

Isomerization of α -Pinene over Clinoptilolite

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The kinetics of the liquid-phase isomerization of α -pinene over a natural zeolite-clinoptilolite has been studied at 100–180°C and nitrogen pressures at 1–20 bar. Up to 80–85 wt% of conversion selectivity toward reaction products was constant with camphene and limonene as the main products. Only at relatively high conversions were other monocyclic and tricyclic products formed. The consumption rate of α -pinene followed first-order kinetics. Temperature dependence of the first-order kinetic constant obeyed Arrhenius dependence with the activation energy equal to 80.9 kJ/mol. Selectivities at particular conversions were seen to be independent of temperature and pressure. A reaction network and mechanism are advanced and the corresponding kinetic equations are derived. The kinetic model gave a good correlation between the theoretical and the experimental data. © 1999 Academic Press

Key Words: α -pinene; isomerization; clinoptilolite; kinetic modeling.

INTRODUCTION

Knowledge in the field of chemical engineering has been acquired over the years regarding heterogeneous catalysis and, in particular, kinetic modeling of various industrially important reactions. In fine and specialty chemical production, contrary to petrochemicals and basic chemicals, much is still based on stoichiometry rather than on catalysis. In recent years, however, there has been increased interest in applying heterogeneous catalysts to conventional organic reactions, which used to be performed under homogeneous conditions. One of the main obstacles to their proper kinetic modeling is the too complicated reaction network with a great variety of formed products.

Among such reactions is isomerization of α -pinene over different heterogeneous catalysts. This reaction over TiO₂ catalysts is a conventional way of producing terpene products. Tricyclic products contain, besides camphene which is an important intermediate in camphor synthesis (1–6), tricyclene and small amounts of fenchenes and bornylene. Under industrial conditions the overall yield of these prod-

ucts is around 75–80%. The reaction product mixture includes, besides several bi- and tricyclic terpenes, monocyclic compounds such as limonene, terpinenes, and terpinolenes (Fig. 1). Conventional titanium oxide catalysts are prepared by treating TiO₂ with an acid to achieve a layer of titanate acid on an oxide surface. Activity and selectivity are associated with the acidity of titanium catalysts (2). Treatment of otherwise inactive TiO₂ with sulfuric acid was a step in the preparation of a catalyst, which possessed activity lower than that prepared from sodium titanate. The latter has a particular advantage, as it can be easily regenerated via extraction and under industrial conditions its consumption is around 0.6 kg per 1 t of α -pinene (2). The effect of the amount of sulfuric acid and activation procedure (e.g., time and temperature) on the initial reaction rate and selectivity of TiO₂ was reported in (6). The initial rate increased when the amount of sulfuric acid increased to a certain value and even decreased at high amounts. An increase in activation time and temperature decreased the initial activity, at the same time selectivity was increasing. Similar to these results it has been shown (7) that selectivity to desired products (camphene and tricyclene) can be increased by blocking specific acid centers of titanium catalysts.

As the reaction rate on TiO₂ is rather low, industrial interest is in finding catalytic systems that could possess much higher catalytic activity and selectivity.

Isomerization of α -pinene in the vapor phase over alumina catalysts with varying acid strength was studied (8). The acid strength had a profound influence on product distribution with the strong acid sites favoring the formation of monocyclic compounds.

Natural zeolites were also applied as catalysts (9–11) in α -pinene isomerization. In a recent study (11), synthetic zeolites Y and X with a Si/Al composition in a range from 1.4 to 200 were investigated. It was concluded that tricyclene products are formed on Lewis centers, while monocyclic products are formed on the Brønsted centers.

Dealuminated mordenite and faujasite zeolites were tested in liquid-phase α -pinene isomerization with limonene and camphene as the main products (12). Contrary to that on 13% amorphous aluminosilicate, selectivity to this product was rather low. Note that all the selectivity data as

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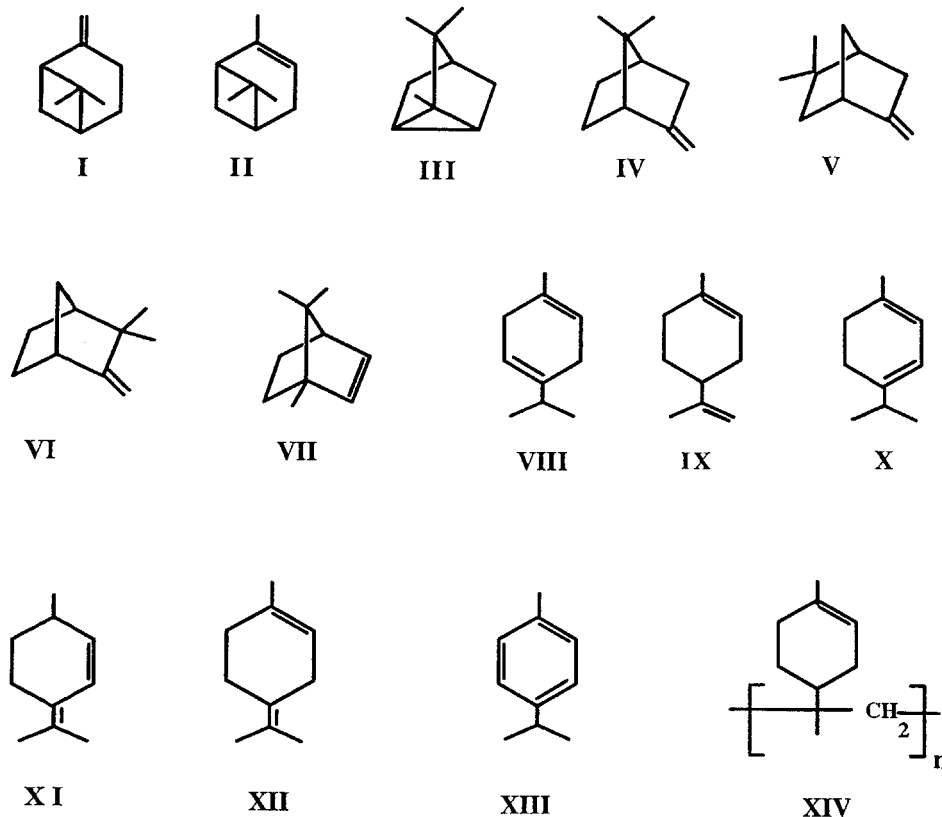


FIG. 1. I, β -pinene; II, α -pinene; III, tricyclene; IV, β -fenchene; V, α -fenchene; VI, camphene; VII, bornylene; VIII, γ -terpinene; IX, limonene (dipentene); X, α -terpinene; XI, isoterpinolene (*p*-metadiene-2,4); XII, terpinolene; XIII, *p*-cymene; XIV, polymers.

a function of conversion for both zeolite structures could be fitted by a unique set of curves regardless of the zeolite topology.

Although isomerization of α -pinene has a long industrial history, rather few kinetic studies on TiO_2 were reported (3, 13, 14) and there are virtually no papers in the literature in which quantitative descriptions via parameter estimation are presented. For instance, the detailed mechanism advanced in (2) was not supported by any kinetic modeling.

More recently, kinetic modeling of α -pinene isomerization on titanium oxide was performed (6). The big granular sizes of the catalysts used could be a reason for the possible influence of internal as well as external diffusion. The main product was camphene, greatly exceeding all other products, which allowed the authors to simplify the reaction scheme by lumping various bicyclic and monocyclic species together and considering, besides these lumped products, only camphene, dipentene (limonene), and terpinolene.

The performance of a new zeolite-based active and selective catalyst for isomerization of α -pinene was studied recently (15–17). The effects of catalyst pretreatment, pressure, and temperature have been investigated, as well as the kinetics of pinene isomerization on clinoptilolite with the formation of several products in a batch reactor at at-

mospheric pressure (15). Initially, mainly camphene and limonene were produced, and only at relatively high conversions were other secondary products formed. Selectivity values at particular conversions were seen to be independent of catalyst pretreatment, although the activity was different. The observed kinetic regularities were modeled on the basis of an elementary step mechanism.

The aim of the present paper is to investigate the kinetics of α -pinene isomerization on a zeolite-based catalyst at different pressures and temperatures and to present a kinetic model, which is consistent with mechanistic data from the literature and observed kinetic regularities.

EXPERIMENTAL METHOD

The zeolite tuffs rich in clinoptilolite obtained from Bigardic (Balikesir/Turkey) were activated prior to use in the catalytic experiments. Zeolite samples were washed with distilled water to remove impurities, dried for 2 h in an oven at 110°C , and subsequently calcined at 520°C . Chemical analysis of the samples was done by an atomic absorption spectrometer (Varian 10 Plus) except gravimetrically analyzed SiO_2 and water. The chemical composition found is 74.86% SiO_2 , 0.42% Fe_2O_3 , 0.7% MgO , 0.5% Na_2O ,

2.71% K₂O, 9.04% H₂O, 2.42% CaO, 9.35% Al₂O₃ (by weight). The BET surface area of the catalyst was 14 m²/g.

The starting reactant (α -pinene) was purchased from Arizona Chemical OY (Finland), distilled, and kept under vacuum. In all experiments 200 ml of α -pinene, containing 97.29 wt% of α -pinene, 1.21 wt% of camphene, and 1.49 wt% of limonene, was used.

The reaction was carried out in an autoclave under nitrogen pressure. The reaction mixture was stirred vigorously with a mixing speed of 1200 rpm. In a typical run 2 g of catalyst with a fraction size of 50–100 μ m and 200 ml of α -pinene were charged in the reactor, which was flushed with nitrogen before charging for 0.5 h. A fresh portion of catalyst was taken for each experiment. Experiments were carried out under isobaric (1–25 bars) and isothermal (100–160°C) dead-end conditions. Pressure and temperature were kept constant with an accuracy of ± 0.5 bar and $\pm 0.5^\circ\text{C}$, respectively.

A PC controlled the whole reactor. During the course of the reaction, several samples were taken out of the reactor, using a special sampling line. These samples were analyzed by FID gas chromatography (Hewlett Packard 5890A with 0.25 mm \times 60 m CP-Wax 52 CB capillary column). Temperature programming was applied (10 min 60°C, 2°C/min from 60 to 180°C, and 5 min at 180°C). A PC also controlled the GC, and the analytical peaks were calculated by means of available software. Experimental errors were within 1%.

It is known that in three-phase catalytic reactions the following processes occur: dissolving of gases in the liquid, diffusion of reactants to and products from the outer surface of the catalyst, and diffusion in pores (18–21).

The influence of external diffusion was determined following the published procedure (21), which was previously applied to liquid-phase hydrogenation reactions. To this end the external mass transfer coefficient was calculated using the equation proposed in (22). Due to a rather high value of the α -pinene diffusion coefficient ($\sim 10^{-9}$ m²/s), small particle size of catalyst, vigorous stirring (and thus a high value of specific mixing power), and absence of diluent (e.g., high initial concentration of reactant), the rate of external diffusion was sufficient. The influence of internal diffusion for porous materials was estimated using the conventional criteria reported in (23). The results of calculations showed that under our conditions, the influence of internal mass transfer was negligible. Experiments were also performed with catalyst particle sizes of 0.075–0.1 and 1–2 mm. It was quite clear that activity and selectivity depended on particle size, thus giving additional support to the choice of size of the clinoptilolite, which was applied in our kinetic studies.

The general approach, that was used to verify the influence of mass transfer, however, cannot rule out completely possible conformational diffusion effects typical for zeolites. On the other hand, dealuminated mordenite and Y zeolites (12), e.g., zeolites with a cell parameter

18.11 \times 20.13 \times 7.42 and 24.60 Å, correspondingly showed a similar selectivity pattern. Moreover selectivities of these zeolites were very much like our data on clinoptilolite, which has a much lower cell parameter. Therefore, possible conformational diffusion effects that may exist play a minor role.

RESULTS AND DISCUSSION

Catalytic Activity

As noted above, kinetic studies of α -pinene isomerization are rather sparse. The α -pinene consumption on TiO₂ was reported to be of zero order (2). It was also supposed (2) that the apparent reaction order in α -pinene isomerization changes depending on conversion. Two different values of activation energy were reported, for the initial period, 120 kJ/mol, and for the final period, 168 kJ/mol (2).

Typical kinetic curves obtained in our experiments are presented in Figs. 2–5. It was found that with increased temperature the catalytic activity for the isomerization of α -pinene increased. Surprisingly pressure also had an influence on reaction rate in the lower pressure region; after 5–10 bars the reaction rate was totally independent of nitrogen pressure. At high temperatures (above 135°C) no influence of pressure on reaction rate could be observed. The influence of nitrogen pressure on reaction rate cannot be explained by an increase of nitrogen solubility in the reaction mixture, since the solubility is rather low and the mole fraction of nitrogen in the liquid phase can be totally neglected. At the same time catalyst selectivity was not effected by a change in pressure. Dependence of ln of α -pinene concentration on reaction time at different values of temperatures and pressures is presented in Fig. 6. Detailed analysis of experimental data showed that the kinetics of α -pinene consumption can be described by first-order kinetics. Kinetic parameters for the first-order kinetic equation were determined using a least-squares method, incorporated in a parameter estimation software. Dependence of the first-order kinetic constant as a function of temperature is presented in Fig. 7. This strongly supports the assumption of first-order kinetics. The global activation energy of α -pinene consumption was 80.9 kJ/mol.

Selectivity and Reaction Network

It was stated in (2) that the product composition remained unchanged until conversion reached 70 wt%. The same author reported (3) that monocyclic terpenes consist mainly of limonene and terpinolene. Secondary reactions (e.g., transformations of camphene into tricyclene and further isomerization of limonene) were thought to occur only at high conversions.

As follows from our experimental data (Figs. 2–5), the main reaction products were camphene and limonene.

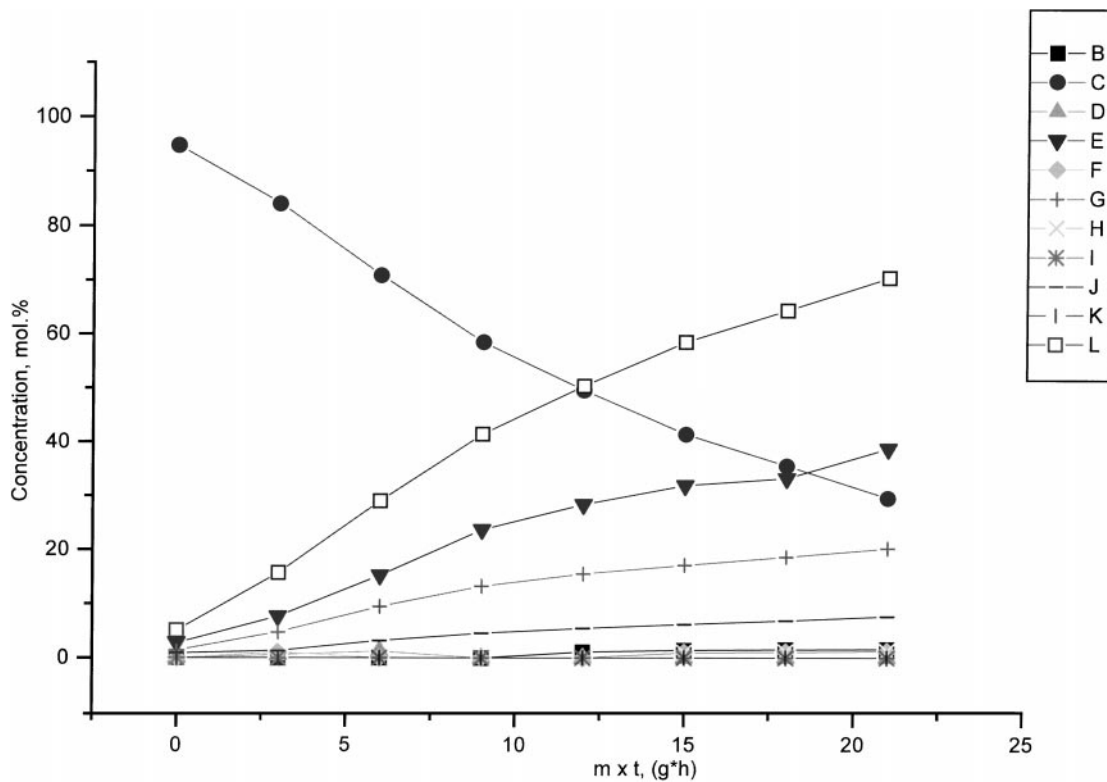


FIG. 2. α -pinene isomerization at 100°C, 5 bar. B, tricyclene; C, α -pinene; D, α -fenchene and β -fenchene; E, camphene; F, α -terpinene; G, limonene; H, γ -terpinene; I, *p*-cymene; J, terpinolene; K, isoterpinolene; L, sum of all products. *m*, catalyst mass, g; *t*, time, h.

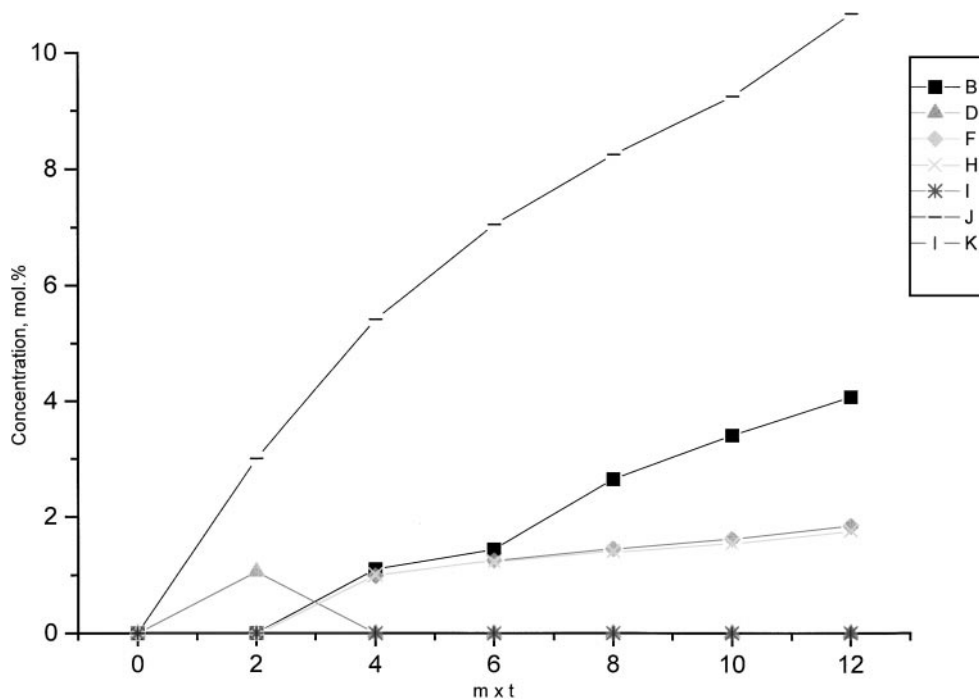


FIG. 3. α -pinene isomerization at 100°C, 11 bar. Only minor products are presented. (Notation as in Fig. 2.)

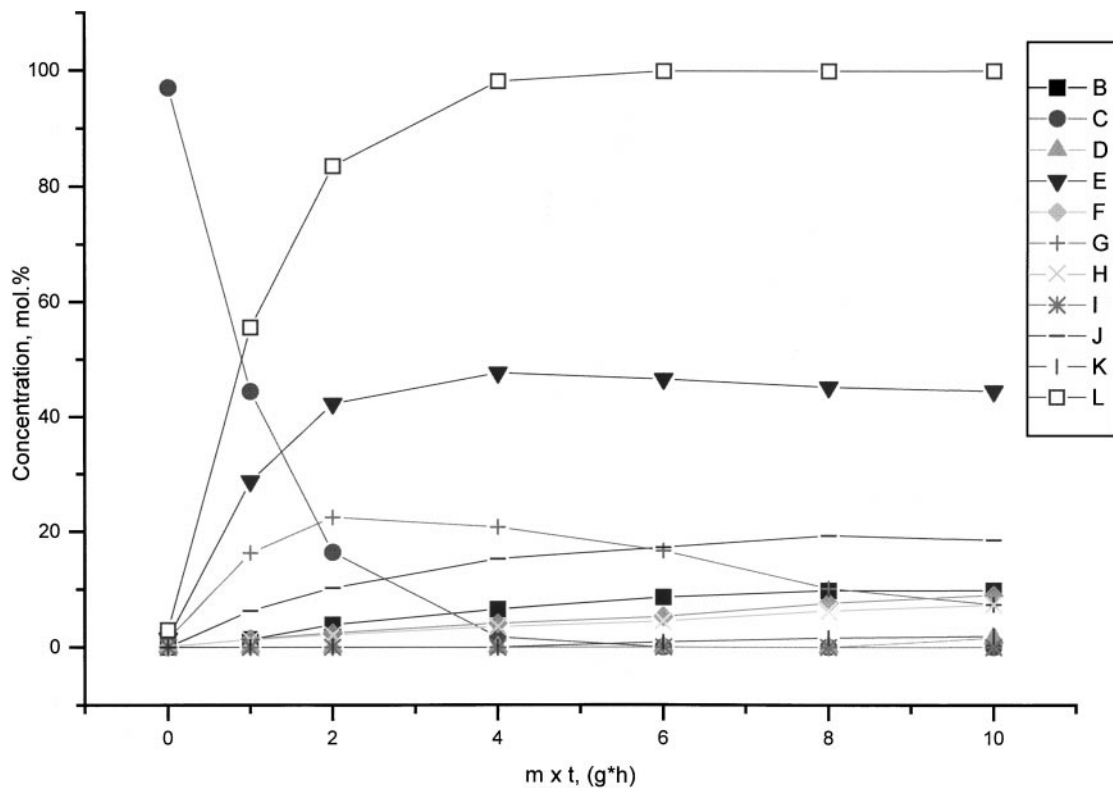


FIG. 4. α -pinene isomerization at 120°C, 10 bar. (Notation as in Fig. 2.)

When α -pinene was consumed, camphene slowly underwent isomerization into tricyclene, finally achieving an equilibrium concentration. Also, at high conversions, limonene isomerizes into secondary products.

Dependence of product concentrations as a function of α -pinene mole fraction is presented in Fig. 8 for all experimental data, e.g., all pressures and temperatures. It follows from Fig. 8 that the selectivity is virtually independent

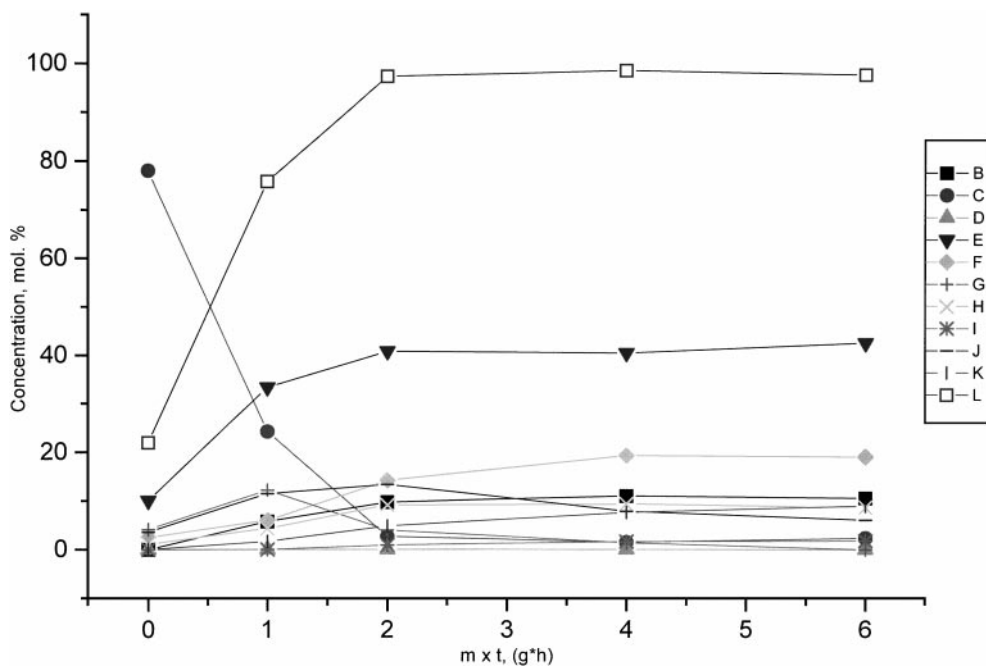


FIG. 5. α -pinene isomerization at 150°C, 10 bar. (Notation as in Fig. 2.)

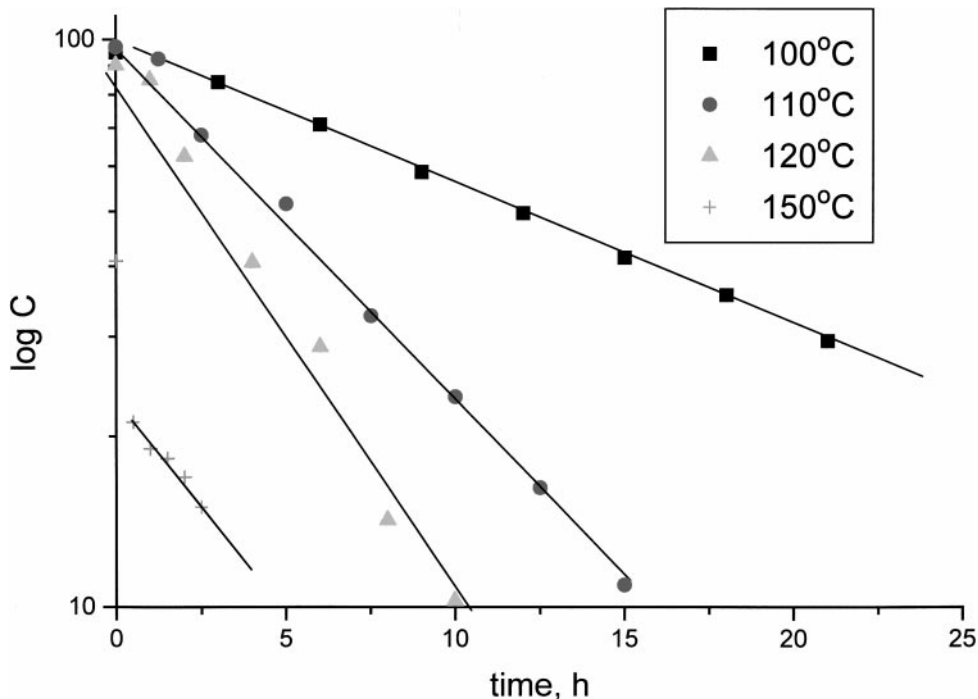


FIG. 6. Temperature dependence of α -pinene consumption.

on pressure and temperature, although the reaction rate depends on these parameters. Previously (16) we observed that the catalytic activity of α -pinene isomerization at 160°C depended on the calcination procedure (e.g., it decreased with increasing calcination time), but that the selectiv-

ity dependence, e.g., product concentration at a particular α -pinene mole fraction, was independent of catalyst activity. We proposed (16) that the activity decrease was caused by loss of a portion of acid sites during dehydration. This was probably due to the fact that the calcination procedure

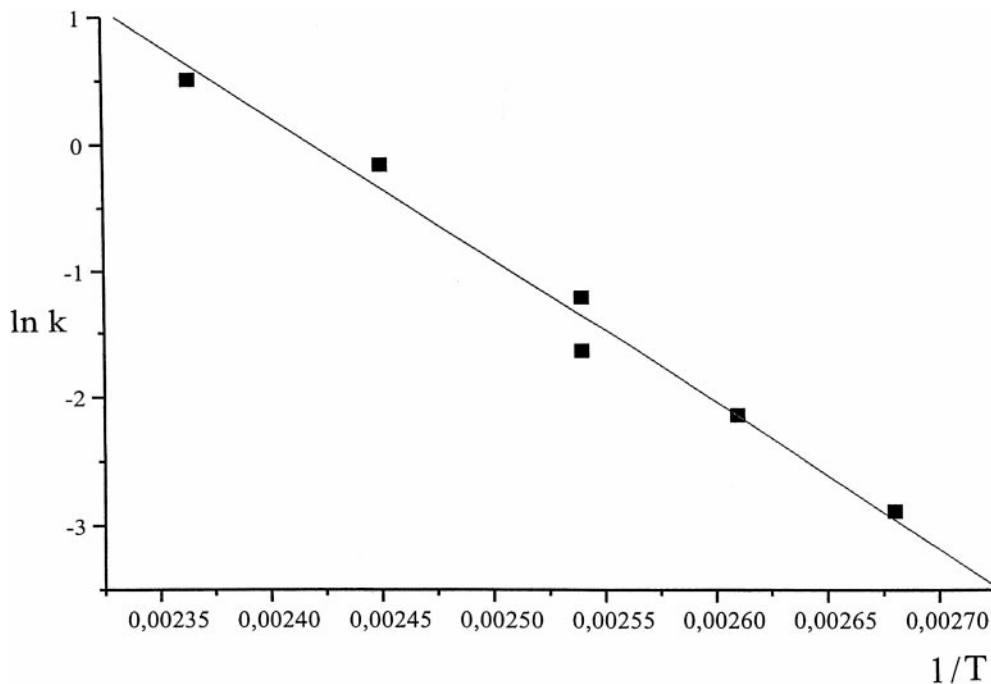


FIG. 7. Activation energy plot.

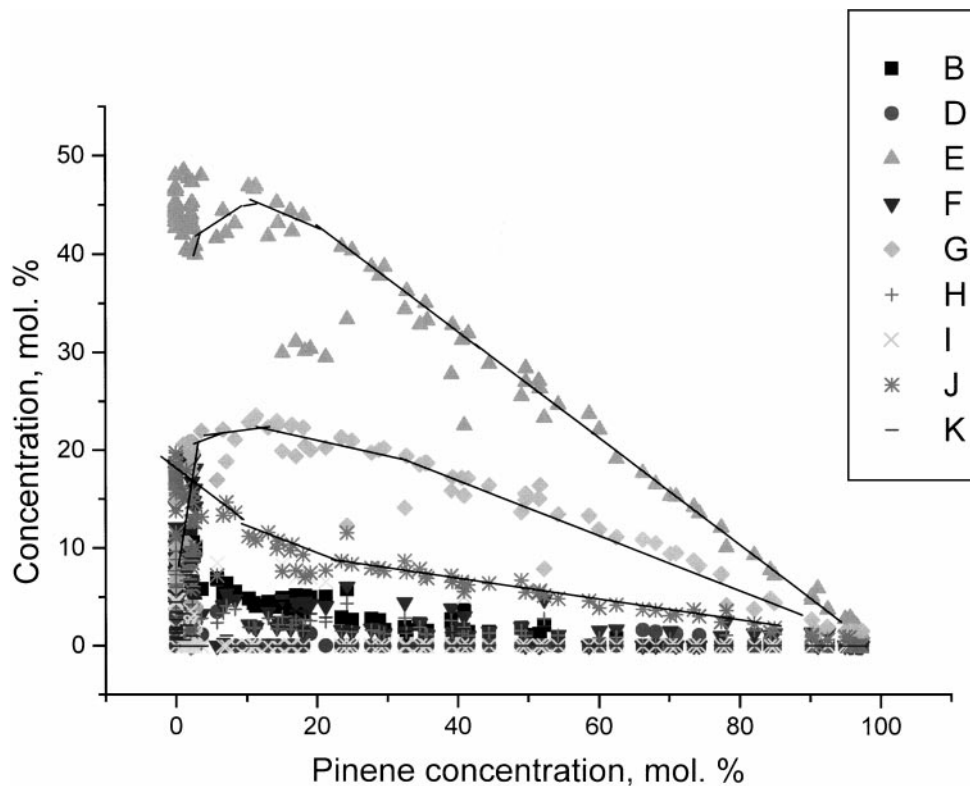
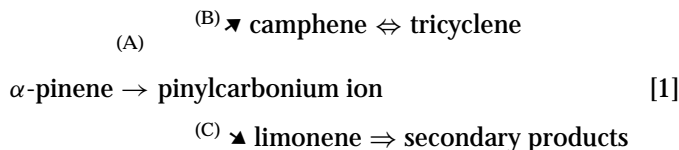


FIG. 8. Product distribution as a function of α -pinene mole fraction. (Notation as in Fig. 2.)

leads to a loss of some acid sites, therefore decreasing the turnover number, but not altering the reaction mechanism.

The reaction network was discussed in (2, 16). To propose the reaction network based on the literature and our own experimental data, the key intermediate is the pinylicarbonium ion, which is formed irreversibly from α -pinene and is the precursor for all of the reaction products, which are produced in turn in consequent steps. Monocyclic and tricyclic terpenes are formed from this ion in parallel irreversible steps. Thus the routes leading to camphene and tricyclene on one side, and limonene and its secondary products on the other side, are not interconnected. This part of the reaction network can be depicted very crudely as follows:



This scheme is supported by the fact that when α -pinene is totally consumed, camphene and tricyclene have almost equilibrium concentrations, whereas secondary reactions of limonene proceed. For instance, if all transformations of limonene occur through the same precursor (i.e., pinylicarbonium ion) as camphene-tricyclene isomerization, then

limonene should produce terpinolene, isoterpinolene, etc., as well as camphene.

The rate of α -pinene isomerization is dependent on T , pressure, and calcination procedure; however, selectivity is independent of conversion. It is reasonable to assume that only the rate of step (A) is influenced by T and P , at the same time the ratio of kinetic constants along steps (B) and (C) remains unchanged.

Secondary transformation (e.g., double bond migration) of limonene proceeds via terpinolene, which in turn gives isoterpinolene and terpenes (Fig. 9). Elucidation of the exact mechanism of double bond migration is not a subject of this paper; at the present time we can only suppose that the double bond migration occurs via addition of H^+ .

Thus, the main transformations of α -pinene are thought to occur through the addition of H^+ to α -pinene with the formation of a pinylicarbonium ion (Fig. 9). This ion has an electron-deficient C(4) atom, which attracts electron density between C(5) and C(7) atoms, leading to Wagner rearrangement with the formation of a bornylcarbonium ion. The latter reacts with the formation of a isocamphylcarbonium ion, with subsequent H^+ subtraction and production of camphene. Another possibility is deprotonation of bornylcarbonium ions, which leads to tricyclene and bornylene. One should also note that tricyclic terpenes can undergo polymerization.

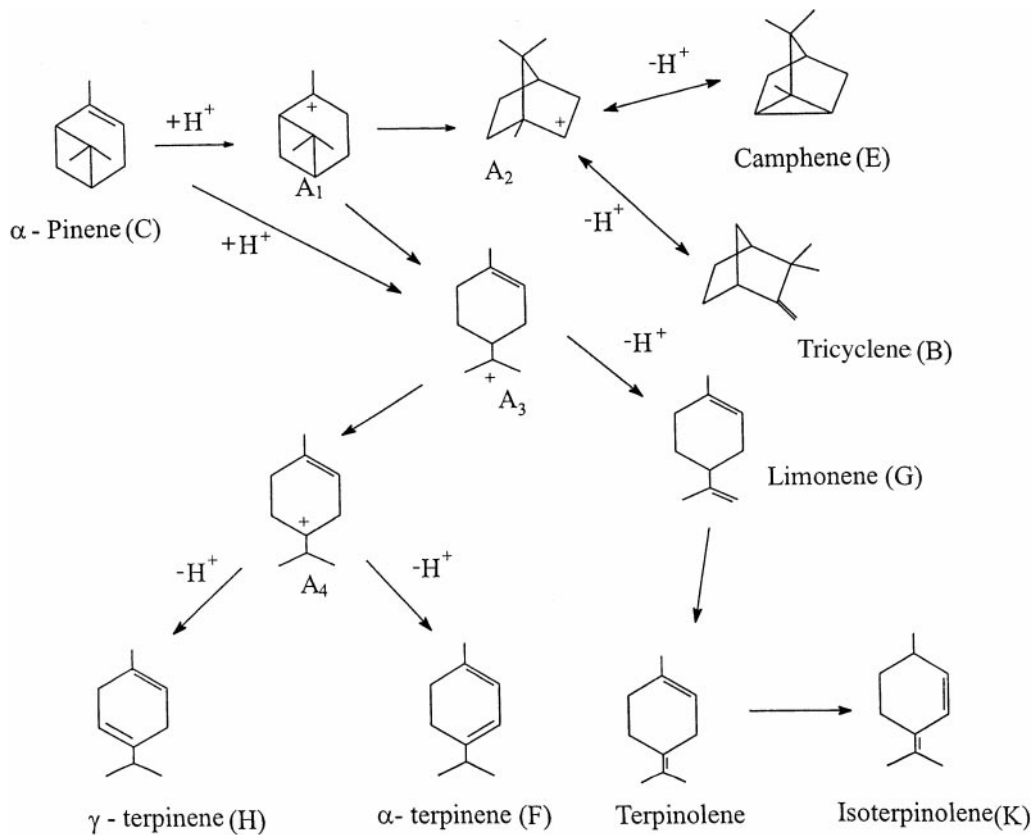


FIG. 9. Reaction network.

The second set of products is due to an irreversible Wagner rearrangement and rupture of a 4-atom cycle between C(5) and C(6), giving rise to various fenchenes, although in minor quantities.

The third group of products is the result of several monocyclic terpenes' formation, where the cycles contain 6 carbon atoms: limonene, terpinolene, α, γ -terpinenes. The pinylcarbonium ion captures an electron pair, which constitutes the bond between C(5) and C(7) atoms and forms a double bond between C(4) and C(5) atoms. H^+ escapes this terpenylcarbonium ion, leading to limonene. One can also imagine the formation of a terpenylcarbonium ion via irreversible rupture of the cyclobutane ring and the addition of a proton to the C(5) atom. We cannot discriminate between these mechanisms solely on the basis of our data, as from a kinetic viewpoint the descriptions of these mechanisms are quantitatively identical.

There is a possibility of a charge transfer within terpenylcarbonium ions from C(7) to C(1) atom, which (after proton subtraction) gives γ - and α -terpinenes. The latter can react with another molecule of α -terpinenes, leading to $\Delta^3 p$ -mentene and p -cymene.

Double bond migration in limonene results subsequently in terpinolene and isoterpinolene formation.

A simplified reaction network is presented in Fig. 10. The corresponding reaction mechanism of α -pinene isomerization can be described by seven reaction routes (sets of stoichiometric numbers of steps) and written as presented in Table 1, where Z denotes surface sites. In Table 1, elementary reactions are grouped into steps, and chemical

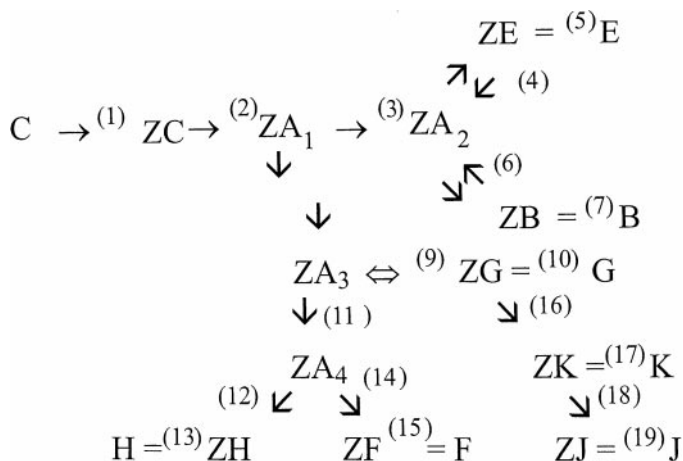


FIG. 10. Reaction network.

TABLE 1
Reaction Mechanism

Elementary steps	Basic routes						
	N(1)	N(2)	N(3)	N(4)	N(5)	N(6)	N(7)
1. $Z + C \rightleftharpoons ZC$	1	1	1	1	1	0	0
2. $ZC \rightleftharpoons ZA_1$	1	1	1	1	1	0	0
3. $ZA_1 \rightleftharpoons ZA_2$	1	1	0	0	0	0	0
4. $ZA_2 \rightleftharpoons ZE$	1	0	0	0	0	0	0
5. $ZE \rightleftharpoons Z + E$	1	0	0	0	0	0	0
6. $ZA_2 \rightleftharpoons ZB$	0	1	0	0	0	0	0
7. $ZB \rightleftharpoons Z + B$	0	1	0	0	0	0	0
8. $ZA_1 \rightleftharpoons ZA_3$	0	0	1	1	1	0	0
9. $ZA_3 \rightleftharpoons ZG$	0	0	1	0	0	0	0
10. $ZG \rightleftharpoons Z + G$	0	0	1	0	0	-1	-1
11. $ZA_3 \rightleftharpoons ZA_4$	0	0	0	1	1	0	0
12. $ZA_4 \rightleftharpoons ZH$	0	0	0	1	0	0	0
13. $ZH \rightleftharpoons Z + H$	0	0	0	1	0	0	0
14. $ZA_4 \rightleftharpoons ZF$	0	0	0	0	1	0	0
15. $ZF \rightleftharpoons Z + F$	0	0	0	0	1	0	0
16. $ZG \rightleftharpoons ZK$	0	0	0	0	0	1	1
17. $ZK \rightleftharpoons Z + K$	0	0	0	0	0	1	0
18. $ZK \rightleftharpoons ZJ$	0	0	0	0	0	0	1
19. $ZJ \rightleftharpoons Z + J$	0	0	0	0	0	0	1

Note. N(1), C = E; N(2), C = B; N(3), C = G; N(4), C = H; N(5), C = F; N(6), G = K; N(7), G = J.

equations of steps contain reactants and surface species. On the right-hand side of these equations, stoichiometric numbers for the different routes are given. The overall reaction equations are obtained by the summation of chemical equations of steps multiplied by stoichiometric numbers; these numbers must be chosen in such a way that the overall equations contain no surface species.

Detailed kinetic modeling with the complete derivation and parameter estimation for a system of differential equations would be a subject of a separate study. Here we present only some of the results.

Kinetic equations can easily be derived for the reaction mechanism presented in Table 1. Below are given only the results of such derivations. Equilibrium of step 1 yields

$$\theta_c = K_1 C_C \theta_O, \quad [2]$$

where θ_c is coverage of pinene and θ_O is the fraction of vacant sites. Similar equations can be derived for other equilibrium steps.

Coverage of surface intermediates can be expressed via θ_O .

$$\theta_{A1} = f_1 K_1 C_C \theta_O \quad [3]$$

$$\theta_{A2} = \theta_O (k_3 f_1 K_1 C_C + k_{-4} C_E / K_5 + k_{-6} C_B / K_7) / (k_4 + k_6) \quad [4]$$

$$\theta_{A3} = \theta_O (k_8 f_1 K_1 C_C + f_2 C_G) / (k_9 + k_{11}), \quad [5]$$

where

$$f_1 = k_2 / (k_3 + k_8) \quad f_2 = k_{-9} / K_{10}. \quad [6]$$

For an analysis of selectivity dependence, we rearranged some of the equations for reaction rates:

$$-dC_G/dC_C = f_3 - f_4 C_G / C_C \quad [7]$$

$$d(C_G + C_K + C_J) / d(C_H + C_F) = k_9 / k_{11} - f_2 (k_9 + k_{11}) C_G / k_{11} (k_8 f_2 K_1 C_C + f_2 C_G) \quad [8]$$

$$-d(C_B + C_E) / dC_C = f_5 \quad [9]$$

$$dC_H / dC_F = f_6, \quad [10]$$

where

$$f_3 = f_1 k_2 K_1 k_8 k_9 / (k_9 + k_{11}) \quad [11]$$

$$f_4 = (f_2 + k_{-16} / K_{10}) / k_2 K_1 - f_2 k_2 K_1 k_9 / (k_9 + k_{11}) \quad [12]$$

$$f_5 = k_3 / (k_3 + k_8) \quad [13]$$

$$f_6 = k_{13} / k_{15}. \quad [14]$$

The ratio of camphene and tricyclene is given by

$$dC_E / dC_B = (k_4 \theta_{A2} - k_{-4} \theta_E) / (k_4 \theta_{A2} - k_{-4} \theta_E). \quad [15]$$

Thus we have

$$N_G = f_3 / (1 - f_4) (N_C^{f_4} - N_C) \quad [16]$$

$$N_H = f_6 N_F \quad [17]$$

$$(N_B + N_E) / (N_C^0 - N_C) = f_5. \quad [18]$$

We performed parameter estimations, comparing experimental and calculated data for Eqs. [16]–[18]. The following values of dimensionless parameters were obtained: $f_3 = 0.32 \pm 0.01$, $f_4 = 0.16 \pm 0.02$, $f_5 = 0.536 \pm 0.004$, $f_6 = 0.93 \pm 0.22$ and the comparison between experimental and calculated data for Eq. [16] is presented in Fig. 11. It follows from Fig. 11 that the model describes the experimental data quite well.

CONCLUSIONS

The kinetics of the liquid-phase isomerization of α -pinene over a natural zeolite-clinoptilolite has been studied. Experiments were carried out under isobaric (1–25 bars) and isothermal (100–180°C) dead-end conditions under nitrogen pressure. The influence of mass transfer was negligible. The catalytic activity for the isomerization of α -pinene increased with increasing temperature. Pressure had an influence on reaction rate in the lower pressure region, but after 10 bars the reaction rate was totally independent of nitrogen pressure. The kinetics of α -pinene consumption was described by first-order kinetics with an activation energy of 80.9 kJ/mol.

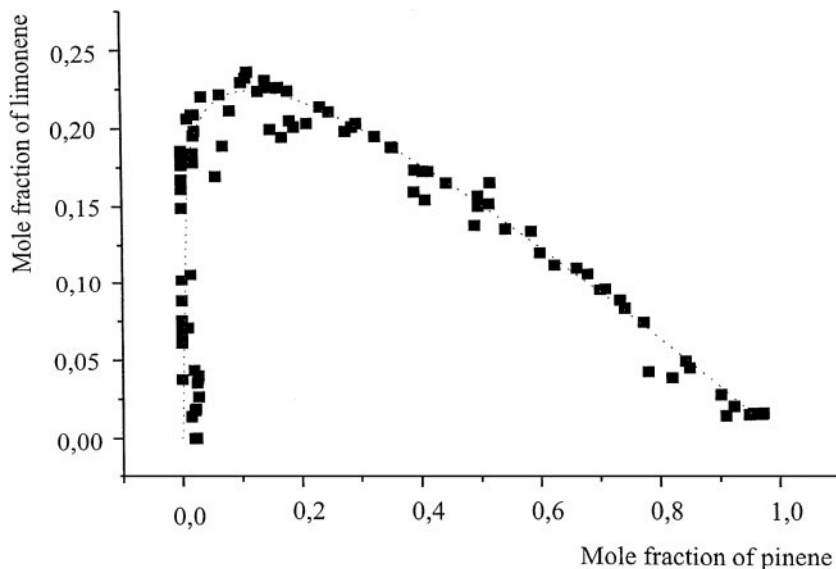


FIG. 11. Comparison between experimental and calculated data.

The main reaction products were camphene and limonene. When α -pinene was consumed, camphene slowly underwent isomerization into tricyclene, finally achieving equilibrium concentrations. Also, at high conversions, limonene isomerizes into secondary products. Selectivities at particular conversion were seen to be independent of temperature and pressure.

A reaction network and mechanism are advanced. The key intermediate is the pinylicarbonium ion, which is formed irreversibly from α -pinene and is the precursor for all of the reaction products. Monocyclic and tricyclic terpenes are formed from this ion in parallel irreversible, noninterconnected steps. Double bond migration in limonene proceeds via terpinolene, which further isomerizes into isoterpinolene and terpenes.

Corresponding kinetic equations were derived and compared with experimental data. The kinetic model gave a good correlation between the theoretical and the experimental data.

APPENDIX: NOMENCLATURE

B	tricyclene	J	terpinolene
C	α -pinene	K	terpinolene
D	α -fenchene and β -fenchene	m	catalyst mass, g
E	camphene	t	time, h
F	terpinolene	k	kinetic constant
G	limonene	Z	surface site
H	γ -terpinene	θ	surface coverage
I	p -cymene	θ_0	fraction of vacant sites

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