Isomerization of α -Pinene Oxide: Solvent Effects, Kinetics and Thermodynamics

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Abstract

Kinetics and thermodynamics of α -pinene oxide isomerization was investigated both theoretically and experimentally in different solvents in the temperature range of 50–140 °C using different zeolites, iron modified zeolites, Fe–H–MCM-41 and micro-mesoporous ZSM-5 derived catalysts. The aim was to elucidate the effect of solvent basicity and polarity on the product distribution in this reaction giving as the main value-added products campholenic aldehyde and *trans*-carveol, which are used as fragrances and perfumes. A generic kinetic first order model was developed composed of both parallel and consecutive routes. A thermodynamic analysis showed that product selectivity is determined by kinetic control and not by thermodynamics. Formation of campholenic aldehyde was favored in non-polar solvents, whereas basic solvents promoted formation of *trans*-carveol independent on temperature.

Graphical Abstract

Keywords α -Pinene oxide · Isomerization · Solvent effect · Kinetic modelling · Thermodynamics

List of Symbols

c	Concentration (mol/l)
E_A	Activation energy (kJ/mol)
E_N^T	Solvent polarity
K_j^0	Equilibrium constant at standard conditions for reaction j
k	Rate constant
n	Moles (mol)
P	Pressure (bar)
P^0	Standard pressure (bar)

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r_0	Initial rate (mmol/min/g _{cat})
R	Ideal gas constant (J/K/mol)
R^2	Degree of explanation
r	Reaction rate
T	Absolute temperature (K)
T^0	Absolute standard temperature (K)
t	Time (s)
$\hat{y}$	Estimate of concentration

Greek Symbols

ΔG_f^0	Gibbs free energy of formation at standard conditions (J/mol)
ΔG_r^0	Gibbs free energy of reaction at standard conditions (J/mol)
$\Delta G_{r,j}^\Phi$	Gibbs free energy of reaction at 1 bar and a chosen temperature (J/mol)
ΔH_f^0	Enthalpy of formation at standard conditions (J/mol)
ΔH_r^0	Enthalpy of reaction at standard conditions (J/mol)
θ	Objective function
ν_{ij}	Stoichiometric matrix composed by i components and j reactions

1 Introduction

Isomerization of α -pinene oxide has been intensively studied in the recent years over several homogeneous and heterogeneous catalysts [1–9]. The two main valuable products are campholenic aldehyde and *trans*-carveol finding applications in perfumes and flavors [10]. Isomerization of α -pinene oxide is a complex reaction including both parallel and consecutive routes (Scheme 1). For production of different compounds it is important to select both optimum reaction conditions, such as solvent and temperature as well as to use

Scheme 1 Reaction scheme for α -pinene oxide isomerization adapted from [3]

a catalyst with the desired properties. Solvent selection can be crucial, since it can be polar or apolar, protic or aprotic [11]. In addition, solvents can be basic or neutral [7]. Typically synthesis of campholenic aldehyde has been performed in neutral solvents at relatively low temperatures, i.e. 70 °C [5, 6]. Furthermore, weakly acidic illite clays promoted formation of fencholenic aldehyde at 30 °C in cyclohexane [12]. On the other hand, *trans*-carveol was produced using a basic solvent, *N,N*-dimethylacetamide (DMA) at a higher temperature 140 °C [1, 4]. A rather selective catalyst for *trans*-carveol ($S = 43\%$) has been, for example Fe–H-beta exhibiting both Brønsted and Lewis acid sites [4], when the reaction was performed in DMA at 140 °C. On the other hand campholenic aldehyde has been formed on Fe–SiO₂ in toluene as a solvent [6] and on Fe–Y-12 in toluene [7]. It was, however, observed very recently, that very high selectivity to campholenic aldehyde can be achieved over MCM-22 in α -pinene oxide isomerization in a basic solvent, *N,N*-dimethylacetamide at 140 °C [8]. Recently ZSM-5 based micro-mesoporous materials were demonstrated to have moderate selectivity to both campholenic aldehyde and *trans*-carveol, around 30–50% [3].

Effect of solvents has been scarcely investigated in α -pinene oxide isomerization apart from few studies [2, 7]. Moreover, the specific effects of temperature and solvents are not fully understood, although there is an indication that temperature does not substantially influence α -pinene oxide isomerization in DMA as a solvent [2] over H₃PW₁₂O₄₀ as a catalyst. High selectivity to *trans*-carveol was reported in [2] where several solvents with varying dielectric coefficients, such as cyclohexane, 1,4-dioxane, *N,N*-dimethylacetamide and acetone were used. The highest yields of campholenic aldehyde were obtained at 70 °C with cyclohexane as a solvent, whereas both dimethylformamide and *N,N*-dimethylacetamide afforded 90% and 86% yield respectively *trans*-carveol at 140 °C [2]. Moreover, in our previous work [7] it was shown that selectivity to *trans*-carveol increased and selectivity to campholenic aldehyde was decreased systematically with increasing solvent polarity when toluene, acetonitrile, tetrahydrofuran, *n*-pentanol, *N,N*-dimethylacetamide and *N*-methylpyrrolidone were used as solvents in α -pinene oxide isomerization over Ce–Si–MCM-41 catalysts [7]. In that study, however, only a relatively high reaction temperature, 140 °C was used with DMA and dimethylpyrrolidone (DMP). As a conclusion it can be stated that the product distribution in α -pinene oxide isomerization is very sensitive to several parameters, such as temperature, catalyst and solvent.

According to our knowledge there is only one study on kinetic analysis and thermodynamic evaluation of α -pinene oxide isomerization [9]. In that work [9] kinetic modelling was done for experimental data in the temperature range of 298–358 K over Zn-triflate supported on three different supports K60, K100 and hexagonal mesoporous silica HMS₂₄.

Thermodynamic analysis was limited to calculations of Gibbs free energy for formation of campholenic aldehyde at 25 °C.

The aim in this work was to compare kinetic results with thermodynamic evaluation, which done by the Joback's method [13, 14] in order to elucidate the effect of different parameters, such as temperature, solvent polarity and basicity in α -pinene oxide isomerization. A generic kinetic model was developed for α -pinene oxide isomerization and applied for modelling of experimental data made in this work and taken from [5, 6] for a range of iron and iron-free catalysts with different acidity, including Fe–H–MCM-41 [6], mildly acidic H-Beta-300 (the number denotes SiO₂/Al₂O₃ ratio) [6], iron modified H-Beta-300 [5] and micro-mesoporous ZSM-5 [3] based catalysts. The rate constants obtained from kinetic modelling were compared with the initial rates calculated from the kinetic results in order to assess the ability of the generic kinetic model to quantitatively describe the kinetic data.

2 Experimental Section

Isomerization of α -pinene oxide (97%, Aldrich) was performed in this work with two catalysts, H-Beta-300 and Fe–H-Beta-300. The preparation and characterization of catalysts, H-Beta-300 and Fe–H-Beta-300, used in this work, are reported in [4, 5].

The kinetic experiments were performed in a glass reactor using *N,N*-dimethylacetamide and toluene as solvents at 323 K and 343 K. In a typical experiment isomerization was performed in a glass reactor equipped with efficient motor stirring and a reflux cooler. The catalyst was heated to 523 K for 30 min in argon atmosphere prior to the reaction. The initial concentration of α -pinene oxide was 0.013 mol/l and the catalyst amount was 75 mg. The experiments were performed in the kinetic regime with small catalyst particles (below 63 μ m) with the stirring speed of 400 rpm. The samples were taken after a certain time intervals (1, 5, 10, 20, 40, 60, 120 and 180 min) and analyzed with a gas chromatograph (HP 6890 series) equipped with a HP-5 column (30 m, 320 μ m, 0.50 μ m) using the following temperature programme: 333 K (2 min) – 5 K/min – 301 K (15 min) using the split ratio of 20:1. The products were quantified calculating the response factors for the following compounds: campholenic aldehyde (86%, Hangzhou Dayangchem Co Ltd), *trans*-carveol (95%, SAFC), *p*-cymene (90%, Fluka) and *trans* pinocarveol (Aldrich, > 96%). The products were confirmed by GC-MS (Agilent technologies GC-MS 6890N) equipped with DP-5 column (30 m, 320 μ m, 0.50 μ m).

The initial formation rates of campholenic aldehyde and *trans*-carveol were calculated during the first 10 min reaction time as follows:

$$r_{0,i} = \frac{(n_{1,i} - n_{0,i})}{t \times m_{cat}} \quad (1)$$

in which $r_{0,i}$ is the initial formation rate of i , t time and m_{cat} catalyst mass.

3 Results and Discussion

3.1 Enthalpy and Gibbs Free Energy Changes for α -Pinene Oxide Isomerization

Enthalpy (ΔH_r^0) and Gibbs free energy (ΔG_r^0) at standard conditions were calculated following a thermodynamic approach [15, 16], starting from the standard enthalpy (ΔH_f^0) and Gibbs free energy (ΔG_f^0) of formation from the elements estimated with the Joback approach [13, 14]:

$$\Delta H_{r,j}^0 = \sum_j v_{i,j} \times \Delta H_{f,i}^0 \quad (2)$$

$$\Delta G_{r,j}^0 = \sum_j v_{i,j} \times \Delta G_{f,i}^0 \quad (3)$$

The equilibrium constant of each reaction was calculated from its definition:

$$K_j^0 = \exp\left(-\frac{\Delta G_{r,j}^0}{RT}\right) \quad (4)$$

Dependence of the reaction free Gibbs energy on temperature was calculated by implementing the Gibbs–Helmholtz equation valid at $P = 1$ bar ($\Delta G_{r,j}^\phi$):

$$\frac{\Delta G_{r,j}^\phi(T)}{T} = \frac{\Delta G_{r,j}^0}{T^0} + \Delta H_{r,j}^0 \left(\frac{1}{T} - \frac{1}{T^0}\right) \quad (5)$$

The calculated enthalpy and Gibbs free energy formation for each component (i) are reported in Table 1. The stoichiometric matrix was built based on the reaction scheme reported in Scheme 1.

Starting from these values, the enthalpy and Gibbs free energy for each reaction (j) at standard conditions, equilibrium constants at standard conditions (K_j^0), enthalpy and Gibbs free energy at different temperatures and pressure were calculated. A temperature range of $T_{min} = 353.15$ K and $T_{max} = 423.15$ K was investigated. The results of the calculations are reported in Table 2 and Fig. 1.

Table 1 Enthalpy and Gibbs free energy formation for each component (*i*) and stoichiometric matrix for component *i* for reaction *j*

Component	ΔH_f^0 (kJ/mol)	ΔG_f^0 (kJ/mol)	<i>i</i>	<i>j</i>						
				1	2	3	4	5	6	7
α -Pinene oxide	−167	115	1	−1	−1	−1	−1	−1	−1	0
Campholenic aldehyde	−234	−22.5	2	1	0	0	0	0	0	0
Fencholenic aldehyde	−234	−22.5	3	0	1	0	0	0	0	0
Isopinocamphe	−273	−0.78	4	0	0	1	0	0	0	0
Pinocarveol	−204	38.1	5	0	0	0	1	0	0	0
2,8-Menthadien-1-ol	−99	9.0	6	0	0	0	0	1	0	0
<i>trans</i> -Carveol	−206	12.9	7	0	0	0	0	0	1	−1
Water	−242	−228	8	0	0	0	0	0	0	−1
<i>p</i> -Cymene	−30.0	134	9	0	0	0	0	0	0	1

Table 2 Enthalpy and Gibbs free energy for each reaction (*j*) at standard conditions, equilibrium constants at standard conditions (K_j^0)

<i>j</i>	$\Delta H_{r,j}^0$ (kJ/mol)	$\Delta G_{r,j}^0$ (J/mol)	K_j^0
1	−66.3	−138	1.31×10^{24}
2	−66.3	−138	1.31×10^{24}
3	−106	−116	2.04×10^{20}
4	−36.4	−77.1	3.19×10^{13}
5	−12.0	−98.2	1.57×10^9
6	−38.7	−102	8.33×10^9
7	418	349	6.54×10^{-62}

Fig. 1 Gibbs free energy for each reaction (*j*) in α -pinene isomerization as a function of temperature

Formation of *p*-cymene from *trans*-carveol (reaction 7) does not occur spontaneously in the investigated temperature range. The Gibbs energy values for reactions 1 and 2, formation of campholenic and fencholenic aldehyde, are overlapped, as the Joback's approach does not distinguish among these two products showing the minima Gibbs free energy values, thus the related products are the most favorable to

be obtained. At 370 K there is a shift between the product distribution: at $T < 370$ K the reaction 3, formation of isopinocamphe shows the lower free energy, while reaction 2, formation of fencholenic aldehyde at $T > 370$ K. The Gibbs free energy for formation of campholenic aldehyde was -138 kJ/mol being comparative to that given in [9] where Gibbs energy change for formation of campholenic aldehyde calculated using the group contribution method was reported being -109.35 kJ/mol at 298 K. When comparing the Gibbs free energy for formation of campholenic aldehyde with *trans*-carveol, it can clearly be seen that even if both are thermodynamically feasible, formation of campholenic aldehyde is even more favorable than *trans* carveol.

3.2 Qualitative Kinetics

Qualitative kinetics of α -pinene oxide isomerization was investigated previously by our group over different catalysts including ZSM-5 based micro-mesoporous catalysts (Fig. 2) [3], mesoporous Fe-MCM-41 (Fig. 3), zeolites H-Beta-300 and Fe-Beta-300 (Fig. 4) [4, 5]. These catalysts exhibited different properties (Table 3). Several mesoporous catalysts, such as Al-SBA-15, Fe-H-MCM-41, 7MMAS and 4MMAS were also used to compare different mesopore sizes varying from 2.7 to 25 nm (Table 3, entries 1–4). 7MMAS exhibited also large amounts of strong acid sites. In addition to mesoporous materials also H-Beta-300 and Fe-Beta-300 were applied in this reaction. Among these catalysts Fe-MCM-41 exhibited the lowest acidity. Iron modification typically decreased the Brønsted acidity and increased the Lewis acidity, especially for Fe-MCM-41 (Table 3, entry 4).

Over these micro-mesoporous ZSM-5 derived catalysts the initial formation rates of campholenic aldehyde and *trans*-carveol in α -pinene oxide isomerization in DMA at 140 °C were rather small and there were no large differences in the initial rates for formation of campholenic aldehyde and *trans*-carveol (Table 4, entries 1–3). The highest initial rate for campholenic aldehyde and *trans*-carveol among

Fig. 2 Kinetic modelling of α -pinene oxide isomerization over Al-SBA-15, 7MMAS and 4MMAS catalysts at 413 K in *N,N*-dimethylacetamide as a solvent. Notation: (o, dark blue) α -pinene oxide (APO), (diamond, pink) *trans*-carveol (TCV), (+, red) campholenic aldehyde (CA), (*) fencholenic aldehyde (FA), (pentagon, green) pinocarveol, (inverted triangle, dashed red) 2,8-menthadien-1-ol, (star, dark blue) *p*-cymene and (hexagon, light blue) other

Fig. 3 Kinetic modelling of α -pinene oxide isomerization over Fe-MCM-41 at 343 K in toluene as a solvent. Notation: (o, dark blue) α -pinene oxide (APO), (diamond, pink) *trans*-carveol (TCV), (+, red) campholenic aldehyde (CA), (*) fencholenic aldehyde (FA), (pentagon, green) pinocarveol, (inverted triangle, dashed red) pinocamphone, (diamond, dotted, pink) *cis* carveol, (star, dark blue) *p*-cymene and (hexagon, light blue) other

these three catalysts was obtained with a mildly acidic Al-SBA-15. Conversion of α -pinene oxide was the lowest with 4MMAS exhibiting the smallest mesopores (Table 4, entry 3). These results show that it was possible to regulate the catalytic activity by changing pore structure [3].

Over these micro-mesoporous ZSM-5 derived catalysts only a slightly higher selectivity to *trans*-carveol were obtained in comparison with campholenic aldehyde at 140 °C in DMA as a solvent (Table 4, entries 1–3, Fig. 2). The third major product over ZSM-5 derived catalysts was 2,8-menthadien-1-ol confirmed by GC-MS [3]. As a comparison, microporous H-Beta-300 gave a quite similar ratio between the selectivities of *trans*-carveol to campholenic aldehyde as 7MMAS (Table 3, entry 2) despite their different structures. Formation of *p*-cymene was very minor over these catalysts in DMA as a solvent despite a high reaction temperature, 140 °C and utilization of micro-mesoporous catalysts (Fig. 2).

Mesoporous mildly acidic Fe-MCM-41 was very active transforming α -pinene oxide to mainly campholenic aldehyde (Table 4, entry 4, Fig. 3). The initial formation rate of campholenic aldehyde was 2.4 fold higher than the initial formation rate of *trans*-carveol, confirming that formation of campholenic aldehyde was favored in a neutral solvent, toluene at 70 °C. Noteworthy is that with this catalyst also *trans*-carveol was reacting further to *p*-cymene (Fig. 3) showing clearly that this type of mesoporous catalyst containing a low amount of Brønsted acid sites is able to catalyze dehydration of *trans*-carveol. Moreover, the amounts of

Fig. 4 Kinetic modelling of α -pinene oxide isomerization over **a** H-Beta-300 at 343 K and **b** at 413 K in DMA, **c** over Fe-H-Beta-300 at 323 K and **d** at 343 K in toluene. Notation: (o, dark blue) α -pinene oxide (APO), (diamond, pink) *trans*-carveol (TCV), (+, red)

campholenic aldehyde (CA), (*) fencholenic aldehyde (FA), (pentagon, green) pinocarveol, (inverted triangle, dashed red) pinocamphone, (diamond, dotted, pink) *cis* carveol, (star, dark blue) *p*-cymene and (hexagon, light blue) other

Table 3 Catalyst characterization data

Entry	Catalyst	Specific surface area (m ² /g _{cat})	Mesopore size (nm)	Brønsted acid sites ($\mu\text{mol/g}_{\text{cat}}$)			Lewis acid sites ($\mu\text{mol/g}_{\text{cat}}$)			References
				250 °C	350 °C	450 °C	250 °C	350 °C	450 °C	
1	Al-SBA-15	530	9.2	9	0	0	32	39	15	[3]
2	7 MMAS	410	25	47	37	8	18	22	9	[3]
3	4MMAS	605	2.7	19	8	0	57	52	36	[3]
Entry	Catalyst	Specific surface area (m ² /g _{cat})		Brønsted acid sites ($\mu\text{mol/g}_{\text{cat}}$)			Lewis acid sites ($\mu\text{mol/g}_{\text{cat}}$)			References
				250 °C	350 °C	450 °C	250 °C	350 °C	450 °C	
4	2.9 wt% Fe-MCM-41	807		22	8	0	45	9	0	[6]
5	1.1 wt% Fe-H-Beta-300	761		54	49	23	28	9	4	[5]
7	H-Beta-300	805		82	67	10	30	4	4	[4]

Table 4 Results from α -pinene oxide isomerization over different catalysts

Entry	Catalyst	Conditions	Initial rate for formation of CA (mmol/min/g _{cat})	Initial rate for formation of TCV (mmol/min/g _{cat})	Conversion (%) after 10 min	Selectivity to CA (%) at 70% conversion	Selectivity to TCV (%) at 70% conversion	References
1	Al-SBA-15	140 °C, DMA C ₀ =0.02 mol/l, 60 mg	0.24	0.33	70	42	36	[3]
2	7 MMAS	140 °C, DMA C ₀ =0.02 mol/l, 0.06 g	0.06	0.06	59	27 (X=50%)	45 (X=50%)	[3]
3	4MMAS	140 °C, DMA C ₀ =0.02 mol/l, 0.06 g	0.04	0.03	15	26	26	[3]
4	Fe-MCM-41	70 °C, toluene C ₀ =0.013 mol/l, 75 mg	3.6	1.5	90	60	20	[6]
5	Fe-H-Beta-300	70 °C, toluene C ₀ =0.013 mol/l, 75 mg	3.6	0.33	92	43	6	[5]
6	Fe-H-Beta-300	50 °C, toluene C ₀ =0.013 mol/l, 75 mg	2.0	0.38	64	42	7	This work
7	H-Beta-300	70 °C, DMA C ₀ =0.02 mol/l, 75 mg	0.04	0.09	12	36	52	This work
8	H-Beta-300	140 °C, DMA C ₀ =0.02 mol/l, 75 mg	0.57	01.1	95	32	43	[4]

the formed *p*-cymene and fencholenic aldehydes are about the same after 180 min over mildly acidic Fe-H-MCM-41.

Fe-H-Beta-300 was also active in α -pinene oxide isomerization giving the same initial formation rate of campholenic aldehyde as Fe-H-MCM-41 under the same conditions in toluene and high conversion (Fig. 4; Table 4, entry 5). Most probably, the amount of acid sites located outside Beta framework is adequate to catalyze this reaction, since the maximum sphere which can diffuse into Beta structure is 0.595 nm [17], whereas the diameters including van der Waals diameters of α -pinene oxide, campholenic aldehyde and *trans*-carveol are 0.71 × 0.83 nm, 0.79 × 1.01 nm and 0.77 × 1.09 nm, respectively [8]. It was also interesting to observe that *p*-cymene formation was lower in microporous Fe-H-Beta-300 (Fig. 4c, d) than over mesoporous Fe-H-MCM-41 (Fig. 3) most probably due to the pore size, i.e. in the microporous catalyst the consecutive reaction of *trans*-carveol is less prominent due to steric hindrance.

The effect of temperature was quite prominent between 50 °C and 70 °C over a mildly acidic Fe-H-Beta-300 in α -pinene oxide isomerization in toluene, since the initial formation rate of campholenic aldehyde and conversion increased from 2.0 mmol/min/g_{cat} to 3.6 mmol/min/g_{cat} and from 60 to 92%, respectively (Table 4, entries 5, 6).

The effect of temperature was also investigated over H-Beta-300 using a basic DMA as a solvent in α -pinene oxide isomerization at 70 °C and 140 °C (Table 4, entries 7 and 8). In this case both the initial rate and conversion were increased substantially. On the other hand, it was confirmed that temperature did not have any major effect on product distribution analogously to [2]. The ratio between the initial formation rates for formation of *trans*-carveol and campholenic aldehyde was 2.25 at 70 °C, whereas it was 1.9 at 140 °C in DMA as a solvent. Noteworthy is also that over H-Beta-300 only traces of *p*-cymene were formed in DMA as a solvent at 140 °C (Fig. 4a, b).

The use of *N,N*-dimethylacetamide resulted in a rather high selectivity to *trans*-carveol even at 70 °C (Table 4, entry 7). The highest selectivity to *trans*-carveol over H-Beta-300 obtained at 140 °C in DMA was 43% being higher than that for campholenic aldehyde [4]. These results are in line with the work of [2], who obtained high selectivity to *trans*-carveol in DMA over H₃PW₁₂O₄₀ in the temperature range of 25–140 °C. These results confirm that the basic nature of the solvent is decisive for formation of *trans*-carveol with its formation being independent on temperature. When comparing these results with thermodynamics presented above it can also be stated that high selectivity to *trans*-carveol can be obtained in α -pinene oxide isomerization even at a

Fig. 5 Selectivity to *trans*-carveol in α -pinene oxide isomerization as a function of temperature. The data generated in this work are denoted as (circle). In addition to the data from this work other data has been taken from [2, 7]

low reaction temperature in a basic solvent even if, from the viewpoint of thermodynamics, formation of campholenic aldehyde is more favourable (Fig. 5).

In order to better understand the role of solvent, temperature and catalyst selection in α -pinene oxide isomerization, both the initial rate for α -pinene oxide transformation and the selectivity to *trans*-carveol were plotted as a function of solvent polarity (Fig. 6) [9]. The initial α -pinene oxide transformation rate was calculated from the kinetic data presented in this work and in [3–7] by dividing the moles of converted α -pinene oxide during the first 10 min by consumed time and catalyst mass. The results revealed that the initial transformation rate of α -pinene oxide decreased with increasing solvent polarity (Fig. 6a). The highest initial rates were obtained at 70 °C with the mildly acidic Fe–H–Beta-300 in toluene followed by Fe–H–MCM-41 at 70 °C in toluene. In DMA much lower initial transformation rates were obtained, although the reaction temperature was usually very high, 140 °C. Noteworthy is also that the initial transformation rate of α -pinene oxide was very low in DMA at 70 °C over mildly acidic H–Beta-300, although this catalyst exhibited rather high initial rate for α -pinene oxide transformation at 140 °C. Several solvents were used in α -pinene oxide isomerization at their boiling points using a mildly acidic composite material, 32 wt% Ce–Si–MCM-41 as a catalyst. The initial rates decreased in this series also with increasing solvent polarity, except for DMA, which gave a very low initial rate despite its polarity.

Only time for 100% conversion of α -pinene oxide was reported for its isomerization over $\text{H}_3\text{PW}_{12}\text{O}_{40}$ at different temperatures [2]. In that work the shortest time for complete conversion of α -pinene oxide was obtained at

Fig. 6 **a** Initial rate for transformation of α -pinene oxide over different catalysts, solvents and temperatures as a function of solvent polarity E_N^T [18], data is from this work and from [3–7], **b** Selectivity to *trans*-carveol in α -pinene oxide isomerization as a function of solvent polarity E_N^T [18]. The data generated in this work are denoted as (circle). In addition to the data from this work (Table 3) and from [3–7]. Notation: DMA *N,N*-dimethylacetamide, NMP *N*-methylpyrrolidone, THF tetrahydrofuran

25 °C in cyclohexane and in acetone at 5 min. These solvents exhibit the E_N^T values of 0.006 and 0.355, respectively, showing that even acetone as a solvent with a relatively high polarity value gave high isomerization rates of α -pinene oxide [2]. Thus, it can be concluded that the initial transformation rate decreased with increasing solvent polarity with some exceptions, such as DMA with Ce–Si–MCM-41 as a catalyst, which can be related to catalytic properties *per se*.

In addition to temperature and basicity, selectivity to *trans*-carveol was also plotted as a function of solvent polarity taken from [9] (Fig. 6b) showing that there was no direct correlation between *trans*-carveol selectivity and solvent polarity. When comparing the initial transformation rates of α -pinene oxide (Fig. 6a) and selectivity to

trans-carveol (Fig. 6b) it can be stated that, for example, the initial rate was low in THF giving also low selectivity to *trans*-carveol indicating that there is no direct correlation between a low initial rate and selectivity to *trans*-carveol.

3.3 Kinetic Modelling

A kinetic model was developed for α -pinene oxide isomerization in [9] using an integral method. In that work both consecutive and parallel routes were proposed, even if the data fitting was only based on α -pinene oxide conversion resulting in a zero order model with respect to the reactant concentration.

Kinetic modelling of α -pinene oxide isomerization in the current study is based on the rate equations, which were derived for the reaction scheme (Scheme 1) assuming a low coverage of reactant on the surface of catalysts:

$$r_1 = k_1 \times C_{APO} \quad (6)$$

$$r_2 = k_2 \times C_{APO} \quad (7)$$

$$r_3 = k_3 \times C_{APO} \quad (8)$$

$$r_4 = k_4 \times C_{APO} \quad (9)$$

$$r_5 = k_5 \times C_{APO} \quad (10)$$

$$r_6 = k_6 \times C_{APO} \quad (11)$$

$$r_7 = k_7 \times C_{TCV} \quad (12)$$

$$r_8 = k_8 \times C_{APO} \quad (13)$$

The corresponding mass balances for the batch reactor for different compounds (with the notation: APO α -pinene oxide, CA campholenic aldehyde, FA fencholenic aldehyde, TCV *trans*-carveol, PCP isopinocampheol, PCV pinocarveol, MDI 2,8-menthadien-1-ol, CCV *cis*-carveol, PCY *p*-cymene) are:

$$\frac{dc_{APO}}{dt} = r_1 - r_2 - r_3 - r_4 - r_5 - r_6 - r_8 \quad (14)$$

$$\frac{dc_{CA}}{dt} = r_1 \quad (15)$$

$$\frac{dc_{FA}}{dt} = r_2 \quad (16)$$

$$\frac{dc_{PCP}}{dt} = r_3 \quad (17)$$

$$\frac{dc_{PCV}}{dt} = r_4 \quad (18)$$

$$\frac{dc_{MDI}}{dt} = r_5 \quad (19)$$

$$\frac{dc_{TCV}}{dt} = r_6 - r_7 \quad (20)$$

$$\frac{dc_{PCY}}{dt} = r_7 \quad (21)$$

Over other catalysts selected for kinetic modelling, i.e. H-Beta-300, Fe-H-Beta-300, Fe-H-MCM-41, no 2,8-menthadien-1-ol was found, while *cis*-carveol was formed [4–7], which can further react to *p*-cymene. In this case, the model was modified by taking into account formation of *cis*-carveol:

$$r_9 = k_9 \times C_{CCV} \quad (22)$$

$$\frac{dc_{CCV}}{dt} = r_5 - r_9 \quad (23)$$

and *p*-cymene

$$\frac{dc_{PCY}}{dt} = r_7 + r_9 \quad (25)$$

The differential equations were solved using the backward difference method and the parameter estimation was performed with the simplex and Levenberg–Marquardt methods. The numerical tools are built into the used optimization software Modest [19] in which the objective function was defined as

$$\theta = \sum (y_i - \hat{y}_i)^2 \quad (26)$$

and the degree of explanation R^2 is defined as

$$R^2 = 1 - \frac{\sum (y_i - \hat{y}_i)^2}{\sum (y_i - \bar{y})^2} \quad (27)$$

Table 5 The estimated parameters for isomerization of α -pinene oxide at 140 °C in *N,N*-dimethylacetamide as a solvent over Al–Si–SBA-15. The degree of explanation is 98.8%

Parameter	Estimate	Standard error	Standard error (%)
k_1	2.19×10^{-2}	2.91×10^{-3}	13.3
k_2	2.81×10^{-3}	6.59×10^{-4}	23.5
k_3	1.10×10^{-2}	1.05×10^{-3}	9.5
k_4	5.90×10^{-4}	6.22×10^{-4}	Large
k_5	5.55×10^{-5}	6.20×10^{-4}	Large
k_6	2.50×10^{-2}	1.96×10^{-3}	7.8
k_7	6.07×10^{-10}	2.25×10^{-4}	Large
k_8	4.62×10^{-4}	6.21×10^{-4}	Large

Table 6 The estimated parameters for isomerization of α -pinene oxide at 140 °C in *N,N*-dimethylacetamide as a solvent over 7MMAS. The degree of explanation is 99.76%

Parameter	Estimate	Standard error	Standard error (%)
k_1	1.78×10^{-3}	3.03×10^{-4}	9
k_2	2.31×10^{-4}	4.00×10^{-5}	9.3
k_3	8.08×10^{-4}	4.22×10^{-5}	5.2
k_4	5.39×10^{-5}	3.96×10^{-5}	73.6
k_5	1.61×10^{-6}	3.96×10^{-5}	Large
k_6	1.84×10^{-3}	6.15×10^{-5}	3.3
k_7	3.65×10^{-4}	3.15×10^{-4}	86.2
k_8	2.33×10^{-6}	3.96×10^{-5}	Large

Table 7 The estimated parameters for isomerization of α -pinene oxide at 140 °C in *N,N*-dimethylacetamide as a solvent over 4MMAS. The degree of explanation is 98.88%

Parameter	Estimate	Standard error	Standard error (%)
k_1	5.32×10^{-3}	9.46×10^{-4}	9.8
k_2	5.55×10^{-4}	1.26×10^{-4}	22.8
k_3	1.94×10^{-3}	1.52×10^{-4}	7.9
k_4	4.18×10^{-5}	1.23×10^{-4}	Large
k_5	9.25×10^{-11}	1.22×10^{-4}	Large
k_6	4.61×10^{-3}	2.53×10^{-4}	5.5
k_7	6.75×10^{-6}	3.52×10^{-4}	Large
k_8	1.82×10^{-4}	1.24×10^{-4}	68

Table 8 The estimated parameters for isomerization of α -pinene oxide at 70 °C in toluene as a solvent over Fe–H–MCM-41. The degree of explanation is 91.7%

Parameter	Estimate	Standard error	Standard error (%)
k_1	1.70×10^{-1}	3.44×10^{-2}	20.2
k_2	2.55×10^{-2}	4.96×10^{-3}	19.4
k_3	2.04×10^{-2}	4.18×10^{-3}	20.5
k_4	1.55×10^{-3}	2.23×10^{-3}	Large
k_5	1.83×10^{-3}	2.23×10^{-3}	Large
k_6	4.82×10^{-2}	8.37×10^{-3}	9.4
k_7	7.28×10^{-3}	9.93×10^{-4}	13.6
k_8	1.25×10^{-2}	3.11×10^{-3}	24.9
k_9	2.25×10^{-2}	4.67×10^{-7}	Large

where y_i and $\hat{y}_i$ are experimental and modelled concentrations. The parameter estimation results and modelling are shown in Tables 5, 6, 7, 8, 9 and 10 and Figs. 2, 3 and 4. The model fitting is adequate for all cases (Fig. 2, 3 and 4b, c and d) except for Fig. 4a. In α -pinene oxide isomerization over Fe–H–MCM-41 the largest error was for k_5 for which the original data for *trans*-carveol are slightly scattered. On the

Table 9 The estimated parameters for isomerization of α -pinene oxide in toluene at 50 °C and 70 °C over Fe–H–Beta-300. The degree of explanation is 96.6%. E_A in kJ/mol

Parameter	Estimate	Standard error	Standard error (%)
k_1	1.02×10^{-1}	8.57×10^{-3}	8.4
k_2	6.05×10^{-2}	4.04×10^{-3}	6.7
k_3	5.85×10^{-3}	1.12×10^{-3}	19.2
k_4	2.80×10^{-3}	1.02×10^{-3}	36.4
k_5	1.20×10^{-2}	1.71×10^{-3}	14.3
k_6	1.04×10^{-2}	1.94×10^{-3}	18.7
k_7	9.07×10^{-4}	4.84×10^{-3}	Large
k_8	2.75×10^{-2}	2.05×10^{-3}	7.4
k_9	2.38	4.71	Large
E_{A1}	60.2	7.66	12.7
E_{A2}	47.7	6.03	12.6
E_{A3}	38.9	9.5	45
E_{A4}	59.4	33.5	56.4
E_{A5}	79.9	13.0	16.2
E_{A6}	20.0	16.9	84.5
E_{A7}	66.6	4.9	Large
E_{A8}	66.1	6.76	10.2
E_{A9}	60.2	68.1	Large

Table 10 The estimated parameters for isomerization of α -pinene oxide in *N,N*-dimethylacetamide at 70 °C and 140 °C over H–Beta-300. The degree of explanation is 97.7%. E_A in kJ/mol

Parameter	Estimate	Standard error	Standard error (%)
k_1	5.95×10^{-3}	3.06×10^{-3}	51.5
k_2	2.76×10^{-3}	4.66×10^{-4}	16.9
k_3	9.67×10^{-5}	1.37×10^{-5}	14.2
k_4	1.59×10^{-4}	2.60×10^{-4}	Large
k_5	1.38×10^{-7}	2.15×10^{-7}	Large
k_6	3.19×10^{-4}	4.94×10^{-4}	Large
k_7	1.09×10^{-7}	1.23×10^{-7}	112.7
k_8	7.78×10^{-4}	9.67×10^{-4}	124.3
k_9	9.98	20.8	Large
E_{A1}	81.8	16.6	20.3
E_{A2}	84.0	5.46	6.5
E_{A3}	22.8	19.6	85.9
E_{A4}	51.2	55.2	Large
E_{A5}	74.5	85.5	Large
E_{A6}	192	> 100	26.2
E_{A7}	37.7	319	Large
E_{A8}	133	40.0	30
E_{A9}	36.6	58.2	Large

other hand, the highest values for k_7 and k_9 were correctly estimated for Fe–H–MCM-41 giving the highest amounts of p-cymene (Tables 5, 6, 7, 8) for Fe–H–Beta-300 and

Fig. 7 Comparison of calculated initial rates for CA and TCV (Table 4) and the modelled k_1 and k_6 for different catalysts (Tables 4, 5, 6). Notation: Al-SBA-15, 7MMAS and 4MMAS at 140 °C, Fe-H-MCM-41 and Fe-H-Beta-300, and H-Beta-300. Initial rates for Fe-H-MCM-41 and Fe-Beta-300 and H-Beta-300 were calculated at 70 °C. Notation; (1) DMA, (2) toluene as a solvent

H-Beta-300 (Tables 9, 10) low amounts of p-cymene were formed resulting in poor identifiability of the corresponding constants and the error became large. Because of a limited data set for H-Beta-300 varying temperature the errors in k_5 and E_{A5} for formation of *trans*-carveol were rather high (Table 10).

In order to qualitative compare the values of the initial formation rates of campholenic aldehyde and *trans*-carveol over different catalysts (Table 4) and the values of k_1 and k_6 obtained kinetic modelling (Tables 5, 6, 7, 8, 9, 10), they were plotted in a bar diagram (Fig. 7). It can be seen from Fig. 7 that for example in the case of Al-SBA-15 when the reaction was carried out in DMA at 140 °C, $r_{0, CA, calc}$ was smaller than $r_{0, TCV, calc}$ and the same trend was valid for $k_{1, mod}$ and $k_{6, mod}$. On the other hand, in a neutral solvent toluene Fe-H-MCM-41 gave higher $r_{0, CA, calc}$ than $k_{1, mod}$ analogously to $r_{0, TCV, calc}$ and $k_{6, mod}$, indicating that qualitative trends with the generic model can be well described. Furthermore, the rates were higher in neutral solvent than in the basic one. At the same time, when the reaction proceeds rapidly, the main product is campholenic aldehyde, whereas in a basic solvent, when the rate is low, the main product was *trans*-carveol.

4 Conclusions

The effect of the solvent properties, such as basicity and polarity as well as the reaction temperature was investigated in α -pinene oxide isomerization using Fe-H-Beta-300 and H-Beta-300 catalysts both exhibiting mild acidity. The results

showed that main product typically in non-polar solvents, such as toluene, is campholenic aldehyde, whereas *trans*-carveol formation is favored in basic solvents independent on temperature. The selectivity to *trans*-carveol was independent on the solvent polarity. The kinetic results were compared with the thermodynamic calculations showing that campholenic aldehyde formation is more feasible than formation of *trans*-carveol. Dehydration of *trans*-carveol to p-cymene is thermodynamically not feasible. The kinetic results showed also that product selectivity in α -pinene oxide isomerization is governed by the kinetic control.

A generic kinetic model for isomerization of α -pinene oxide containing parallel first order kinetic equations for formation of different primary products from the reactants and a consecutive route for p-cymene formation from *trans*- and *cis*-carveol was developed. The kinetic model was describing well the kinetic data for both micro- and mesoporous catalysts. The values of the kinetic constants were qualitatively compared with the initial formation rates of campholenic aldehyde and *trans*-carveol showing similar trends and explaining well the prominent solvent effect of a basic solvent favoring formation of *trans*-carveol.

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