Isomerization of α-Pinene to Camphene

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ABSTRACT: The catalytic isomerization reaction of α-pinene to camphene over a clinoptilolite catalyst was investigated in a batch reactor open to the atmosphere between 130 and 155°C. The catalyst was selective to the isomerization of α-pinene to camphene. The effects of several variables, such as reaction temperature, amount of catalyst, stirring speed and catalyst particle size, on the conversion of α-pinene and selectivity to camphene were determined. The reaction fits a first-order parallel reaction with rate constants of $k_1 = 3.020 \cdot 10^{-2} \, e^{-33381.6/RT}$ for the production of camphene and of $k_2 = 1.576 \cdot 10^{-2} \, e^{-31096.53/RT}$ for the production of limonene.
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KEY WORDS: Camphene, isomerization, kinetics of isomerization of α-pinene, selective catalyst.

The purpose of this study was to investigate the effects of several variables, such as reaction temperature, amount of catalyst, stirring speed and catalyst particle size, on the conversion of α-pinene to camphene (X_c), and on the overall selectivity for camphene over an activated clinoptilolite zeolite catalyst, which was found as the most selective after a selectivity screening test. We also wanted to develop a suitable rate equation for the isomerization of α-pinene to camphene.

Camphene is an important industrial chemical from which many products of commerce, such as toxaphene, isobornyl acetate, isoborneol, and camphor are made. Comparatively small amounts are used to produce fragrance chemicals by reaction with phenols.

Camphene is produced commercially by treatment of α-pinene over acidic catalysts in the absence of water (Scheme 1). It can be produced similarly from β-pinene and from pinene-containing materials, such as gum turpentine, wood turpentine and sulfate turpentine, which are obtained in the manufacture of paper from delignification of wood. Iso-

merization of α-pinene is generally carried out at reflux temperature in the presence of titania, minerals that contain a specific group of silicates (halloysite, zeolites), or activated clays. Preparation of the catalyst has a great influence on product yields and composition. The chief by-products of the isomerization are tricyclene, which is always obtained with camphene as an equilibrium product, and *p*-menthadienes.

Many one-step methods with catalysts have been suggested in the literature (1) for the preparation of camphene. Various types of catalysts, both organic and inorganic, as well as mineral, have been reported to promote the isomerization of pinene directly to camphene. The catalysts must be treated with an acid to activate the surface. The time for complete conversion of the terpene being isomerized varies with the nature and amount of the catalyst used and the temperature employed. Carson (2) used chlorites, and Kirkpatrick (3) tried halloysite as catalyst for the isomerization of pinene to camphene and obtained a yield of 60% by weight. Korotov *et al.* (4) prepared camphene by isomerization of pinene in the presence of TiO_2. Afanas'eva and coworkers (5,6) studied the continuous isomerization of technical pinene into camphene under laboratory and pilot plant conditions in a vertical column through which a liquid suspension of a Ti catalyst in camphene flowed downward, while α-pinene vapor moved upward. In a Japanese patent (7), isomerization of pinene to camphene by a $TiO_2 - Ti(OH)_4$ catalyst was described. They obtained an oil with 65% camphene. Davis and McBride (8) used activated carbon, and Nazir *et al.* (9) employed clay as catalyst to produce camphene. Popov and Vyrodov (10) investigated the isomerization of pinenes, which contained 92.1% α-pinene, at 110°C in the presence of activated titanium dioxide. The yields of camphene and tricyclene were 76.2 and 14.2%, respectively. Kullaj (11,12) studied the isomerization of α-pinene into camphene and tricyclene with different samples of Albanian clay activated by 10% HCl. In one work (13), it was found that selectivity on an industrial titanium catalyst for isomerization of α-pinene into camphene increased with the amount of Na_2O on its surface, whereas catalytic activity of the sample decreased with increasing Na_2O loading, and catalysts containing 1.6% Na_2O gave 87% yields of desired products. Özek (14) studied the production of odorous compounds, such as camphene, from the natural monoterpenes over titanium catalysts.
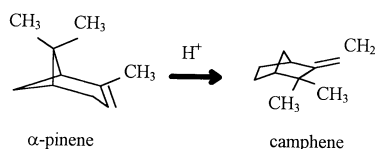
SCHEME 1

The quoted studies, in general, describe the invention of a new catalyst for the production of camphene from α-pinene, but knowledge of the effects of several parameters, such as temperature and catalyst amount and of the reaction kinetics is lacking, and it was the aim of the present work to improve this knowledge.

MATERIALS AND METHODS

Catalyst preparation. Halloysite, clay, titanium dioxide, and natural zeolite (clinoptilolite) were employed for preparation of the catalysts to be used in selectivity studies. Halloysite catalyst was prepared by the method of Kirkpatrick (3). A quantity of halloysite, composed of 27% Al_2O_3, 57% SiO_2 and 16% H_2O (by weight), was reduced into the powder form and was contacted with a weak solution of acetic acid (14.3% by wt) under continuous stirring for 1 h (Halloysite 1) or 2 d (Halloysite 2).

For preparation of the activated carbon catalyst, the method given by Davis and McBride (8) was employed.

The clay catalysts were activated by the treatment of clay with HCl solution (9,11,12,15). Activated clay 1 was obtained from the margarine department of Taris Oil Company in Izmir, Turkey. Activated clay 2 and activated clay 3 were obtained by activating clay from Madak Company (Balıkesir, Turkey) and green clay from the Ankara region, respectively, by the dry method. Titanium-based catalysts were prepared by treatment of a mixture of titanium dioxide and silica gel in the mole ratio of 1:1 with an HCl solution of 9% or by the treatment of 1 mole titanium dioxide by acetic acid after heating in 25% aqueous solution of NaOH (16).

The zeolite tuffs, rich in clinoptilolite and obtained from Bigadic (Balikesir/Turkey), also were used as catalyst and activated as follows: A quantity of clinoptilolite was contacted with distilled water for 2 h and then dried at 105°C. It was reduced into powder form by grinding and then activated at 300°C for 24 h. The composition of the catalyst was 74.86% SiO_2, 0.42% Fe_2O_3, 0.70% MgO, 0.50% Na_2O, 2.71% K_2O, 9.04% H_2O, 2.42% CaO, and 9.35% Al_2O_3.

Experimental setup. A schematic diagram of the experimental setup is given in Figure 1. The experiments were done in a three-neck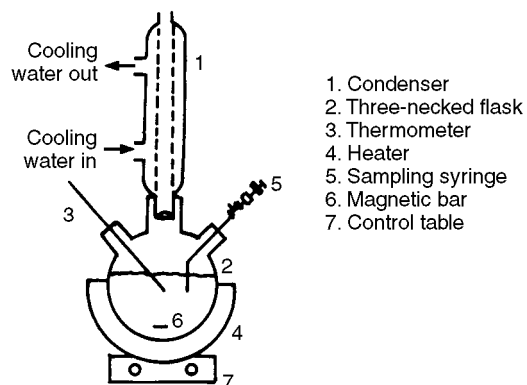ed 250-mL flask. The necks housed a sampling syringe, a condenser open to the atmosphere, and a thermometer to measure the temperature of the reaction mixture. The flask was heated with a thermostated heating mantle (Electrothermal Engineering Ltd., Essex, United Kingdom) and was stirred magnetically.

For a typical run, a known amount of catalyst and wood turpentine, containing α-pinene, was charged to the reactor and equilibrated to the reaction temperature. Throughout the run, the temperature was maintained constant within about ±1°C. The mixture was stirred vigorously to slurry the catalyst uniformly throughout the liquid. The condenser's cooling water was started. Representative samples were withdrawn periodically with a syringe (Birgi, İstanbul, Turkey), and the catalyst was immediately separated from the liquid phase by centrifuging. The sample of liquid phase was analyzed by a Hewlett-Packard gas chromatograph (Palo Alto, CA) with flame-ionization detector on a capillary column of HP-FFFAP. From the composition of wood turpentine before each run, the percentage yield of camphene, *Y*, was calculated (Equation 1):

$$Y(\%) = \frac{\text{Weight of camphene obtained}}{\text{Weight of } \alpha\text{-pinene in the original material}} \times 100 \quad [1]$$

RESULTS AND DISCUSSION

Selectivity studies. Wood turpentine (100 g) (Ortaş, Edremit, Turkey), containing 85 wt% α-pinene, was used as the α-pinene source in all runs given below. The results of the selectivity screening test are given in Table 1. The following was noted from the selectivity studies: (i) During the preparation of the halloysite catalysts, increasing the treatment time with acetic acid from 1 h to 2 d did not make any significant difference in the yield of camphene. (ii) Activated carbon was inactive in the production of camphene. (iii) It was difficult to control the temperature during the runs with activated clay. When the amount of catalyst was decreased from 2.5 to 1.0 g, the reaction temperature could be maintained within the desired range. Activated clay 3 was more active than the others. (iv) Titanium catalysts treated with NaOH were not active. Catalysts prepared by contact with HCl were rather selective in the production of camphene. (v) Natural zeolite catalyst in the form of clinoptilolite was the most selective catalyst when compared with the others used in the study at the level of 2.5 g. Although activated clay 3 seems to be the most selective in terms of the amount of catalyst used in the test, we selected clinoptilolite as the most selective catalyst because of the existence of zeolite tuffs reserves rich in clinoptilolite in Bigadic (Balikesir/Turkey). Also, acid clay-catalyzed isomerization reactions of α-pinene are rather uncontrollable and often lead to severe explosions.

The effect of temperature. Figure 2 shows the effect of temperature on camphene yield at a catalyst level of 2.5 g and a reaction time of 2 h between 130–150°C. Below 130°C, the yield of camphene was almost zero. Above 130°C, a sharp in-

FIG. 1. Experimental setup.

Cooling water out — 1

Cooling water in

3

5

2

6

4

7

1. Condenser
2. Three-necked flask
3. Thermometer
4. Heater
5. Sampling syringe
6. Magnetic bar
7. Control table

TABLE 1
Results of the Selectivity Screening Test

Type of catalyst	Reaction time (h)	Amount of catalyst (g)	Temperature (°C)	Camphene yield (%)
Halloysite 1	2	2.5	155	24.71
Halloysite 1	2	2.5	155	27.63
Halloysite 1	2	2.5	155	28.30
Halloysite 2	2	2.5	155	23.87
Halloysite 2	2	2.5	155	26.92
Halloysite 2	2	2.5	155	31.00
Activated carbon	2	2.5	155	0.90
Activated carbon	2	2.5	155	0.39
Activated carbon	2	2.5	155	3.18
Activated clay 1	0.16	2.5	155[a]	30.60
Activated clay 1	0.16	2.5	155[a]	41.13
Activated clay 2	0.16	2.5	155[a]	31.92
Activated clay 3	0.16	2.5	155[a]	33.76
TiO_2-SiO_2	2	2.5	155	42.41
TiO_2-SiO_2	2	2.5	155	34.57
TiO_2-SiO_2	2	2.5	155	29.07
TiO_2-NaOH	2	2.5	155	4.07
TiO_2-NaOH	2	2.5	155	0.54
TiO_2-NaOH	2	2.5	155	0.87
TiO_2-SiO_2-NaOH	2	2.5	155	0.47
TiO_2-SiO_2-NaOH	2	2.5	155	0.25
TiO_2-SiO_2-NaOH	2	2.5	155	0.52
Clinoptilolite	2	2.5	155	43.73
Clinoptilolite	2	2.5	155	37.92
Clinoptilolite	2	2.5	155	43.50
Clinoptilolite	2	2.5	155	43.90
Activated clay 1	2	1	155[a]	31.13
Activated clay 1	2	1	155[a]	31.98
Activated clay 1	2	1	155[a]	32.11
Activated clay 2	2	1	155[a]	34.85
Activated clay 2	2	1	155[a]	35.05
Activated clay 2	2	1	155[a]	32.76
Activated clay 3	2	1	155[a]	37.53
Activated clay 3	2	1	155[a]	38.74
Activated clay 3	2	1	155[a]	39.56

[a]Sudden temperature increase up to 180°C in 0.16 h and overflow of the reaction mixture.
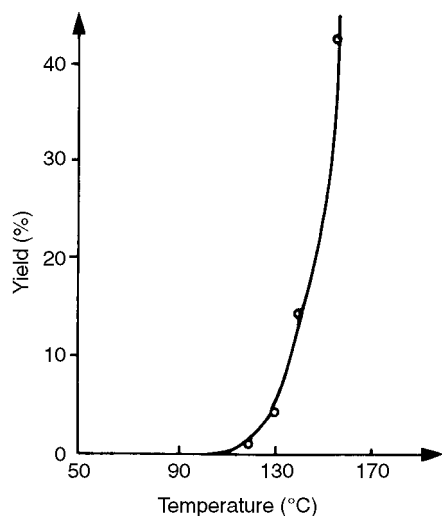
FIG. 2. Variation of the yield of camphene with temperature at 2.5 g catalyst after 2 h for 100 g of turpentine.

crease in camphene yield was obtained with increasing temperature.

The effect of catalyst amount. The effect of catalyst amount was investigated at 155°C for 2 h. The results are given in Figure 3. Figure 3 indicates that the yield of camphene increases with increasing catalyst amount until a level of 2.5 g is reached. Between 2.5 and 5 g, yield remains constant, and then yield begins to decrease with increasing catalyst loading. Figure 3 clearly shows that the optimal catalyst amount at 155°C is 2.5 g and that the conversion obtained is 42.84%. The decrease in camphene yield above 5 g catalyst may arise from the inhibition effect of products on the formation rate of camphene. But this matter is outside the scope of this study. At temperatures below 155°C, an increase in yield with catalyst amount is observed (16).

The effect of the catalyst particle size. In heterogeneous catalytic reactions, a decrease in particle size increases the rate of the reaction by decreasing the internal diffusion resistance (17).

For the isomerization of α-pinene to camphene, it has been noted (2) that, although reaction rates increase with increase in the fineness of the catalyst, few further effects are observed above a grain size of about 0.075 mm. That is why catalyst particles with a size between 0.075–0.1 mm were used in all runs in the present work. The investigation on the effect of particle size on camphene yield at 155°C and 2.5 g of catalyst after 2 h for 100 g turpentine gave the following results: $d_p <$ 0.040, 37.86; $0.075 \leq d_p \leq 0.1$, 42.84; $1 \leq d_p \leq 2$, 16.37, particle size (mm) and camphene yield (%), respectively. At a particle size above 1 mm, the camphene yield is smaller than that with a size of 0.075 mm. The decrease in size from 0.075 to 0.040 mm causes a small decrease in yield from 42.84 to 37.86%, which may be due to the agglomeration of catalyst particles.

The effect of stirring speed. In liquid-phase heterogeneous catalytic reactions, the reaction mixture should be stirred vigorously to slurry the catalyst uniformly throughout the liquid and eliminate the external diffusion resistance. The effects of stirring speed on the camphene yield at 155°C and 2.5 g of catalyst after 2 h for 100 g of turpentine were: 3, 41.93; 5 (stirring speed used in all runs of the present work), 42.84; 7,
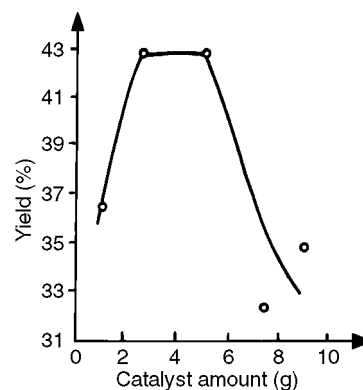
FIG. 3. Variation of the yield of camphene with catalyst level at 155°C after 2 h for 100 g of turpentine.
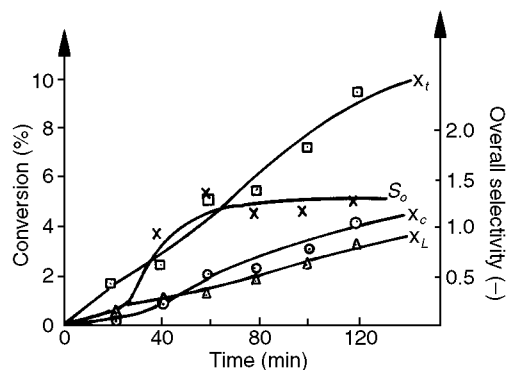
FIG. 4. Variation of the overall selectivity and conversion to products with time at 130°C at a catalyst level of 2.5 g for 100 g of turpentine.

FIG. 6. Variation of the overall selectivity and conversion to products with time at 155°C at a catalyst level of 2.5 g for 100 g of turpentine.

43.10, position of stirrer switch and camphene yield (%), respectively. The effect of stirring speed on camphene yield is not significant in the range studied.

Temperature effect on the overall selectivity to camphene. In the isomerization of α-pinene, under the reaction conditions studied, camphene and limonene were observed as main products (16). The overall selectivity of camphene, S_o, is then the ratio of the yields of camphene and limonene. Because the amount of product is proportional to the yield, for the overall selectivity, Equation 2 can be written as:

$$S_o = X_c/X_L \qquad [2]$$

where X_c is the fraction of α-pinene converted to camphene, that is, the yield of camphene, and X_L is the yield of limonene.

The overall selectivity of camphene was investigated as a function of time at a catalyst level of 2.5 g between 130 and 150°C. Figures 4–6 show the variation of S_o, X_t (total conversion of α-pinene), X_c and X_L with time at different temperatures. Selectivity to camphene and conversion to products increase with time and with temperature. Selectivity is the highest at 155°C and approaches 1.7. The similarity of conversion vs. time curves for the parallel reactions indicates that the isomerization reaction of α-pinene may be considered as a parallel reaction system.
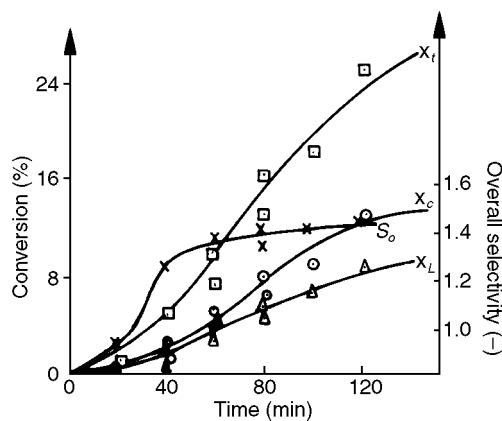

FIG. 5. Variation of the overall selectivity and conversion to products with time at 140°C at a catalyst level of 2.5 g for 100 g of turpentine.
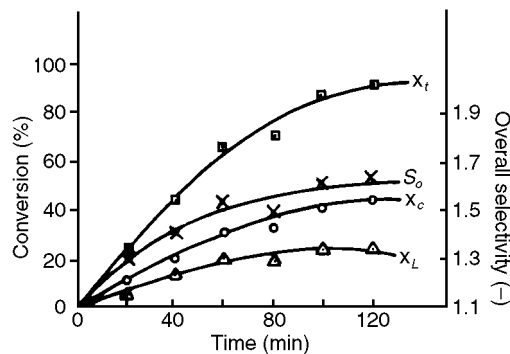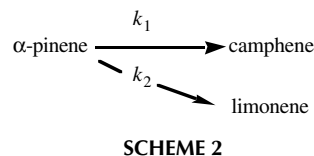

SCHEME 2

Kinetics of the isomerization reaction of α-pinene to camphene. The heterogeneous catalytic isomerization reaction of α-pinene was considered as a first-order parallel reaction system because of the observed trend of conversion vs. time curves. Neglecting the formation of by-products, which are minor (16), the reaction may be given as in Scheme 2. Eliminating the external and internal diffusion resistances by sufficient agitation and by reducing the catalyst particle size, respectively, surface concentrations may be taken equal to the bulk concentrations. So, the rate of isomerization of α-pinene per unit mass of catalyst is given in Equation 3.

$$\frac{V_l}{M_c}\frac{dC_p}{d_t} = (k_1 + k_2)C_p \qquad [3]$$

where V_l = volume of liquid (L), M_c = amount of catalyst (g), C_p = concentration of α-pinene (mol/L), t = time (s), k_1 = rate constant for production of camphene (L/g·s), and k_2 = rate constant for production of limonene (L/g·s). The production rates of camphene and limonene are in Equations 4 and 5.

$$\frac{V_l}{M_c}\frac{dC_c}{d_t} = k_1 C_p \qquad [4]$$

$$\frac{V_l}{M_c}\frac{dC_L}{d_t} = k_2 C_p \qquad [5]$$

where C_c = concentration of camphene (mol/L) and C_L = concentration of limonene (mol/L).

The ratio of Equation 4 to Equation 5 gives:

$$\frac{dC_c}{dC_L} = \frac{k_1}{k_2} \qquad [6]$$

Equations 3 and 6 are integrated with the conditions that $t = 0$, $C_p = C_{p0}$, $C_c = C_{c0}$, and $C_L = C_{L0}$ (determined by gas chromatographic analysis before each run) to give Equation 7 and Equation 8, respectively:

$$-\ln\frac{C_p}{C_{p0}} = \left(k_1 + k_2\right)\frac{M_c}{V_1} \qquad [7]$$

$$\frac{C_c - C_{c0}}{C_L - C_{L0}} = \frac{k_1}{k_2} \qquad [8]$$

where C_{p0} = initial concentration of α-pinene (mol/L). Equation 8 is equal to the ratio of the yield of camphene to the yield of limonene, given by Equation 9:

$$\frac{X_c}{X_L} = \frac{k_1}{k_2} \qquad [9]$$

this plot for different temperatures. Plotting the conversion of camphene vs. the conversion of limonene, according to Equation 9, k_1/k_2 is obtained from the slope of the straight line. Figure 8 presents these lines. From $k_1 + k_2$ and k_1/k_2 values, calculated at the different temperatures, k_1 and k_2 can be determined separately. The results are presented in Table 2. The Arrhenius plots for k_1 and k_2 are presented in Figures 9 and 10: between 130 and 150°C, for the production of camphene (Equation 10)

$$k_1 = 3.020\cdot10^{-2}\, e^{-33381.6/RT} \qquad [10]$$

and for the production of limonene (Equation 11)

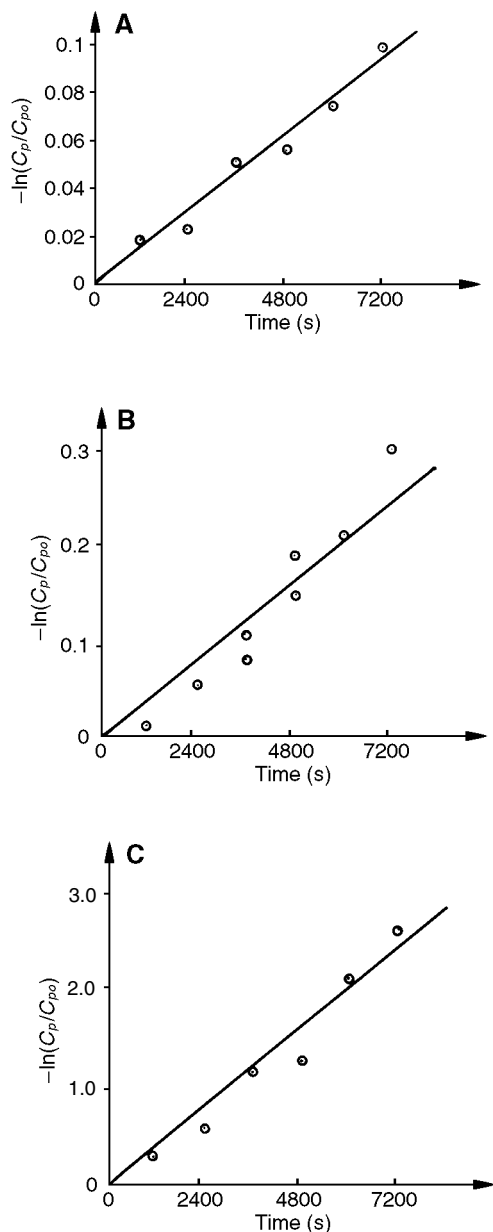$$k_2 = 1.576\cdot10^{-2}\, e^{-31096.5/RT} \qquad [11]$$

FIG. 7. Variation of −ln (C_p/C_{p0}) with time at different temperatures. (A) 130°C; (B) 140°C; (C) 155°C where C_p = concentration of α-pinene (mol/L) and C_{p0} = initial concentration of α-pinene (mol/L).
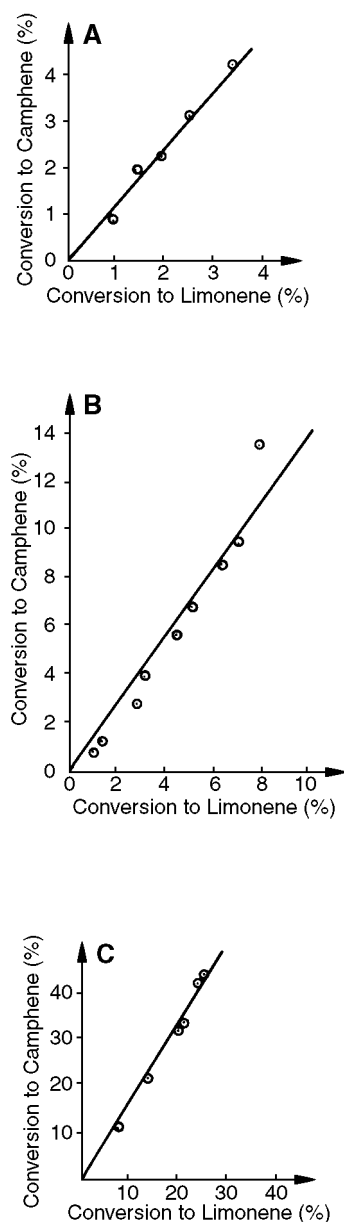
FIG. 8. Variation of conversion to camphene (X_c) with conversion to limonene (X_L) at different temperatures. (A) 130°C; (B) 140°C; (C) 155°C.
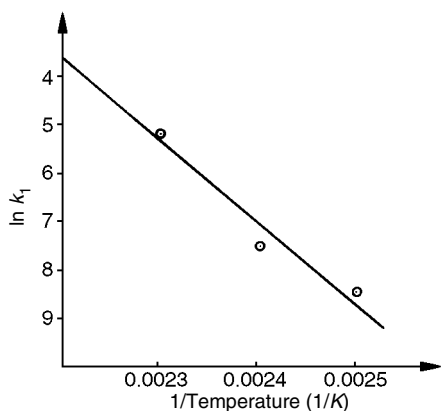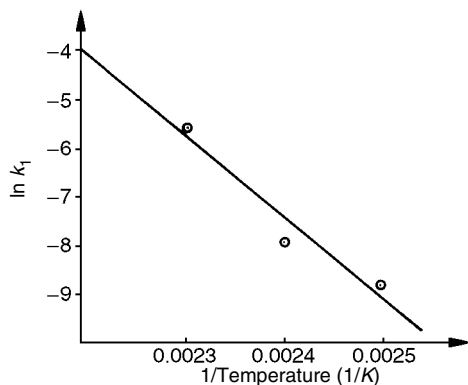
TABLE 2
Rate Constants for Different Temperatures[a]

Temperature (°C)	k_1 (L/g·s)	k_2 (L/g·s)
130	$2.082 \cdot 10^{-4}$	$1.683 \cdot 10^{-4}$
140	$5.663 \cdot 10^{-4}$	$4.060 \cdot 10^{-4}$
150	$6.002 \cdot 10^{-3}$	$3.823 \cdot 10^{-3}$

[a]k_1, rate constant for production of camphene; k_2, rate constant for production of limonene.

TABLE 3
Ratio of Rate Constants and Overall Selectivities of Camphene with Respect to Limonene at Different Temperatures

Temperature (°C)	$S_p = k_1/k_2$	$S_o = X_c/X_L$
130	1.24	1.28[a]
140	1.39	1.45[a]
150	1.57	1.66[a]

[a]From Figures 5–7, for 2 h reaction time. S_p, ratio of rate constants; S_o, overall selectivity of camphene; X_c, fraction of α-pinene converted to camphene; X_L, yield of limonene. See Table 2 for other abbreviations.

where R is the gas constant in cal/gmol K and T is temperature in K. The validity of Equation 10 and Equation 11 is limited to the ranges of operating conditions studied. The turbulence created around the catalyst particles by vigorous stirring of the reaction mixture helps to eliminate the external diffusion resistance between the bulk liquid and surface of the catalyst. Internal diffusion resistance is also negligible because of the small size of catalyst particles (0.075 mm ≤ d_p ≤ 0.1 mm) used in the runs. The model fits the experimental data fairly well. Figures 9 and 10 show that the straight lines obtained on the Arrhenius plots are rather good and that the model is satisfactory. The external diffusion resistances are negligible, and the activation energies calculated are true activation energies.

On the other hand, Table 3 presents the ratio of the rate constants, $S_p = k_1/k_2$, and overall selectivities of camphene with respect to limonene at different temperatures. S_p and overall selectivities are identical for first-order parallel reaction systems (17). The comparison of S_p and overall selectivities of camphene in Table 3 shows that both selectivity values are close to each other, so the isomerization reaction of α-pinene can be considered as a first-order parallel reaction system.

In conclusion, in the heterogeneous catalytic isomerization reaction of α-pinene to camphene, the most selective catalyst was the clinoptilolite-based zeolite composed of 74.86% SiO_2, 0.42% Fe_2O_3, 0.70% MgO, 0.50% Na_2O, 2.71% K_2O, 9.04% H_2O, 2.42% CaO, and 9.35% Al_2O_3. Camphene yield was increased by increasing reaction temperature between 130 and 155°C. The highest selectivity to camphene was obtained at 155°C. Increasing catalyst amount from 2.5 to 5 g did not change the yield of camphene at 155°C, and above 5 g of catalyst, a decrease in camphene yield was observed. The optimal conditions for the isomerization of α-pinene (for 100 g of wood turpentine with 85% α-pinene in weight) were: reaction temperature, 155°C; amount of catalyst, 2.5 g; reaction time, 2 h; and catalyst particle size, 0.075 ≤ d_p ≤ 0.1 mm.

The isomerization reaction of α-pinene to camphene was considered as a parallel reaction system with main products of camphene and limonene. Such a model fits the experimental data fairly well. The rate constants were $k_1 = 3.020 \cdot 10^{-2} e^{-33381.6/RT}$ for the production rate of camphene and $k_2 = 1.576 \cdot 10^2 e^{-31096.5/RT}$ for the production of limonene under the operating conditions of the study.

FIG. 9. Arrhenius plot for rate constant for production of camphene (k_1).

FIG. 10. Arrhenius plot for rate constant for production of limonene (k_2).

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