of catalyst samples to camphene, decreasing the selectivity to limonene, probably forcing limonene to secondary reactions at high conversions.

The kinetics of α-pinene consumption was described by first-order kinetics. Two kinetic models were tested for the reaction mechanism and one model was found to give a good correlation between the theoretical and experimental data. In the models, the key intermediate was the pinylcaronium ion, which was formed irreversibly from α-pinene.

Number and distribution of Lewis and Brønsted acid sites affect the formation of bicyclic and monocyclic products.

Keywords: Reaction kinetics; Catalyst; Isomerization; Natural zeolite; Alpha-pinene

Introduction
Camphene, which is an important intermediate in camphor synthesis, is produced commercially by isomerization of α-pinene at reflux temperature over acidic
catalysts. Various types of acidic catalysts prepared from titanium dioxide, clay, halloysite, natural zeolite, activated carbon, synthetic zeolite, silica-supported rare earth oxide, and sulfated zirconium oxide have been reported in the literature for the isomerization of \( \alpha \)-pinene. Carson (1945) studied isomerization of \( \alpha \)-pinene over the mineral catalysts called chlorites. A yield of 60 wt\% of solid camphene was obtained, and the remainder was chiefly monocyclic terpenes. Kirkpatrick (1945) used halloysite as catalyst for the isomerization of pinene to camphene. It was found that 90% conversion of the \( \alpha \)-pinene was obtained at 170°C in 10 minutes to yield 60% camphene. The time for complete conversion of the terpene varied with the amount of catalyst used and the temperature employed. Korotov et al. (1969) prepared camphene by isomerization of pinene in the presence of TiO\(_2\). Pinene vapors in the inert gas were passed through a layer of Ti catalyst suspension in camphene at a flow rate of 9 mL/s. They obtained a product containing 96% camphene.

Afanaseva and coworkers (1970a,b) studied the continuous isomerization of commercial alpha-pinene into camphene under laboratory conditions and on a pilot plant over a TiO\(_2\) catalyst. The effects of vapor feed rate, temperature, and \( \alpha \)-pinene concentration in the feed on the production of camphene were investigated.

A Japanese patent (Matsubara et al., 1970) described isomerization of pinene to camphene using TiO\(_2\)–Ti(OH)\(_4\) catalyst. An oil containing 65% camphene was obtained in two hours at 145°C. In one study (Davis and McBride, 1974) activated carbon was used as catalyst to produce camphene. The reaction mixture obtained was rich in camphene, free of polymers, and low in terpene by-product formation.

China and Albanian clays were also used in the isomerization of \( \alpha \)-pinene. Clay was treated with acid, but a relation could not be established between pH, surface area of clays, and the rate of reaction. Nazır et al. (1976), Kullaj (1985, 1989), and Battolova et al. (1990) found that the selectivity on a titanium catalyst for isomerization of \( \alpha \)-pinene into camphene increased with the amount of Na\(_2\)O on its surface, whereas catalytic activity of the sample decreased with increasing Na\(_2\)O loading. Findik and Gündüz (1997) studied the effects of reaction time, amount of catalyst, stirring speed, and catalyst particle size on the conversion of \( \alpha \)-pinene and selectivity to camphene over a natural zeolite rich in clinoptilolite. The reaction fitted a first-order parallel reaction for production of camphene and limonene. Stefanis et al. (1995) investigated the reactions of \( \alpha \)-pinene, limonene, and \( \alpha \)-terpinene in several alumina-pillared clays and a layered \( \alpha \)-tin phosphate analogue under Lewis acid conditions and compared with the mid-pore zeolites USY, NH\(_4\)\(^+\)-ZSM-5, and H\(^+\)-mordenite.

Severino and coworkers (1996) found that extra-lattice aluminium (EFAL) species had a promoting effect on the activity of catalysts prepared by hydrothermal treatment of zeolites Y and X in the liquid phase isomerization of \( \alpha \)-pinene at 150°C. Selectivity towards camphene was strongly affected by EFAL species, decreasing at high values of the number of framework aluminum atoms per unit cell and increasing with high EFAL content. It was concluded that tricyclene products such as camphene and tricyclene were formed on Lewis acid centers, while monocyclic products such as limonene were formed on the Brönsted centers.

Allahverdiev and coworkers (1998) investigated the kinetics of pinene isomerization over zeolite tuffs rich in clinoptilolite calcined at 520°C for different durations. Initially mainly camphene and limonene were produced and only at relatively high conversions were other secondary products formed. Selectivity values at particular conversions were independent of catalyst pretreatment although activity was different. A kinetic model based on the elementary step mechanism fitted the experimental data well.
In another study by Allahverdiev et al. (1999) the kinetics of liquid phase isomerization of \( \alpha \)-pinene over natural zeolite catalyst was investigated at 100–180°C at nitrogen pressure of 1–20 bar. Consumption rate of \( \alpha \)-pinene was found to follow first-order kinetics. Selectivities at particular conversions were seen to be independent of temperature and pressure. A reaction network and mechanism were advanced and the corresponding kinetic equations were derived.

Yamamoto et al. (1999) studied the generation of acid sites on silica-supported rare earth oxide catalysts for \( \alpha \)-pinene isomerization. These catalysts exhibited solid acidity for catalysis of pinene isomerization and the activities depended on the supported element. The same authors (Yamamoto et al., 2000) also investigated acid-base properties of silica-supported ytterbium oxide catalyst in \( \alpha \)-pinene isomerization. Grzona et al. (2000) reported that sulfated zirconium oxide catalysts were active for producing camphene when they presented Brønsted acidity and when zirconium oxide crystallized in the tetragonal phase. Beşin et al. (2002) studied alpha-pinene isomerization over acid-treated montmorillonite clays and investigated the relationship between structure changes in clays with acid treatment and product distribution in the reaction.

Most of these studies describe the invention of a new catalyst for the production of camphene from \( \alpha \)-pinene. There are not as many investigations of the kinetic parameters and reaction mechanism. In some studies (Yamamoto et al., 1999, 2000) \( \alpha \)-pinene isomerization has been utilized as a test reaction for the acid-base properties of catalysts. Isomerization of \( \alpha \)-pinene has not yet been studied over acid-treated natural zeolite rich in clinoptilolite. The aim of this work is mainly to study the consumption kinetics of \( \alpha \)-pinene, to find a kinetic model fitting the experimental data well, and to investigate the effect of acid treatment, Lewis and Brønsted acid sites, on \( \alpha \)-pinene isomerization.

**Experimental**

**Catalyst Preparation**

Zeolite tuffs rich in clinoptilolite obtained from Bigadiç (Balikesir, Turkey) were employed for preparation of the catalysts. Chemical analysis of the tuff samples was done by an atomic absorption spectrometer, Varian 10 Plus, except for gravimetric analysis of SiO\(_2\) and water. The chemical composition found was 78.05% SiO\(_2\), 2.57% Na\(_2\)O, 1.82% K\(_2\)O, 0.45% Fe\(_2\)O\(_3\), 2.31% CaO, 6.34% Al\(_2\)O\(_3\), 0.33% MgO, and 8.14% H\(_2\)O.

The zeolite tuff samples crushed to the size of 0.5 mm were washed with distilled water twice for 2 hours at room temperature to remove impurities, then dried at 160°C for 24 hours. Washed samples (4 g) were suspended at 30°C or at 60°C for 3 or 24 hours in 100 mL of aqueous solution of HCl at different concentrations ranging from 0.1 M to 5 M; after filtration the zeolite portions were washed with bidistilled water until there was no Cl\(^-\) ions left and then dried at 160°C for 24 hours.

**Reaction Studies**

Prepared catalysts were tested in the isomerization reaction of \( \alpha \)-pinene. Reaction was carried out at atmospheric pressure under nitrogen flow to provide an inert atmosphere in a glass reactor with a reflux condenser and an efficient stirrer. The
flask was heated with a heating mantle (Electrothermal) with a temperature controller. One gram of catalyst and 50 mL of wood turpentine (Ortas¸, Edremit, Turkey) containing about 85 wt% α-pinene, 3.9 wt% camphene, and 5.2 wt% limonene (the rest consists of tricyclene, α- and γ-terpinene, terpilonene, p-cymene, α- and β-phellandrene, and borneol) were charged in the reactor. Adding the catalyst started the reaction and all experiments were carried out under isothermal (155°C) conditions. Samples of the reaction mixture were taken during the course of the reaction and analyzed by flame ionization detector (FID) gas chromatography (Hewlett Packard 5980 with 25 m long and 0.32 mm id HP-FFAP capillary column) connected to a mass spectrometer with electron energy 70 eV and mass rate 35–425 m/z. Temperature programming (increase at a rate of 2°C/min from 60 to 130°C and then at a rate of 3°C/min until 215°C) was applied for separation at 1 mL/min N2 flow. A kinetic run took 3.25 hours.

**Catalyst Characterization**

Surface areas of the catalyst samples were measured by the Coulter Omnisorp 100 CX adsorption equipment using a diffusion pump. The static dose method was used and the samples were degassed at 300°C under high vacuum condition (∼10−5 mbar) for 3 hours. X-ray diffraction (XRD) studies were carried out for some catalyst samples on a JSDX 100S4 diffractometer using CuKα radiation with a Ni filter.

Hammett indications were used for the measurement of acid strength of catalyst samples. The acid strength was expressed by the Hammett acidity function, H0. Lower values of H0 correspond to greater strength of the solid.

Pyridine adsorption was carried out to identify the acid centers of the catalysts. For this purpose pyridine was adsorbed on catalyst samples for 12 hours prior to measurements. After that, the excess amount of pyridine was vaporized in a vacuum at 50°C for 48 hours. Wafers were prepared by pressing a mixture of 8 mg of catalyst and 100 mg of KBr. Infrared (IR) spectra of pyridine-adsorbed samples were recorded by a Shimadzu 470 instrument at room temperature and atmospheric pressure.

**Results and Discussion**

**Reaction Studies**

In the isomerization reaction of α-pinene, the main products were camphene and limonene while tricyclene, terpinolene, and α- and γ-terpinene were also formed. Figure 1 presents the structural formulae of some mono-, bi-, and tricyclic terpenes in the reaction mixture. The typical product-time curves are presented in Figure 2.

Selectivity to camphene and limonene were determined in the following ways:

\[
\text{Selectivity to product} = S_C(S_L) = \frac{\text{Moles of product } C \text{ or } L \text{ formed}}{\text{Moles of converted } \alpha\text{-pinene}} \times 100
\]

The selectivity values are presented for the catalysts studied in Table I.

It can be stated as a trend that activity of catalysts as well as total conversions of α-pinene decreases slightly with increasing acid concentration. Table I shows that acid treatment makes the catalysts unselective to limonene, probably forcing limonene to secondary reactions. The completion of the isomerization of pinene is
preferred, because the separation of α-pinene and camphene by the ordinary methods of fractional distillation is unfeasible when the reaction is not completed. From this point of view, catalyst 11 is the best one for camphene production. Figure 3 presents the percentage of camphene and tricyclene as a function of α-pinene conversion.

Figure 1. A. α-Pinene; D. camphene; B. tricyclene; E. limonene; F₁. terpinolene; C₂. α-terpinene; C₁. γ-terpinene; G. p-cymene; H₁. β-phellandrene; H₂. α-phellandrene.

Figure 2. Isomerization of α-pinene over the acid-treated natural zeolite with 5 M HCl at 60°C for 24 h.
for all catalysts studied. It is seen that selectivity to bi/tricyclic products was almost independent of conversion on all catalysts studied irrespectively of the acid treatment procedure. Similar results have been reported in the literature (Allahverdiev et al., 1998; Lopez et al., 1998). As seen in Figure 4, selectivity to limonene was very much dependent on conversion. For conversions lower than about 80\%\textsuperscript{a}, limonene increases with conversion. At higher conversion levels, limonene decreases rapidly due to the secondary reactions of limonene, with special emphasis to terpinenes

\begin{table}
\centering
\caption{The results of conversion and selectivity studies (after a reaction time of 3.25 hr)}
\begin{tabular}{|c|c|c|c|}
\hline
Code & Catalyst samples & X\textsubscript{T} & S\textsubscript{C} & S\textsubscript{L} \\
\hline
1 & Natural zeolite & 100,00 & 37,76 & 4,51 \\
2 & 1 M HCl 3 h 30\degree\textsuperscript{C} & 99,61 & 38,52 & \textsuperscript{a} \\
3 & 0,1 M HCl 24 h 30\degree\textsuperscript{C} & 99,61 & 37,18 & \textsuperscript{a} \\
4 & 0,5 M HCl 24 h 30\degree\textsuperscript{C} & 99,59 & 36,50 & \textsuperscript{a} \\
5 & 1 M HCl 24 h 30\degree\textsuperscript{C} & 99,48 & 39,22 & \textsuperscript{a} \\
6 & 0,5 M HCl 3 h 60\degree\textsuperscript{C} & 99,58 & 39,55 & \textsuperscript{a} \\
7 & 1 M HCl 3 h 60\degree\textsuperscript{C} & 99,35 & 37,19 & \textsuperscript{a} \\
8 & 5 M HCl 3 h 60\degree\textsuperscript{C} & 99,29 & 39,40 & \textsuperscript{a} \\
9 & 0,1 M HCl 24 h 60\degree\textsuperscript{C} & 99,65 & 33,26 & \textsuperscript{a} \\
10 & 0,5 M HCl 24 h 60\degree\textsuperscript{C} & 98,16 & 40,55 & 2,50 \\
11 & 1 M HCl 24 h 60\degree\textsuperscript{C} & 100,00 & 39,22 & \textsuperscript{a} \\
12 & 5 M HCl 24 h 60\degree\textsuperscript{C} & 99,49 & 39,76 & \textsuperscript{a} \\
\hline
\end{tabular}
\label{table:results}
\end{table}

\textsuperscript{a}(-) means that the amount of limonene in the reaction mixture after 3.25 h is less than its initial value.

Figure 3. Concentrations of camphene and tricycylene as a function of \(\alpha\)-pinene conversion for all studied catalysts (reaction temperature = 155\degree\textsuperscript{C}, 1 g catalyst, 50 mL wood turpentine).
Figure 4. Concentration of limonene as a function of α-pinene conversion. Legend numbers correspond to the codes of catalysts in Table I.
and terpinolenes. The amount of limonene over untreated natural zeolite is always higher than that over all acid-treated zeolite samples. This observation might be explained by the slower secondary reactions of limonene over natural zeolite.

**Kinetic Studies**

Alpha-pinene was reported by Rudakov et al. (1975) to be of zero order over titanium catalyst. Severino et al. (1996) over HY and HZ zeolites and Allahverdiev et al. (1999) over differently pretreated natural zeolites described the kinetics of α-pinene consumption by a first-order equation. In the light of this information, several orders such as first, half, and zero have been tested in the present study. The following rate equations, Equations (1) and (2), were used for kinetic analysis:

\[-\frac{dC_A}{dt} = k_RC_A \quad \text{(for first order)} \tag{1}\]

\[\frac{C_A^{1-n} - C_{A_0}^{1-n}}{n-1} = k_Rt \quad \text{(for orders different from one)} \tag{2}\]

A first-order dependency on α-pinene consumption was observed on the acid-treated zeolite samples. Reaction rate constant was found to be 1.83 h\(^{-1}\) with a regression coefficient \(R^2 = 0.88\).

The reaction mixture was stirred vigorously, thus eliminating external diffusion resistance between the bulk liquid and the catalyst surface. The turbulence created by the nitrogen stream around the catalyst particles also helps to eliminate external diffusion resistance. A high value of the α-pinene diffusion coefficient (≈10\(^{-9}\) m\(^2\)/s) permits a sufficient rate of external diffusion. The value of the Thiele modulus was calculated for a first-order consumption kinetics of α-pinene and was found to be 0.14, indicating that the effectiveness factor was equal to 1. It shows that the intraparticle resistance on rate can be neglected. In the present study, two mechanisms based on the studies of Allahverdiev et al. (1998, 1999) were tested. In these mechanisms, which slightly differ from each other, the key intermediate is the pinylcarbocation ion, which is formed with the addition of H\(^+\) to α-pinene and is the precursor for all of the reaction products, which are produced in turn in subsequent steps. Monocyclic and bi-, tricyclic terpenes are formed from this ion in two parallel steps. The first one is a ring expansion path and gives rise to bi- and tricyclic products such as camphene and tricyclene; the second path yields monocyclic products such as limonene, terpinolenes, and terpinenes.

The reaction network of the first mechanism is given in Scheme 1, where \(Z\) denotes surface sites. Steps \(ZA_2 \rightarrow ZD\) and \(ZA \rightarrow ZC\) have been neglected in the present study. It was considered that the rates leading to camphene (and tricyclene) and limonene (and its secondary products) are not interconnected, which was supported by the fact that when α-pinene is totally consumed, camphene and tricyclene have almost equilibrium concentrations, whereas secondary reactions of limonene proceed. Terpinolene and isoterpinolene are formed by the reversible transformation of limonene, whereas terpinenes are produced from terpinolenes by an irreversible reaction.

For the mechanism used, there are 13 step equations, 9 intermediate, and 5 basic routes (Table II). A set of stoichiometric numbers of steps is defined as a reaction
route. Derivation of kinetic equations of the first mechanism is a routine procedure and was given elsewhere (Allahverdiev et al., 1998).

By rearranging the kinetic equations for selectivity, Equations (3)–(7) are obtained:

\[
\begin{align*}
-\frac{dC_B}{dC_A} & = f_1 \left( f_2 + f_3 \frac{C_B}{C_A} + f_4 \frac{C_D}{C_A} \right) - f_3 \frac{C_B}{C_A} \\
-\frac{dC_C}{dC_A} & = f_5 \frac{C_F}{C_A} \\
-\frac{dC_D}{dC_A} & = (1 - f_1) \left( f_2 + f_3 \frac{C_B}{C_A} + f_4 \frac{C_D}{C_A} \right) \\
-\frac{dC_E}{dC_A} & = f_6 - f_7 \frac{C_E}{C_A} + f_8 \frac{C_F}{C_A} \\
-\frac{dC_F}{dC_A} & = f_7 \frac{C_E}{C_A} - f_8 \frac{C_F}{C_A} - f_5 \frac{C_F}{C_A}
\end{align*}
\]

**Scheme 1.** Reaction network of the first mechanism: A, \(\alpha\)-pinene; B, tricyclene; C, \(\alpha\)- and \(\gamma\)-terpinene; D, camphene; E, limonene; F, terpinolene and isoterpinolene.

**Table II** Reaction mechanism for the first model

<table>
<thead>
<tr>
<th>Elementary steps</th>
<th>N(1) A = B</th>
<th>N(2) A = D</th>
<th>N(3) A = E</th>
<th>N(4) A = F</th>
<th>N(5) F = C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Z + A (\equiv) ZA</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>2 ZA (\Rightarrow) ZA_1</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3 ZA (\Rightarrow) ZA_2</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>4 ZA_1 (\Leftrightarrow) ZB</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5 ZA_1 (\Leftrightarrow) ZD</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6 ZB (\equiv) Z + B</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>7 ZD (\equiv) Z + D</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>8 ZA_2 (\Rightarrow) ZE</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>9 ZE (\Leftrightarrow) ZF</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>10 ZF (\Rightarrow) ZC</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>11 ZC (\equiv) Z + C</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>12 ZE (\equiv) Z + E</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>13 ZF (\equiv) Z + F</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>(-1)</td>
</tr>
</tbody>
</table>
where

\[ f_1 = \frac{k_4}{(k_4 + k_3)} \]
\[ f_2 = \frac{k_2}{Y} \]
\[ f_3 = \frac{k_-4}{K_6 K_1 Y} \]
\[ f_4 = \frac{k_-5}{K_7 K_1 Y} \]
\[ f_5 = \frac{k_{10}}{K_{13} K_1 Y} \]
\[ f_6 = \frac{k_3}{Y} \]
\[ f_7 = \frac{k_9}{K_{12} K_1 Y} \]
\[ f_8 = \frac{k_-9}{K_{13} K_1 Y} \]
\[ Y = k_2 + k_3 \]

The system of differential equations was solved, and the numerical values of dimensionless parameters are given in Table III with their standard errors.

The second mechanism (Allahverdiev et al., 1999) used for kinetic modeling is presented in Scheme 2.

Although the path that leads to the formation of camphene and tricyclene is the same as in the first mechanism, the path that leads to the formation of limonene, terpinolene, isoterpinolene, and \( \alpha \)-and \( \gamma \)-terpinenes differs. In the second mechanism the monocyclic terpenes of \( \alpha \)- and \( \gamma \)-terpinenes are formed by an irreversible route.

<table>
<thead>
<tr>
<th>Parameter*</th>
<th>Estimated value</th>
<th>Standard error (±)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( f_1 )</td>
<td>0.1860</td>
<td>0.3713</td>
</tr>
<tr>
<td>( f_2 )</td>
<td>0.4367</td>
<td>0.1703</td>
</tr>
<tr>
<td>( f_3 )</td>
<td>1.90E-07</td>
<td>1.59E-07</td>
</tr>
<tr>
<td>( f_4 )</td>
<td>2.89E-06</td>
<td>3.76E-07</td>
</tr>
<tr>
<td>( f_5 )</td>
<td>2.01E-06</td>
<td>1.41E-06</td>
</tr>
<tr>
<td>( f_6 )</td>
<td>0.3762</td>
<td>0.0065</td>
</tr>
<tr>
<td>( f_7 )</td>
<td>1.4174</td>
<td>0.1373</td>
</tr>
<tr>
<td>( f_8 )</td>
<td>0.2836</td>
<td>0.0541</td>
</tr>
</tbody>
</table>

*Dimensionless.
different from the limonene formation route. Double-bond migration in limonene results in terpinolene and isoterpinolene formation (Allahverdiev et al., 1999), whereas, according to the first mechanism, terpinolenes are formed from limonene by a reversible path and terpinenes are from terpinolenes. Table IV presents 19 step equations, 13 intermediates, and 7 basic routes. On the right-hand side of the equations stoichiometric numbers for the different routes are given.

Kinetic equations can easily be derived (Allahverdiev et al., 1999) for the reaction mechanism displayed in Table IV.

By arranging the reaction rate equations for the selectivity dependence, Equations (8)–(11) are obtained:

\[-\frac{dC_E}{dC_A} = f_3 - f_4 \frac{C_E}{C_A}\]  
\[\frac{d(C_E + C_{F1} + C_{F2})}{d(C_{C1} + C_{C2})} = \frac{k_9}{k_{11}} \left( \frac{f_2(k_9 + k_{11})C_E}{k_{11}(k_8f_2K_1C_A + f_2C_E)} \right)\]  
\[-\frac{d(C_B + C_D)}{dC_A} = f_5\]  
\[\frac{dC_{C2}}{dC_{C1}} = f_6\]

where

\[f_1 = \frac{k_2}{(k_3 + k_8)}\]  
\[f_2 = \frac{k_9}{K_{10}}\]  
\[f_3 = \frac{f_1k_2K_1k_8k_9}{(k_9 + k_{11})}\]
Table IV Reaction mechanism for the second model

<table>
<thead>
<tr>
<th>Elementary steps</th>
<th>N(1)</th>
<th>N(2)</th>
<th>N(3)</th>
<th>N(4)</th>
<th>N(5)</th>
<th>N(6)</th>
<th>N(7)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A = D</td>
<td>A = B</td>
<td>A = E</td>
<td>A = C₂</td>
<td>A = C₁</td>
<td>E = F₁</td>
<td>E = F₂</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>Z + A $\equiv$ ZA</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>ZA $\Rightarrow$ ZA₁</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>ZA₂ $\Leftrightarrow$ ZD</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<td>0</td>
</tr>
<tr>
<td>5</td>
<td>ZD $\equiv$ Z + D</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>ZA₂ $\Leftrightarrow$ ZB</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>ZB $\equiv$ Z + B</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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</tr>
<tr>
<td>8</td>
<td>ZA₁ $\Rightarrow$ ZA₃</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>ZA₃ $\Rightarrow$ ZE</td>
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<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>ZE $\equiv$ Z + E</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>-1</td>
</tr>
<tr>
<td>11</td>
<td>ZA₃ $\Rightarrow$ ZA₄</td>
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<td>0</td>
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<td>1</td>
<td>0</td>
</tr>
<tr>
<td>12</td>
<td>ZA₄ $\Rightarrow$ ZC₂</td>
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<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>13</td>
<td>ZC₂ $\equiv$ Z + C₂</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>14</td>
<td>ZA₄ $\Rightarrow$ ZC₁</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>15</td>
<td>ZC₁ $\equiv$ Z + C₁</td>
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<td>0</td>
<td>0</td>
</tr>
<tr>
<td>16</td>
<td>ZE $\Rightarrow$ ZF₁</td>
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<td>0</td>
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<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>17</td>
<td>ZF₁ $\equiv$ Z + F₁</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>18</td>
<td>ZF₁ $\Rightarrow$ ZF₂</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>19</td>
<td>ZF₂ $\equiv$ Z + F₂</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>
\[ f_4 = \frac{f_2 + k_{16}/K_{10}}{k_2 K_1} - \frac{f_2 k_2 K_1 k_9}{(k_9 + k_{11})} \]

\[ f_5 = \frac{k_3}{(k_3 + k_8)} \]

\[ f_6 = \frac{k_{13}}{k_{15}} \]

Integrating Equations (8), (10), and (11) gives Equations (12), (13), and (14):

\[ C_E = \left( \frac{f_3}{1 - f_4} \right) C_A^0 \left( \left( \frac{C_A}{C_A^0} \right)^{f_4} - \left( \frac{C_A}{C_A^0} \right) \right) + C_E^0 \left( \frac{C_A}{C_A^0} \right)^{f_4} \quad (12) \]

\[ (C_B - C_B^0) + (C_D - C_D^0) = f_5 (C_A - C_A) \quad (13) \]

\[ (C_{C2} - C_{C2}^0) = f_6 (C_C - C_C^0) \quad (14) \]

The values of the dimensionless parameters in Equations (12), (13), and (14) were calculated and are given in Table V.

Comparison of Tables III and V shows that the standard error of the second mechanism is less than that of the first one. It means that the second model fits the experimental data better than the first mechanism.

**Catalyst Characterization Studies**

Table VI presents the BET surface areas of the prepared samples. It is seen that increasing the acid leaching temperature causes an increase in the BET surface area. On the other hand, acid leaching causes the BET surface area to increase because new pores, where nitrogen is able to pass, are established due to the removal of several cations from the zeolite framework, such as Al\(^{3+}\), Fe\(^{3+}\), Mg\(^{2+}\), Ca\(^{2+}\), Na\(^{+}\), and K\(^{+}\). The change in zeolite structure due to acid leaching will be presented elsewhere (Ünveren et al., submitted). Figure 5 illustrates the XRD patterns of acid-treated natural zeolite rich in clinoptilolite. Comparison of XRD results of samples 1 (natural zeolite), 2, and 7 shows that significant decreases are observed at diffraction peaks appearing at \(2\theta = 10\) and \(22\)° and an appreciable increase at the peak at \(2\theta = 27\)° and an appreciable decrease at the peak at \(2\theta = 30\)°, with acid treatment increasing the temperature from \(30°\) to \(60^°\). The diffraction peaks appearing at

<table>
<thead>
<tr>
<th>Parameter(^a)</th>
<th>Estimated value</th>
<th>Standard error (±)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(f_3)</td>
<td>0.3062</td>
<td>6.0 E-06</td>
</tr>
<tr>
<td>(f_4)</td>
<td>0.4234</td>
<td>4.2 E-04</td>
</tr>
<tr>
<td>(f_5)</td>
<td>0.4540</td>
<td>0.0035</td>
</tr>
<tr>
<td>(f_6)</td>
<td>0.5757</td>
<td>0.0049</td>
</tr>
</tbody>
</table>

\(^a\)Dimensionless.
2θ = 10°, 2θ = 22°, and 2θ = 30° are characteristic to clinoptilolite (C) and heulandite (H) and peak at 2θ = 27° to clinoptilolite.

As the duration of treatment increases from 3 h to 24 h (comparison of XRD results of samples 7 and 11), albite (A) is formed due to the changes in zeolite structure.

As acid concentration increases from 1 M to 5 M at 60°C for 24 h (comparison of XRD results of samples 11 and 12), the surface with a diffraction index of 3.31 (2θ = 27°) becomes appreciable.

The acid strength of natural zeolite increased with acid treatment and the range of acid strength (Hammett acidity function, H_o) broadened from 5.00–3.30 to 6.80–0.80 (Ünveren, 2001). The amount of acid sites on the solid surface of catalyst samples was measured by amine titration. Acid treatment increased the amount of acid sites of natural zeolite, as expected.

IR spectroscopic studies of ammonia and pyridine adsorbed on solid surfaces make it possible to distinguish between Brønsted and Lewis acids and to assess their amounts independently. In this study, pyridine was used as a proton acceptor. The spectrum of pyridine coordinatively bonded to the surface (Lewis acidity) is very different from that of the pyridinium ion (Brønsted acidity). This fact permits differentiation between acid types on the surface of a solid acid.

The density of the sites is evaluated by the intensity (absorbance) of the respective bands, e.g., pyridine bound to Brønsted acid sites is associated with an IR band at 1545 cm⁻¹ and that bound to Lewis sites with a band at 1450 cm⁻¹. A band at 1490 cm⁻¹ arises due to pyridine adsorbed on both Brønsted and Lewis sites (Severino et al., 1996). Table VII presents the intensities of the spectra of pyridine-adsorbed samples at given wave numbers corresponding to Lewis (L) and Brønsted (B) acid sites.

Table VII shows that Brønsted acidity increases with acid leaching. Camphene, which is a bicyclic product, forms easily over catalysts with low Brønsted acidity. A catalyst is active for producing camphene when it presents Brønsted acidity (Grzona et al., 2000). As Brønsted acidity increases, formation of monocyclic product is favored because reaction rates on Brønsted sites are higher than on Lewis sites. Relative concentration of Lewis acid sites, L/B, becomes important to yield bicyclic

### Table VI BET surface areas of prepared catalysts

<table>
<thead>
<tr>
<th>Code</th>
<th>Catalyst samples</th>
<th>BET surface area, m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Natural zeolite</td>
<td>30,514</td>
</tr>
<tr>
<td>2</td>
<td>1 M HCl 3 h 30°C</td>
<td>38,879</td>
</tr>
<tr>
<td>3</td>
<td>0.1 M HCl 24 h 30°C</td>
<td>52,993</td>
</tr>
<tr>
<td>4</td>
<td>0.5 M HCl 24 h 30°C</td>
<td>36,326</td>
</tr>
<tr>
<td>5</td>
<td>1 M HCl 24 h 30°C</td>
<td>90,903</td>
</tr>
<tr>
<td>6</td>
<td>0.5 M HCl 3 h 60°C</td>
<td>60,320</td>
</tr>
<tr>
<td>7</td>
<td>1 M HCl 3 h 60°C</td>
<td>90,991</td>
</tr>
<tr>
<td>8</td>
<td>5 M HCl 3 h 60°C</td>
<td>83,627</td>
</tr>
<tr>
<td>9</td>
<td>0.1 M HCl 24 h 60°C</td>
<td>110,960</td>
</tr>
<tr>
<td>10</td>
<td>0.5 M HCl 24 h 60°C</td>
<td>143,300</td>
</tr>
<tr>
<td>11</td>
<td>1 M HCl 24 h 60°C</td>
<td>140,660</td>
</tr>
<tr>
<td>12</td>
<td>5 M HCl 24 h 60°C</td>
<td>136,830</td>
</tr>
</tbody>
</table>
Figure 5. XRD patterns of natural zeolite with and without acid treatment.
products such as camphene. Only when L/B is high enough does the selectivity to camphene grow significantly (Stefanis et al., 1995; Severino et al., 1996). Figure 6 presents the change in selectivity to camphene by the relative concentration of Lewis sites, L/B. For low values of Brønsted acidity, the L/B ratio has no significant effect on the selectivity because at low values of Brønsted acidity, formation of camphene is favored (Figure 6(a)). Selectivity to camphene increases with L/B ratio at high values of Brønsted acidity, except for catalyst 4 (Figure 6(b)). Slight decrease in selectivity with increasing L/B ratio at the same Brønsted acidity over catalyst 4 compared to catalyst 7 is likely due to the lower amount of acid sites of catalyst 4 than that of catalyst 7. The amount of acid sites of catalysts 7, 4, and 3 are 0.65, 0.55, and 0.55 mmol/g catalyst (Ünveren, 2001). L/B ratio becomes more dominant on the camphene selectivity for rather high values of Brønsted acidity (Figure 6(c)).

At the same L/B ratio selectivity to camphene decreases with high increase in Brønsted acidity, probably due to formation of limonene and of its fast secondary reactions. As observed from the comparison of the selectivities to camphene over catalysts 4 and 9, selectivity decreases from 36.50 to 33.26 with increase in Brønsted acidity from 37.65 to 75.29 at the same L/B ratio of 0.02.

**Conclusions**

Isomerization of α-pinene was studied at atmospheric pressure under nitrogen flow over several acid-treated natural zeolite catalysts rich in clinoptilolite. Catalysts prepared were characterized by XRD studies, surface area, and acidity measurements.

Two main groups of product were formed: bi/tricycle products (camphene and tricyclene) and monoterpenes (especially limonene). At high conversions, limonene isomerizes to other terpenes.

Acid treatment decreases the selectivity to limonene. Low selectivity to limonene is likely mainly due to the fact that secondary reactions of limonene proceed faster on acid-treated zeolite catalysts.

### Table VII Intensities of spectra of pyridine-adsorbed samples at given wave numbers

<table>
<thead>
<tr>
<th>Code</th>
<th>Catalyst samples</th>
<th>Lewis at 1450 cm(^{-1})</th>
<th>Brønsted at 1545 cm(^{-1})</th>
<th>Lewis to Brønsted, L/B</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Natural zeolite</td>
<td>1.75</td>
<td>12.00</td>
<td>0.14</td>
</tr>
<tr>
<td>2</td>
<td>1 M HCl 3 h 30°C</td>
<td>4.40</td>
<td>40.00</td>
<td>0.110</td>
</tr>
<tr>
<td>3</td>
<td>0.1 M HCl 24 h 30°C</td>
<td>1.38</td>
<td>37.65</td>
<td>0.037</td>
</tr>
<tr>
<td>4</td>
<td>0.5 M HCl 24 h 30°C</td>
<td>0.80</td>
<td>37.65</td>
<td>0.021</td>
</tr>
<tr>
<td>5</td>
<td>1 M HCl 24 h 30°C</td>
<td>0.74</td>
<td>18.12</td>
<td>0.041</td>
</tr>
<tr>
<td>6</td>
<td>0.5 M HCl 3 h 60°C</td>
<td>0.91</td>
<td>25.88</td>
<td>0.035</td>
</tr>
<tr>
<td>7</td>
<td>1 M HCl 3 h 60°C</td>
<td>0.22</td>
<td>37.65</td>
<td>0.006</td>
</tr>
<tr>
<td>8</td>
<td>5 M HCl 3 h 60°C</td>
<td>0.99</td>
<td>23.53</td>
<td>0.042</td>
</tr>
<tr>
<td>9</td>
<td>0.1 M HCl 24 h 60°C</td>
<td>1.69</td>
<td>75.29</td>
<td>0.022</td>
</tr>
<tr>
<td>10</td>
<td>0.5 M HCl 24 h 60°C</td>
<td>6.42</td>
<td>35.29</td>
<td>0.182</td>
</tr>
<tr>
<td>11</td>
<td>1 M HCl 24 h 60°C</td>
<td>1.04</td>
<td>16.47</td>
<td>0.063</td>
</tr>
<tr>
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<td>5 M HCl 24 h 60°C</td>
<td>7.51</td>
<td>78.47</td>
<td>0.096</td>
</tr>
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</table>
Alpha-pinene consumption was explained by a first-order dependency. Two different reaction networks and mechanisms were tested. The key intermediate is the pinyl carbonium ion, which is formed irreversibly from $\alpha$-pinene. Monocyclic and bicyclic terpenes are formed from this ion in parallel irreversible, noninterconnected steps. The kinetic model in which terpinenes and terpilonenes are formed by two different paths fits the experimental data best.

Pyridine adsorption studies show that acid treatment increases the Brønsted acidity. The main factor in the formation of bicyclic products is Lewis to Brønsted acidity ratio, however a catalyst should present Brønsted acidity as well. Lewis to Brønsted acidity ratio becomes more dominant on the selectivity to camphene for rather high values of Brønsted acidity.

It is well known that not only acidity but also textural properties affect product distribution in $\alpha$-pinene isomerization (Stefanis et al., 1995; Lopez et al., 1998). However, it is rather difficult to separate these effects from each other because they are so striking. Our research group will present the change in zeolite structure due to acid leaching and its effect on product distribution elsewhere (Ünveren et al., submitted).

**Acknowledgements**

Funding for this work from the Turkish Scientific Research Council through Grant MISAG-120 and from Ege University Research Fund through Grant 98 BIL 018 is gratefully acknowledged.
Nomenclature

\[ C_A \] concentration of A, etc., \(^{\%}\) wt  
\[ f_1{\text{--}}f_8 \] parameters in Equations 3–14  
\[ k_i \] rate constant of step i  
\[ K_i \] equilibrium constant of step i  
\[ k_R \] rate constant of \( \alpha \)-pinene consumption, \( h^{-1} \)  
\[ n \] reaction order  
\[ S_C \] selectivity to camphene  
\[ S_L \] selectivity to limonene  
\[ t \] time, h  
\[ X_T \] total conversion of \( \alpha \)-pinene, \(^{\%}\)  
\[ X_C \] conversion to camphene, \(^{\%}\)  
\[ X_L \] conversion to limonene, \(^{\%}\)  
\[ 2\theta \] diffraction angle, °

References


