

# Supporting Information

## Isomerization of $\alpha$ - and $\beta$ -pinene epoxides over dendritic ZSM-5 zeolites

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## 1. Experimental conditions

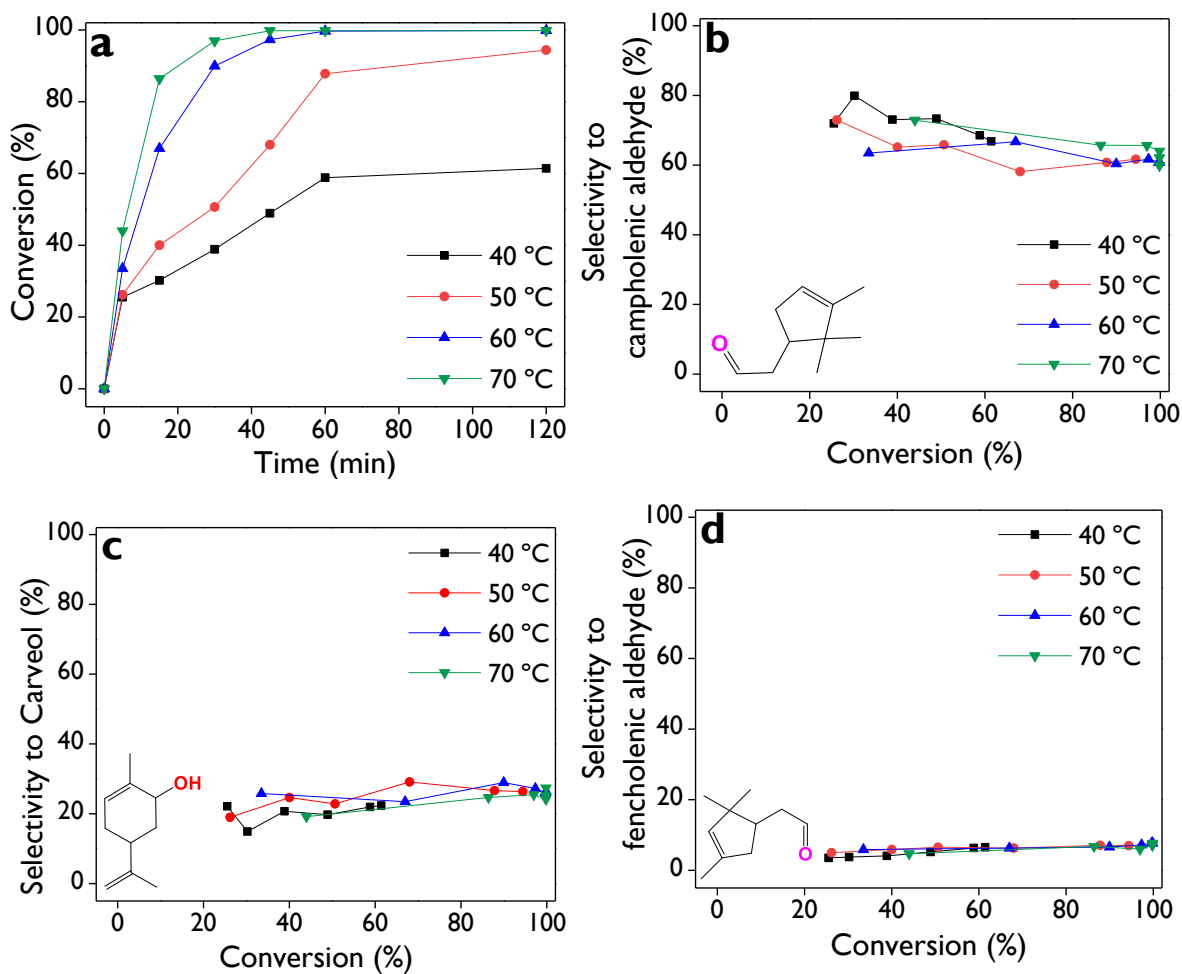
**Table S1.** Experimental conditions for the kinetic modeling of  $\alpha$ -pinene and  $\beta$ -pinene epoxide isomerization.

Entry	Temperature (°C)	Catalyst (mg)
1	40	10
2	50	10
3	60	10
4	70	10
5	40	7
6	40	16

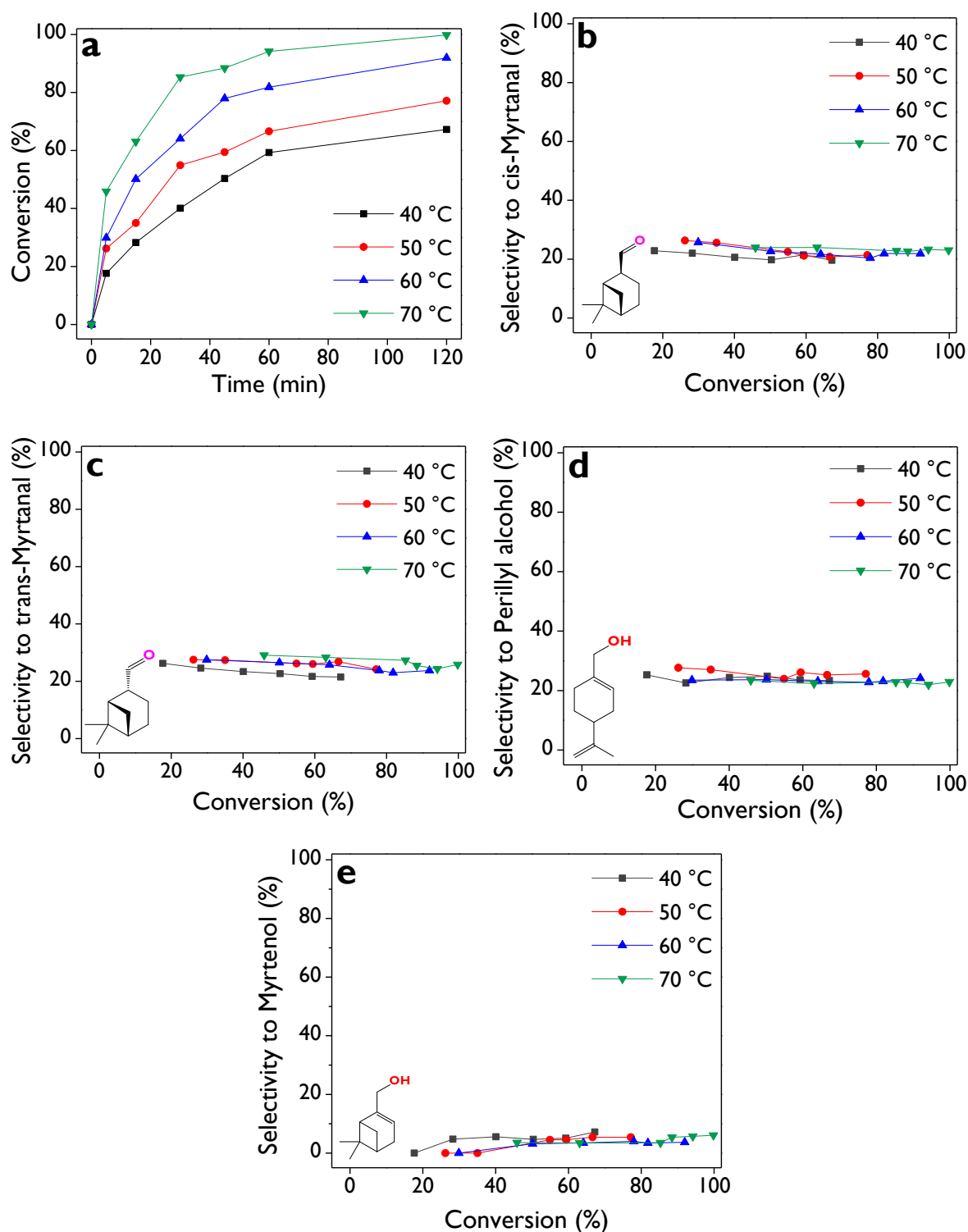
Reaction conditions: 0.25 M epoxide, total volume: 1 mL with APO, 0.5 mL with BPO, 750 rpm.

## 2. Reaction conditions

Figure S1 and Figure S2 shows the effect of temperature on the isomerization of  $\alpha$ - and  $\beta$ -pinene epoxide, respectively, over d-ZSM-5/7d catalyst sample. As expected, an increase in temperature leads to higher conversions, reaching up to 99.8 % at 70 °C. In the case of  $\alpha$ -pinene oxide, the main products were campholenic aldehyde, carveol, and to a lesser extent, fencholenic aldehyde. As the temperature increases, selectivity towards campholenic aldehyde slightly decreases, while that of carveol increases, and the selectivity of fencholenic aldehyde remains constant. This behavior is attributed to a carbocationic mechanism or to minimal entropic changes. Similar effects were observed by Sánchez-Velandia et al. (2020),[1] using a natural zeolite and confirming that these reactions are exothermic and spontaneous, with campholenic aldehyde being the most favored product ( $\Delta G_{\text{rxn}} = -99.6$  kJ/mol). For  $\beta$ -pinene oxide, the three main products (cis- and trans-myrtanal and perillyl alcohol) are obtained with comparable selectivities. An increase in temperature slightly favors the formation of myrtanal, while the selectivities of perillyl alcohol and myrtenol remain practically constant, possibly due to kinetic limitations or weak surface interactions.

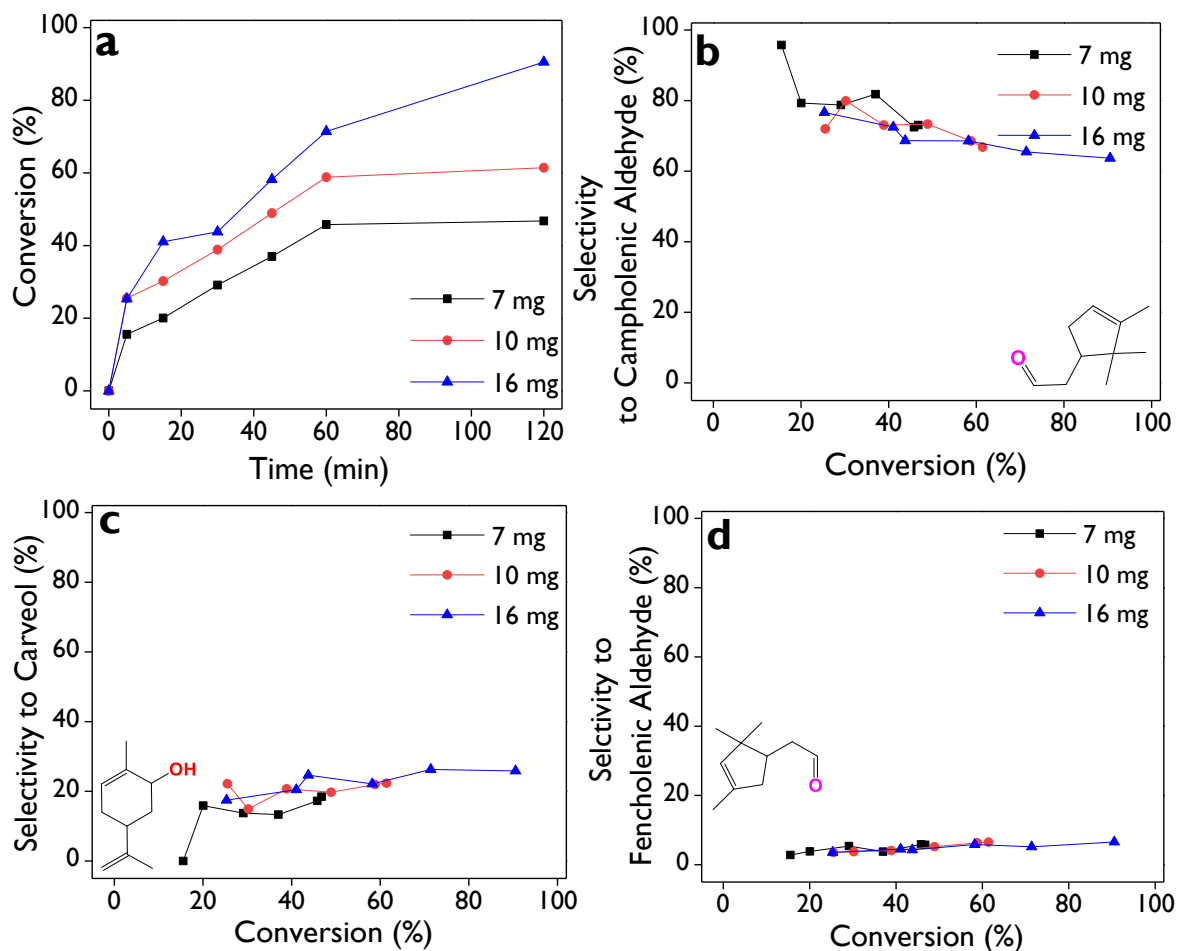


**Figure S1.** Effect of the temperature on the isomerization of  $\alpha$ -pinene epoxide over d-ZSM-5/7d catalyst: (a) conversion as a function of the reaction time; (b) selectivity to campholenic aldehyde, (c) selectivity to carveol, and (d) selectivity to fencholenic aldehyde, as a function of the conversion. Reaction conditions:  $C_{\text{APO},0} = 0.25 \text{ mol L}^{-1}$ , ethyl acetate as the solvent, 10 mg of d-ZSM-5/7d catalyst, 750 rpm.



**Figure S2.** Effect of the temperature on the isomerization of  $\beta$ -pinene epoxide over d-ZSM-5/7d catalyst: (a)  $\beta$ -Pinene epoxide conversion as a function of the reaction time, (b) selectivity to cis-myrtanal, (c) selectivity to trans-myrtanal, (d) selectivity to perillyl alcohol, and (e) selectivity to myrtenol, as a function of the conversion. Reaction conditions:  $C_{BPO,0} = 0.25 \text{ mol L}^{-1}$ , ethyl acetate as the solvent, 10 mg of d-ZSM-5/7d catalyst, 750 rpm.

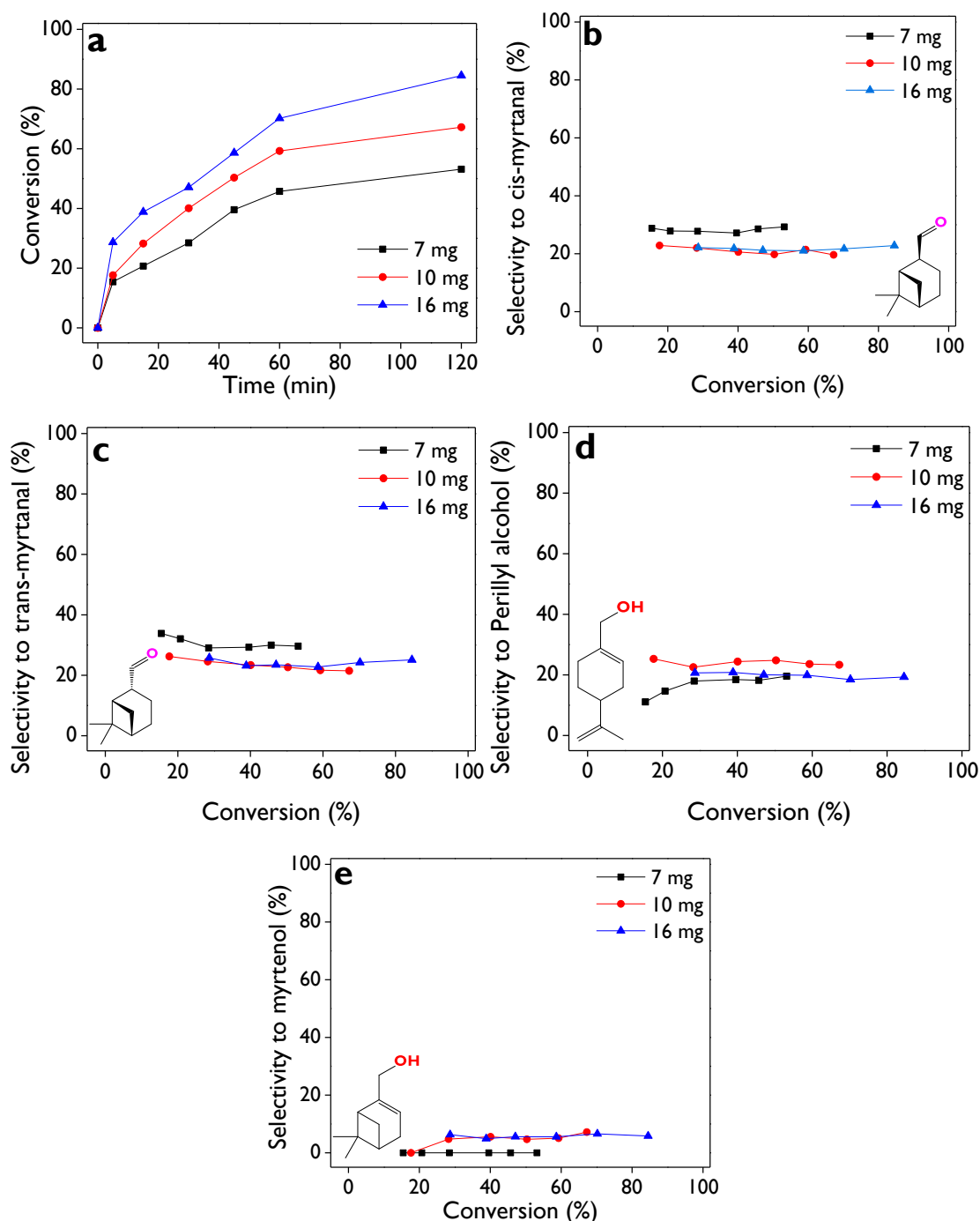
The effect of the amount of catalyst on the isomerization of  $\alpha$ - and  $\beta$ -pinene epoxide is shown in Figure S3 and Figure S4, respectively. The profiles are typical and, as expected, higher conversion is observed with increasing catalyst amount when the reaction is kinetically controlled and free from mass diffusion limitations, which was ensured under the tested reaction conditions using high stirring speed and small catalyst particle size, below 100  $\mu\text{m}$ . Along with the increase in conversion of  $\alpha$ -pinene oxide (APO), a decrease in selectivity towards campholenic aldehyde was observed, while the selectivity towards carveol increased, and that of fencholenic aldehyde remained nearly constant.



**Figure S3.** Effect of the catalyst amount for the isomerization of  $\alpha$ -pinene epoxide over d-ZSM-5/7d catalyst: (a) conversion as a function of the reaction time, (b) selectivity to campholenic aldehyde, (c) selectivity to carveol, and (d) selectivity to fencholenic aldehyde, as a function of the conversion. Reaction conditions:  $C_{\text{APO},0} = 0.25 \text{ mol L}^{-1}$ , ethyl acetate as solvent, 40  $^{\circ}\text{C}$ , 750 rpm.

In the case of  $\beta$ -pinene oxide (BPO), the increase in conversion led to a decrease in selectivity towards the *cis*- and *trans*-myrtanal isomers, as the catalyst amount increased. In contrast, the selectivity towards myrtenol and perillyl alcohol showed an increase. This behavior can be attributed to the fact that a higher amount of catalyst leads to a greater availability of active sites, which not only promotes the primary reaction but also facilitates secondary reaction

pathways. Furthermore, high catalyst loadings can alter the equilibrium between adsorption and desorption of key species on the catalyst surface, modifying the surface reaction dynamics and reducing selectivity towards the desired products. [2]



**Figure S4.** Effect of the catalyst amount for the isomerization of  $\beta$ -pinene epoxide over d-ZSM-5/7d catalyst: (a)  $\beta$ -Pinene epoxide conversion as a function of the reaction time, (b) selectivity to cis-myrtanal, (c) selectivity to trans-myrtanal, (d) selectivity to perillyl alcohol, and (e) selectivity to myrtenol, as a function of the conversion. Reaction conditions:  $C_{\text{BPO},0} = 0.25 \text{ mol L}^{-1}$ , ethyl acetate as the solvent,  $40^\circ\text{C}$ , 750 rpm.



### 3. Internal mass transfer limitations

Due to the hierarchical porosity of the dendritic zeolite material (d-ZSM-5/7d), diffusion limitations may arise in the different pore size levels. In the microporous region, with an average pore size of 0.55 nm, diffusional effects do not apply since the epoxide molecules cannot enter these pores, due to the kinetic diameters being estimated between 0.70 and 0.78 nm [1,3]. This fact implies that the reactions occur over the external surface of the zeolite nanounits in the dendritic structure. In the mesoporous region, two domains can be considered: pores (mainly in the mesopore range) within the dendritic particles and macropores existing between agglomerates of the latter aggregates. It can be assumed that the highest diffusional restrictions may arise during the transport through the mesopores, which have an average pore size of c.a. 6 nm.

Accordingly, the existence of mass transfer limitations in the mesoporous domain, for the isomerization reaction of monoterpene epoxides, have been evaluated using the Weisz-Prater criterion ( $C_{WP}$ ). This parameter is broadly used to check whether the reaction is limited or not by internal diffusion, which uses parameters that are either measured or known. If  $C_{WP} \ll 1$ , the internal diffusion is negligible, but if  $C_{WP} \gg 1$ , internal diffusion limits the reaction severely.  $C_{WP}$  is defined by Eq. (S1) [4,5].

$$C_{WP} = \frac{-r_A' \rho_c R^2}{D_{AB,eff} C_{A,cat}} \quad (S1)$$

where  $-r_A'$  ( $\text{mol g}^{-1} \text{min}^{-1}$ ) is the reaction rate of the monoterpene epoxide,  $\rho_c$  is the density of the catalyst particle ( $1/(V_p + 1/\rho_s) = 0.90 \text{ g/cm}^3$ , being  $V_p$  the total pore volume ( $0.68 \text{ cm}^3 \text{ g}^{-1}$ ) from Table S4 and  $\rho_s = 2.3 \text{ g cm}^{-3}$  [6]),  $R$  is the average radius of the catalyst particle ( $0.52 \text{ }\mu\text{m}$ , calculated assuming spherical particles using a volume of  $0.6 \text{ }\mu\text{m}^3$ , estimated from HR-TEM),  $D_{AB,eff}$  is the effective diffusivity of the epoxide in ethyl acetate, and  $C_{A,cat}$  is the concentration of epoxide at the catalyst surface, which can be assumed to be equal to the bulk concentration ( $C_A$ ) if external mass transfer limitations are removed, which were guaranteed due to the high stirring in the system.

Wilke-Chang equation [7] is an empirical expression used for calculating the diffusion coefficient,  $D_{AB}$  in  $\text{cm}^2 \text{s}^{-1}$  (Eq. (S2)), whereas the effective diffusivity ( $D_{AB,eff}$ ) can be related to the diffusion coefficient ( $D_{AB}$ ) by Eq. (S3):

$$D_{AB} = 7.4 \times 10^{-8} \frac{(\psi_B M_B)^{\frac{1}{2}} T}{\mu_B \bar{V}_A^{0.6}} \quad (S2)$$

$$D_{AB,eff} = \frac{\varphi_p \sigma_c D_{AB}}{\tau} \quad (S3)$$

Here  $\psi_B$  is the dimensionless association parameter for ethyl acetate (1.0 [8]),  $M_B$  is the molecular weight of ethyl acetate (88.11 g mol<sup>-1</sup>),  $T$  is the absolute temperature in K,  $\mu_B$  is the absolute viscosity of ethyl acetate in cP (calculated using Aspen Plus),  $\tilde{V}_A$  is the molar volume of the epoxide at the normal boiling point (188.35 cm<sup>3</sup> mol<sup>-1</sup>, estimated by Aspen Plus for camphor as a model molecule of epoxide, C<sub>10</sub>H<sub>16</sub>O),  $\phi_p$  is the catalyst porosity ( $V_p/(1/\rho_c) = 0.61$  where  $V_p$  is the total pore volume (0.68 cm<sup>3</sup> g<sup>-1</sup>) from Table S4),  $\sigma_c$  is the constriction factor (a value of 0.5 has been estimated for d-ZSM-5/7d according to definition [9] and taking into account its mesopore size distribution), and  $\tau$  is the tortuosity (value between 1-2 is assumed according to definition [9]).

On the other hand,  $r_A'$  should be calculated from the experimental data. Notice that the  $C_{WP}$  criterion gives an upper bound to avoid internal mass transfer limitations, so it is enough to calculate it at the maximum  $-r_A'$ . This value corresponds to the initial reaction rate, as expressed in Eq. (S4), where  $V$  is the total volume of liquid phase,  $C_0$  is the initial molar concentration of epoxide,  $X$  is the conversion after  $\Delta t = 5$  min, and  $m_{cat}$  is the catalyst mass:

$$-r_A' = \frac{VC_0X}{m_{cat}\Delta t} \quad (S4)$$

The value of different parameters, necessary for the application of the Weisz-Prater criterion, is provided in **Table S2** as a function of the temperature. Finally, **Table S3** shows the results of the Weisz-Prater criterion for the isomerization of  $\alpha$ - and  $\beta$ -pinene epoxides, demonstrating that both reactions are fully controlled by the kinetics of the chemical steps rather than by intraparticle mass transport since  $C_{WP} \ll 1$  values have been obtained for both substrates in all the considered cases.

**Table S2.** Value of different parameters estimated for the application of the Weisz-Prater criterion as a function of the temperature.

Entry	T (°C)	Catalyst (mg)	C <sub>0</sub> (mol L <sup>-1</sup> )	$\mu_B$ (cP)	D <sub>AB, WK</sub> (cm <sup>2</sup> s <sup>-1</sup> )	$-r_{APO,0}$ (mol g <sup>-1</sup> min <sup>-1</sup> )	$-r_{BPO,0}$ (mol g <sup>-1</sup> min <sup>-1</sup> )
1	40	10	0.25	0.366	2.563E-05	0.0013	0.0004
2	50	10	0.25	0.330	2.934E-05	0.0013	0.0007
3	60	10	0.25	0.298	3.347E-05	0.0017	0.0007
4	70	10	0.25	0.270	3.804E-05	0.0022	0.0011
5	40	7	0.25	0.366	2.563E-05	0.0011	0.0006
6	40	16	0.25	0.366	2.563E-05	0.0008	0.0004

**Table S3.** Results of the Weisz-Prater criterion for both substrates.

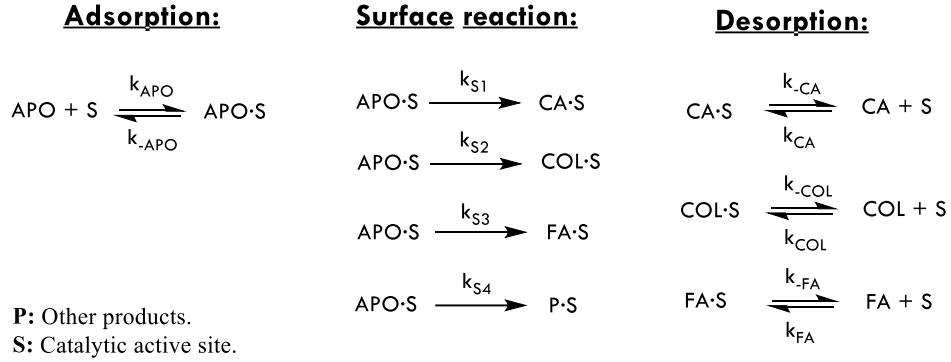
<b>Tortuosity = 1.0</b>			
<b>Entry</b>	<b><math>D_{AB, \text{eff}}</math> (<math>\text{cm}^2 \text{s}^{-1}</math>)</b>	<b><math>C_{WP, APO}</math></b>	<b><math>C_{WP, BPO}</math></b>
1	7.816E-06	2.641E-05	9.124E-06
2	8.948E-06	2.367E-05	1.183E-05
3	1.021E-05	2.654E-05	1.184E-05
4	1.160E-05	3.066E-05	1.599E-05
5	7.816E-06	2.298E-05	1.141E-05
6	7.816E-06	1.638E-05	9.267E-06
<b>Tortuosity = 2.0</b>			
<b>Entry</b>	<b><math>D_{AB, \text{eff}}</math> (<math>\text{cm}^2 \text{s}^{-1}</math>)</b>	<b><math>C_{WP, APO}</math></b>	<b><math>C_{WP, BPO}</math></b>
1	3.908E-06	5.282E-05	1.825E-05
2	4.474E-06	4.735E-05	2.366E-05
3	5.103E-06	5.307E-05	2.367E-05
4	5.801E-06	6.133E-05	3.197E-05
5	3.908E-06	4.596E-05	2.282E-05
6	3.908E-06	3.275E-05	1.853E-05

## 4. Kinetic modeling

### 4.1. Isomerization of $\alpha$ -pinene epoxide

#### 4.1.1. Unimolecular surface reaction

The reaction rate laws for the four reactions of the reaction network for  $\alpha$ -pinene epoxide isomerization (Figure 1) have been obtained, using heterogeneous kinetic models as deduced from the steps considering unimolecular surface reactions, as shown in **Figure S5**:



**Figure S5.** Elemental steps proposed for the reaction network of the isomerization of  $\alpha$ -pinene epoxide, considering unimolecular surface reactions.

S: Surface site on catalyst.

$C_i$ : Concentration of specie i in the bulk of the solution.

$C_v$ : Concentration of available surface sites on the catalyst surface.

$C_{is}$ : Concentration of specie i adsorbed at the surface site.

$C_t$ : Total concentration of sites available on the catalyst surface.

$k_i$ : Reaction rate constant of direct reaction i.

$k_{-i}$ : Reaction rate constant of reverse reaction i.

$K_i$ : Equilibrium constant for step i.

$$r_{APO,ads} = k_{APO} \left[ C_{APO} C_v - \frac{C_{APO\cdot S}}{K_{APO}} \right] \quad (\text{S5})$$

$$r_1 = k_{s1} C_{APO\cdot S} \quad (\text{S6})$$

$$r_2 = k_{s2} C_{APO\cdot S} \quad (\text{S7})$$

$$r_3 = k_{s3} C_{APO\cdot S} \quad (\text{S8})$$

$$r_4 = k_{s4} C_{APO\cdot S} \quad (\text{S9})$$

$$r_{CA,des} = k_{-CA} \left[ C_{CA\cdot S} - \frac{C_{CA} C_v}{K_{CA,d}} \right] \quad (\text{S10})$$

$$r_{\text{COL,des}} = k_{-\text{COL}} \left[ C_{\text{COL}\cdot\text{S}} - \frac{C_{\text{COL}}C_{\text{V}}}{K_{\text{COL,d}}} \right] \quad (\text{S11})$$

$$r_{\text{FA,des}} = k_{-\text{FA}} \left[ C_{\text{FA}\cdot\text{S}} - \frac{C_{\text{FA}}C_{\text{V}}}{K_{\text{FA,d}}} \right] \quad (\text{S12})$$

The Eqs. (S5), and (S10)-(S12) are solved to find the concentrations of adsorbed species ( $C_{\text{is}}$ ) when these are equal to zero, assuming the surface reactions (Eqs. (S6)-(S9)) as the rate-limiting steps.

$$C_{\text{APO}\cdot\text{S}} = K_{\text{APO}} C_{\text{APO}} C_{\text{V}} \quad (\text{S13})$$

$$C_{\text{CA}\cdot\text{S}} = \frac{C_{\text{CA}}C_{\text{V}}}{K_{\text{CA,d}}} = K_{\text{CA}} C_{\text{CA}} C_{\text{V}} \quad (\text{S14})$$

$$C_{\text{COL}\cdot\text{S}} = \frac{C_{\text{COL}}C_{\text{V}}}{K_{\text{COL,d}}} = K_{\text{COL}} C_{\text{COL}} C_{\text{V}} \quad (\text{S15})$$

$$C_{\text{FA}\cdot\text{S}} = \frac{C_{\text{FA}}C_{\text{V}}}{K_{\text{FA,d}}} = K_{\text{FA}} C_{\text{FA}} C_{\text{V}} \quad (\text{S16})$$

The balance of sites is defined by Eq. (S17):

$$C_{\text{t}} = C_{\text{V}} + C_{\text{APO}\cdot\text{S}} + C_{\text{CA}\cdot\text{S}} + C_{\text{COL}\cdot\text{S}} + C_{\text{FA}\cdot\text{S}} \quad (\text{S17})$$

By replacing Eqs. (S13) – (S16) in Eq. (S17) and simplifying, Eq. (S18) is obtained:

$$C_{\text{t}} = C_{\text{V}} + K_{\text{APO}} C_{\text{APO}} C_{\text{V}} + K_{\text{CA}} C_{\text{CA}} C_{\text{V}} + K_{\text{COL}} C_{\text{COL}} C_{\text{V}} + K_{\text{FA}} C_{\text{FA}} C_{\text{V}}$$

$$C_{\text{V}} = \frac{C_{\text{t}}}{1 + K_{\text{APO}} C_{\text{APO}} + K_{\text{CA}} C_{\text{CA}} + K_{\text{COL}} C_{\text{COL}} + K_{\text{FA}} C_{\text{FA}}} \quad (\text{S18})$$

Replacing Eq. (S18) in Eq. (S13):

$$C_{\text{APO}\cdot\text{S}} = \frac{K_{\text{APO}} C_{\text{APO}} C_{\text{t}}}{1 + K_{\text{APO}} C_{\text{APO}} + K_{\text{CA}} C_{\text{CA}} + K_{\text{COL}} C_{\text{COL}} + K_{\text{FA}} C_{\text{FA}}} \quad (\text{S19})$$

The final expressions for the reaction rates of  $r_1$ - $r_4$  are shown below, where  $k_i = k_{\text{si}} K_i C_{\text{t}}$ :

$$r_1 = \frac{k_1 C_{\text{APO}}}{1 + K_{\text{APO}} C_{\text{APO}} + K_{\text{CA}} C_{\text{CA}} + K_{\text{COL}} C_{\text{COL}} + K_{\text{FA}} C_{\text{FA}}} \quad (\text{S20})$$

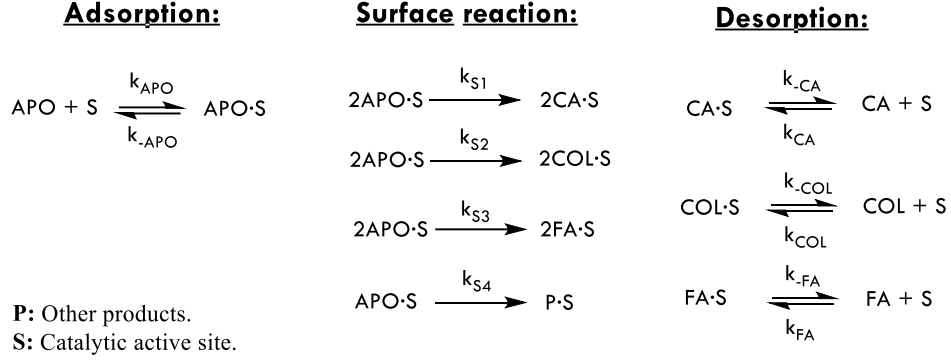
$$r_2 = \frac{k_2 C_{\text{APO}}}{1 + K_{\text{APO}} C_{\text{APO}} + K_{\text{CA}} C_{\text{CA}} + K_{\text{COL}} C_{\text{COL}} + K_{\text{FA}} C_{\text{FA}}} \quad (\text{S21})$$

$$r_3 = \frac{k_3 C_{\text{APO}}}{1 + K_{\text{APO}} C_{\text{APO}} + K_{\text{CA}} C_{\text{CA}} + K_{\text{COL}} C_{\text{COL}} + K_{\text{FA}} C_{\text{FA}}} \quad (\text{S22})$$

$$r_4 = \frac{k_4 C_{\text{APO}}}{1 + K_{\text{APO}} C_{\text{APO}} + K_{\text{CA}} C_{\text{CA}} + K_{\text{COL}} C_{\text{COL}} + K_{\text{FA}} C_{\text{FA}}} \quad (\text{S23})$$

#### 4.1.2. Bimolecular surface reaction

The reaction rate laws for the four reactions of the reaction network for  $\alpha$ -pinene epoxide isomerization (Figure 1) are obtained, using heterogeneous kinetic models as deduced considering **bimolecular surface reactions** for three of the elementary steps and unimolecular reaction for the last one, as shown in **Figure S6**:



**Figure S6.** Elemental steps proposed for the reaction network of the isomerization of  $\alpha$ -pinene epoxide, considering bimolecular surface reactions.

S: Surface site on catalyst.

$C_i$ : Concentration of specie  $i$  in the bulk of the solution.

$C_v$ : Concentration of available surface sites on the catalyst surface.

$C_{is}$ : Concentration of specie  $i$  adsorbed at the surface site.

$C_t$ : Total concentration of sites available on the catalyst surface.

$k_i$ : Reaction rate constant of direct reaction  $i$ .

$k_{-i}$ : Reaction rate constant of reverse reaction  $i$ .

$K_i$ : Equilibrium constant for step  $i$ .

$$r_{\text{APO,ads}} = k_{\text{APO}} \left[ C_{\text{APO}} C_v - \frac{C_{\text{APO}\cdot\text{S}}}{K_{\text{APO}}} \right] \quad (\text{S24})$$

$$r_1 = k_{s1} C_{\text{APO}\cdot\text{S}}^2 \quad (\text{S25})$$

$$r_2 = k_{s2} C_{\text{APO}\cdot\text{S}}^2 \quad (\text{S26})$$

$$r_3 = k_{s3} C_{\text{APO}\cdot\text{S}}^2 \quad (\text{S27})$$

$$r_4 = k_{s4} C_{\text{APO}\cdot\text{S}} \quad (\text{S28})$$

$$r_{\text{CA,des}} = k_{-\text{CA}} \left[ C_{\text{CA}\cdot\text{S}} - \frac{C_{\text{CA}} C_v}{K_{\text{CA,d}}} \right] \quad (\text{S29})$$

$$r_{\text{COL,des}} = k_{-\text{COL}} \left[ C_{\text{COL}\cdot\text{S}} - \frac{C_{\text{COL}} C_v}{K_{\text{COL,d}}} \right] \quad (\text{S30})$$

$$r_{FA,des} = k_{-FA} \left[ C_{FA \cdot S} - \frac{C_{FA} C_V}{K_{FA,d}} \right] \quad (S31)$$

The Eqs. (S24), and (S29)-(S31) are solved to find the concentrations of adsorbed species ( $C_{is}$ ) when these are equal to zero, assuming the surface reactions (Eqs. (S25)-(S28)) as the rate-limiting steps.

$$C_{APO \cdot S} = K_{APO} C_{APO} C_V \quad (S32)$$

$$C_{CA \cdot S} = \frac{C_{CA} C_V}{K_{CA,d}} = K_{CA} C_{CA} C_V \quad (S33)$$

$$C_{COL \cdot S} = \frac{C_{COL} C_V}{K_{COL,d}} = K_{COL} C_{COL} C_V \quad (S34)$$

$$C_{FA \cdot S} = \frac{C_{FA} C_V}{K_{FA,d}} = K_{FA} C_{FA} C_V \quad (S35)$$

The balance of sites is defined by Eq. (S36):

$$C_t = C_V + C_{APO \cdot S} + C_{CA \cdot S} + C_{COL \cdot S} + C_{FA \cdot S} \quad (S36)$$

By replacing Eqs. (S32) – (S35) in Eq. (S36) and simplifying, Eq. (S37) is obtained:

$$C_t = C_V + K_{APO} C_{APO} C_V + K_{CA} C_{CA} C_V + K_{COL} C_{COL} C_V + K_{FA} C_{FA} C_V$$

$$C_V = \frac{C_t}{1 + K_{APO} C_{APO} + K_{CA} C_{CA} + K_{COL} C_{COL} + K_{FA} C_{FA}} \quad (S37)$$

Replacing Eq. (S37) in Eq. (S32):

$$C_{APO \cdot S} = \frac{K_{APO} C_{APO} C_t}{1 + K_{APO} C_{APO} + K_{CA} C_{CA} + K_{COL} C_{COL} + K_{FA} C_{FA}} \quad (S38)$$

The final expressions for the reaction rates of  $r_1$ - $r_4$  are shown below, where  $k_i = k_{si} K_i^2 C_t^2$  for Eqs. (S39)-(S41) and  $k_i = k_{si} K_i C_t$  for Eq. (S42):

$$r_1 = \frac{k_1 C_{APO}^2}{(1 + K_{APO} C_{APO} + K_{CA} C_{CA} + K_{COL} C_{COL} + K_{FA} C_{FA})^2} \quad (S39)$$

$$r_2 = \frac{k_2 C_{APO}^2}{(1 + K_{APO} C_{APO} + K_{CA} C_{CA} + K_{COL} C_{COL} + K_{FA} C_{FA})^2} \quad (S40)$$

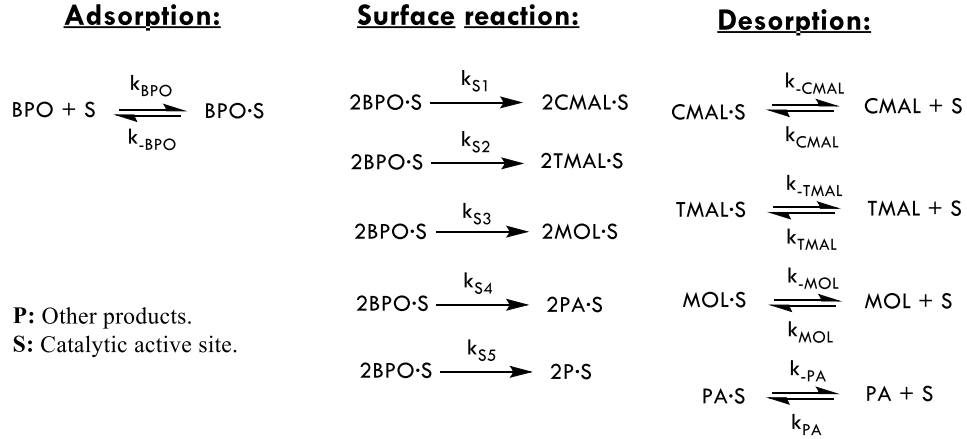
$$r_3 = \frac{k_3 C_{APO}^2}{(1 + K_{APO} C_{APO} + K_{CA} C_{CA} + K_{COL} C_{COL} + K_{FA} C_{FA})^2} \quad (S41)$$

$$r_4 = \frac{k_4 C_{APO}}{1 + K_{APO} C_{APO} + K_{CA} C_{CA} + K_{COL} C_{COL} + K_{FA} C_{FA}} \quad (S42)$$

## 4.2. Isomerization of $\beta$ -pinene epoxide

### 4.2.1. Bimolecular surface reaction

The reaction rate laws for the five reactions of the reaction network for  $\beta$ -pinene epoxide isomerization (Figure 1) are obtained, using heterogeneous kinetic models as deduced considering **bimolecular surface reactions**, as shown in **Figure S7**:



**Figure S7.** Elemental steps proposed for the reaction network of the isomerization of  $\beta$ -pinene epoxide, considering bimolecular surface reactions.

S: Surface site on catalyst.

$C_i$ : Concentration of specie i in the bulk of the solution.

$C_v$ : Concentration of available surface sites on the catalyst surface.

$C_{is}$ : Concentration of specie i adsorbed at the surface site.

$C_t$ : Total concentration of sites available on the catalyst surface.

$k_i$ : Reaction rate constant of direct reaction i.

$k_{-i}$ : Reaction rate constant of reverse reaction i.

$K_i$ : Equilibrium constant for step i.

$$r_{\text{BPO,ads}} = k_{\text{BPO}} \left[ C_{\text{BPO}} C_v - \frac{C_{\text{BPO} \cdot \text{S}}}{K_{\text{BPO}}} \right] \quad (\text{S43})$$

$$r_1 = k_{s1} C_{\text{BPO} \cdot \text{S}}^2 \quad (\text{S44})$$

$$r_2 = k_{s2} C_{\text{BPO} \cdot \text{S}}^2 \quad (\text{S45})$$

$$r_3 = k_{s3} C_{\text{BPO} \cdot \text{S}}^2 \quad (\text{S46})$$

$$r_4 = k_{s4} C_{\text{BPO} \cdot \text{S}}^2 \quad (\text{S47})$$

$$r_5 = k_{s5} C_{\text{BPO} \cdot \text{S}}^2 \quad (\text{S48})$$



$$r_{\text{CMAL,des}} = k_{-\text{CMAL}} \left[ C_{\text{CMAL}\cdot\text{S}} - \frac{C_{\text{CMAL}}C_{\text{V}}}{K_{\text{CMAL,d}}} \right] \quad (\text{S49})$$

$$r_{\text{TMAL,des}} = k_{-\text{TMAL}} \left[ C_{\text{TMAL}\cdot\text{S}} - \frac{C_{\text{TMAL}}C_{\text{V}}}{K_{\text{TMAL,d}}} \right] \quad (\text{S50})$$

$$r_{\text{MOL,des}} = k_{-\text{MOL}} \left[ C_{\text{MOL}\cdot\text{S}} - \frac{C_{\text{MOL}}C_{\text{V}}}{K_{\text{MOL,d}}} \right] \quad (\text{S51})$$

$$r_{\text{PA,des}} = k_{-\text{PA}} \left[ C_{\text{PA}\cdot\text{S}} - \frac{C_{\text{PA}}C_{\text{V}}}{K_{\text{PA,d}}} \right] \quad (\text{S52})$$

The Eqs. (S43), and (S49)-(S52) are solved to find the concentrations of adsorbed species ( $C_{\text{is}}$ ) when these are equal to zero, assuming the surface reactions (Eqs. (S44)-(S48)) as the rate-limiting steps.

$$C_{\text{BPO}\cdot\text{S}} = K_{\text{BPO}}C_{\text{BPO}}C_{\text{V}} \quad (\text{S53})$$

$$C_{\text{CMAL}\cdot\text{S}} = \frac{C_{\text{CMAL}}C_{\text{V}}}{K_{\text{CMAL,d}}} = K_{\text{CMAL}}C_{\text{CMAL}}C_{\text{V}} \quad (\text{S54})$$

$$C_{\text{TMAL}\cdot\text{S}} = \frac{C_{\text{TMAL}}C_{\text{V}}}{K_{\text{TMAL,d}}} = K_{\text{TMAL}}C_{\text{TMAL}}C_{\text{V}} \quad (\text{S55})$$

$$C_{\text{MOL}\cdot\text{S}} = \frac{C_{\text{MOL}}C_{\text{V}}}{K_{\text{MOL,d}}} = K_{\text{MOL}}C_{\text{MOL}}C_{\text{V}} \quad (\text{S56})$$

$$C_{\text{PA}\cdot\text{S}} = \frac{C_{\text{PA}}C_{\text{V}}}{K_{\text{PA,d}}} = K_{\text{PA}}C_{\text{PA}}C_{\text{V}} \quad (\text{S57})$$

The balance of sites is defined by Eq. (S58):

$$C_{\text{t}} = C_{\text{V}} + C_{\text{BPO}\cdot\text{S}} + C_{\text{CMAL}\cdot\text{S}} + C_{\text{TMAL}\cdot\text{S}} + C_{\text{MOL}\cdot\text{S}} + C_{\text{PA}\cdot\text{S}} \quad (\text{S58})$$

By replacing Eqs. (S53) – (S57) in Eq. (S58) and simplifying, Eq. (S59) is obtained:

$$C_{\text{t}} = C_{\text{V}} + K_{\text{BPO}}C_{\text{BPO}}C_{\text{V}} + K_{\text{CMAL}}C_{\text{CMAL}}C_{\text{V}} + K_{\text{TMAL}}C_{\text{TMAL}}C_{\text{V}} + K_{\text{MOL}}C_{\text{MOL}}C_{\text{V}} + K_{\text{PA}}C_{\text{PA}}C_{\text{V}} \quad (\text{S59})$$

$$C_{\text{V}} = \frac{C_{\text{t}}}{1 + K_{\text{BPO}}C_{\text{BPO}} + K_{\text{CMAL}}C_{\text{CMAL}} + K_{\text{TMAL}}C_{\text{TMAL}} + K_{\text{MOL}}C_{\text{MOL}} + K_{\text{PA}}C_{\text{PA}}} \quad (\text{S60})$$

Replacing Eq. (S60) in Eq. (S53):

$$C_{\text{BPO}\cdot\text{S}} = \frac{K_{\text{BPO}}C_{\text{BPO}}C_{\text{t}}}{1 + K_{\text{BPO}}C_{\text{BPO}} + K_{\text{CMAL}}C_{\text{CMAL}} + K_{\text{TMAL}}C_{\text{TMAL}} + K_{\text{MOL}}C_{\text{MOL}} + K_{\text{PA}}C_{\text{PA}}} \quad (\text{S61})$$

The final expressions for the reaction rates of  $r_1$ - $r_5$  are shown below, where  $k_i = k_{\text{si}}K_i^2C_{\text{t}}^2$  for Eqs. (S62)-(S66):

$$r_1 = \frac{k_1C_{\text{BPO}}^2}{(1 + K_{\text{BPO}}C_{\text{BPO}} + K_{\text{CMAL}}C_{\text{CMAL}} + K_{\text{TMAL}}C_{\text{TMAL}} + K_{\text{MOL}}C_{\text{MOL}} + K_{\text{PA}}C_{\text{PA}})^2} \quad (\text{S62})$$

$$r_2 = \frac{k_2 C_{\text{BPO}}^2}{(1 + K_{\text{BPO}} C_{\text{BPO}} + K_{\text{CMAL}} C_{\text{CMAL}} + K_{\text{TMAL}} C_{\text{TMAL}} + K_{\text{MOL}} C_{\text{MOL}} + K_{\text{PA}} C_{\text{PA}})^2} \quad (\text{S63})$$

$$r_3 = \frac{k_3 C_{\text{BPO}}^2}{(1 + K_{\text{BPO}} C_{\text{BPO}} + K_{\text{CMAL}} C_{\text{CMAL}} + K_{\text{TMAL}} C_{\text{TMAL}} + K_{\text{MOL}} C_{\text{MOL}} + K_{\text{PA}} C_{\text{PA}})^2} \quad (\text{S64})$$

$$r_4 = \frac{k_4 C_{\text{BPO}}^2}{(1 + K_{\text{BPO}} C_{\text{BPO}} + K_{\text{CMAL}} C_{\text{CMAL}} + K_{\text{TMAL}} C_{\text{TMAL}} + K_{\text{MOL}} C_{\text{MOL}} + K_{\text{PA}} C_{\text{PA}})^2} \quad (\text{S65})$$

$$r_5 = \frac{k_5 C_{\text{BPO}}^2}{(1 + K_{\text{BPO}} C_{\text{BPO}} + K_{\text{CMAL}} C_{\text{CMAL}} + K_{\text{TMAL}} C_{\text{TMAL}} + K_{\text{MOL}} C_{\text{MOL}} + K_{\text{PA}} C_{\text{PA}})^2} \quad (\text{S66})$$

## 5. Catalyst characterization data

**Table S4.** Characterization data of h-ZSM-5 and d-ZSM-5 catalysts.

Catalyst	Si/Al	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	S <sub>EXT</sub> (m <sup>2</sup> g <sup>-1</sup> )	V <sub>MIC</sub> (cm <sup>3</sup> g <sup>-1</sup> )	V <sub>T</sub> (cm <sup>3</sup> g <sup>-1</sup> )	BA (μmol g <sup>-1</sup> )	LA (μmol·g <sup>-1</sup> )	C <sub>B,ext</sub> (μmol·g <sup>-1</sup> )
h-ZSM-5	40	557	279	0.17	0.66	199	65	41
d-ZSM-5/4d	42	570	360	0.13	0.68	123	88	97
d-ZSM-5/7d	41	553	330	0.14	0.68	131	86	61

Si/Al: molar ratio, S<sub>BET</sub>: BET surface area, S<sub>EXT</sub>: mesopore/external surface area; V<sub>MIC</sub>: micropore volume, V<sub>T</sub>: total pore volume. BA and LA: Brønsted and Lewis acid sites concentration, measured by Pyr-FTIR at 250 °C, and C<sub>B,ext</sub>: BA external concentration measured at 250 °C by DTBPyr-FTIR.

## 6. Benchmarking the productivity of dendritic zeolites

**Table S5.** Productivity towards campholenic aldehyde from the isomerization of  $\alpha$ -pinene epoxide and productivity towards myrtanal from the isomerization of  $\beta$ -pinene epoxide using different catalysts at 70 °C.

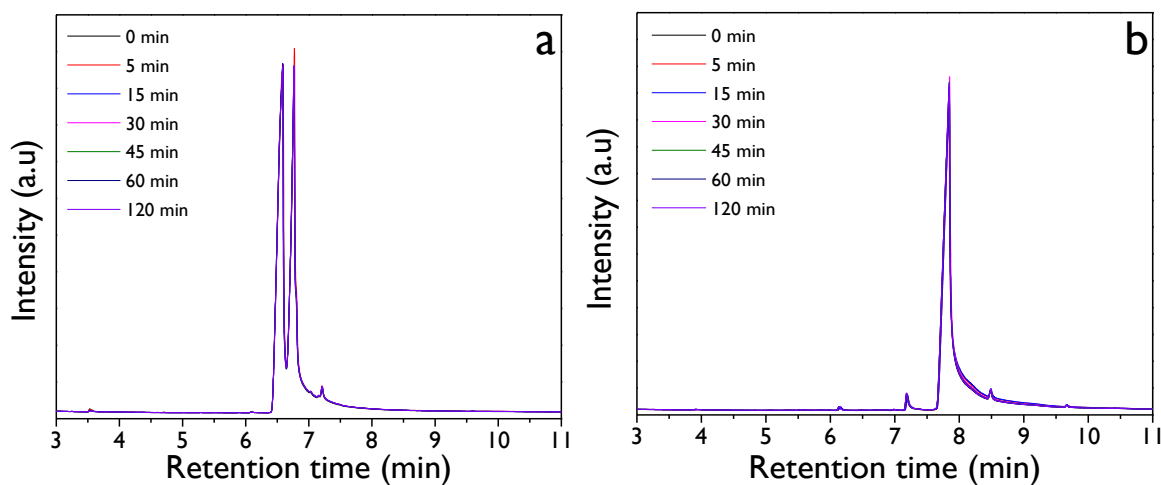
$\alpha$ -pinene epoxide						$\beta$ -pinene epoxide					
Catalyst	Reaction conditions	X <sub>APO</sub> (%)	S <sub>CA</sub> (%)	P <sub>CA</sub> (mmol g <sup>-1</sup> min <sup>-1</sup> )	Ref	Catalyst	Reaction conditions	X <sub>BPO</sub> (%)	S <sub>MAL</sub> (%)	P <sub>MAL</sub> (mmol g <sup>-1</sup> min <sup>-1</sup> )	Ref
FeCl <sub>3</sub> /IL/ACC	0.012 mol/L of $\alpha$ -pinene epoxide, 250 mL of n-hexane, 68 mg of catalyst, 70 °C, 4 h in argon atmosphere (5 bar).	81	54	0.081	[10]	Natural Zeolite	0.25 mol/L of $\beta$ -pinene epoxide, 1 mL of toluene, 25 mg of catalyst, 70 °C, 2.5 h.	97	23	0.015	[3]
1.4/Fe-SBA-15	0.25 mol/L of $\alpha$ -pinene epoxide, 1 mL of toluene, 2 mg catalyst, 70 °C, 24 h.	25	83	0.018	[11]	1.4/Fe-SBA-15	0.25 mol/L of $\beta$ -pinene epoxide, 1 mL of toluene, 2 mg catalyst, 70 °C, 24 h.	60	100	0.052	[11]
1.4/Fe-MCM-41		73	59	0.037		1.4/Fe MCM-41		22	100	0.019	
2.1/Cu-SBA-15		30	100	0.026		2.1/Cu-SBA-15		23	61	0.012	
Natural Zeolite	0.25 mol/L of $\alpha$ -pinene epoxide, 1 mL of toluene, 25 mg of catalyst, 70 °C, 1.5 h.	94	46	0.024	[1]	MCM-41		14	100	0.012	
MoO <sub>3</sub> -Modified Zeolite BETA (20Mo450)	1.10 mol/L of $\alpha$ -pinene epoxide, 6 mL of ethyl acetate, 125 mg of catalyst, 70 °C, 3 h.	97	37	0.127	[12]	Fe-SBA-15	0.25 mol/L of $\beta$ -pinene epoxide, 1 mL of acetonitrile, 10 mg of catalyst, 70 °C, 1 h.	20	82	0.068	[13]
MWW-NA		93	74	0.055	[14]	Fe-MCM-41		23	90	0.086	

$\alpha$ -pinene epoxide						$\beta$ -pinene epoxide					
Catalyst	Reaction conditions	X <sub>APO</sub> (%)	S <sub>CA</sub> (%)	P <sub>CA</sub> (mmol g <sup>-1</sup> min <sup>-1</sup> )	Ref	Catalyst	Reaction conditions	X <sub>BPO</sub> (%)	S <sub>MAL</sub> (%)	P <sub>MAL</sub> (mmol g <sup>-1</sup> min <sup>-1</sup> )	Ref
MWW-AFS	0.02 mol/L of $\alpha$ -pinene oxide, 30 mL of toluene, 25 mg of catalyst, 70 °C, 5 h.	18	80	0.012		Sn-Beta-300	0.012 mol/ L of $\beta$ -pinene epoxide, 150 mL of toluene, 75 mg of catalyst, 70 °C, 2 h.	72	66	0.106	[15]
MCM-56		25	69	0.012		USY	1.4 mol/L of $\beta$ -pinene epoxide, 6 mL acetonitrile, 125 mg of catalyst, 70 °C, 24 h.	88	67	0.027	[16]
USY-40		73	65	0.039		Sn-MCM-41		85	54	0.021	
Beta-25		7	52	0.031		ZnCl2/[N(3-OH-Pr)Py][NTf2]/ACC	0.0096 mol/L of $\beta$ -pinene epoxide, 250 mL of n-hexane, 1.2 g of catalyst, 70°C, 2 h.	100	54	0.009	[17]
ZSM-5		25	60	0.012		ZnCl2/[NB4M Py][BF4]/ACC		100	50	0.008	
H-Beta-300	0.02 mol /L of $\alpha$ -pinene oxide, 1 mL of DMA, 75 mg of catalyst 70 °C, 3 h.	70	36	0.024	[18]	h-ZSM-5	0.25 mol/L of $\beta$ -pinene epoxide, 0.5 mL of ethyl acetate, 10 mg catalyst, 70 °C, 5 min.	29	58	0.421	This work
Fe-H-beta-300-IE.	0.013 mol/L of $\alpha$ -pinene oxide, 150 mL toluene, 75 mg, 70 °C, 1.33 h.	40	49	0.042	[19]	d-ZSM-5/7d		46	53	0.609	This work
h-ZSM-5	0.25 mol/L of $\alpha$ -pinene epoxide, 1.0 mL of ethyl acetate, 10 mg catalyst, 70 °C, 5 min.	45	70	1.59	This work	d-ZSM-5/4d		87	47	1.02	This work
d-ZSM-5/7d		44	73	1.60	This work						
d-ZSM-5/4d		88	57	2.55	This work						

P<sub>CA</sub> and P<sub>MAL</sub> refer to the productivity of campholenic aldehyde and myrtanal, respectively.

## 7. Reversibility tests

The reversibility tests of carveol (L-Carveol, mixture of cis and trans isomers, Sigma-Aldrich, 97 wt%) and perillyl alcohol (Sigma-Aldrich, 96 wt%) were carried out using 10 mg of the d-ZSM-5/7d catalyst. A mixture was prepared consisting of 1 mL of carveol solution and 0.5 mL of perillyl alcohol solution in ethyl acetate, both at a concentration of 0.25 M. The reactions were performed at 40 °C under magnetic stirring (750 rpm) for reaction times ranging from 0 to 120 min. The chromatograms of the obtained results are shown in Figure S8.



**Figure S8.** Chromatograms, along the reaction time, for the reversibility tests using (a) carveol and (b) perillyl alcohol as reactants. Reaction conditions: 10 mg d-ZSM-5/7d, 0.25 M, ethyl acetate as the solvent, 40 °C, 750 rpm.

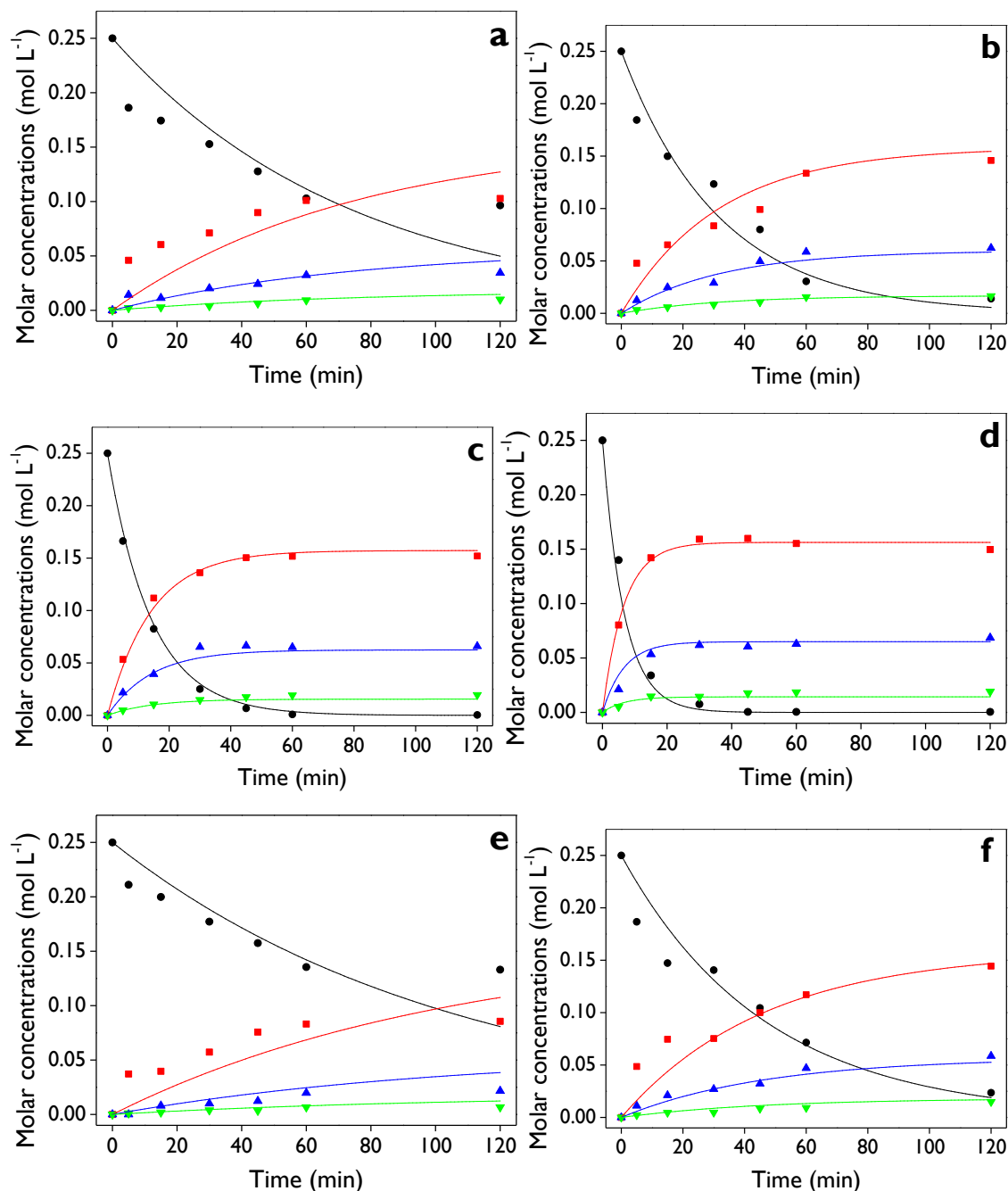
## 8. Kinetic results

### 8.1. Isomerization of $\alpha$ -pinene epoxide

**Table S6.** Optimized kinetic parameters for the kinetic model for  $\alpha$ -pinene epoxide, considering unimolecular surface reactions.

Parameter	Value	Units	Standard error (%)
$k_1$	$4.45 \times 10^{-3}$	$\text{mL mg}^{-1} \text{ min}^{-1}$	3.3
$k_2$	$1.76 \times 10^{-3}$	$\text{mL mg}^{-1} \text{ min}^{-1}$	6.6
$k_3$	$4.36 \times 10^{-4}$	$\text{mL mg}^{-1} \text{ min}^{-1}$	20.9
$k_4$	$4.22 \times 10^{-4}$	$\text{mL mg}^{-1} \text{ min}^{-1}$	44.9
$E_{a1}$	71.5	$\text{kJ mol}^{-1}$	3.8
$E_{a2}$	75.9	$\text{kJ mol}^{-1}$	6.1
$E_{a3}$	64.6	$\text{kJ mol}^{-1}$	23.5
$E_{a4}$	69.1	$\text{kJ mol}^{-1}$	44.3

$k_i$  values were estimated at 60 °C.



**Figure S9.** Concentration profiles of the species ( $C_{APO}$  (—, ●),  $C_{CA}$  (—, ■),  $C_{COL}$  (—, ▲),  $C_{FA}$  (—, ▼)) involved in the isomerization of  $\alpha$ -pinene epoxide over d-ZSM-5/7d catalyst, with experimental values (symbols) and modeled values (solid lines), considering unimolecular surface reactions. Reaction conditions: 0.25 mol L<sup>-1</sup> epoxide. (a) 40 °C and 10 mg of catalyst, (b) 50 °C and 10 mg of catalyst, (c) 60 °C and 10 mg of catalyst, (d) 70 °C and 10 mg of catalyst, (e) 40 °C and 7 mg of catalyst, (f) 40 °C and 16 mg of catalyst.

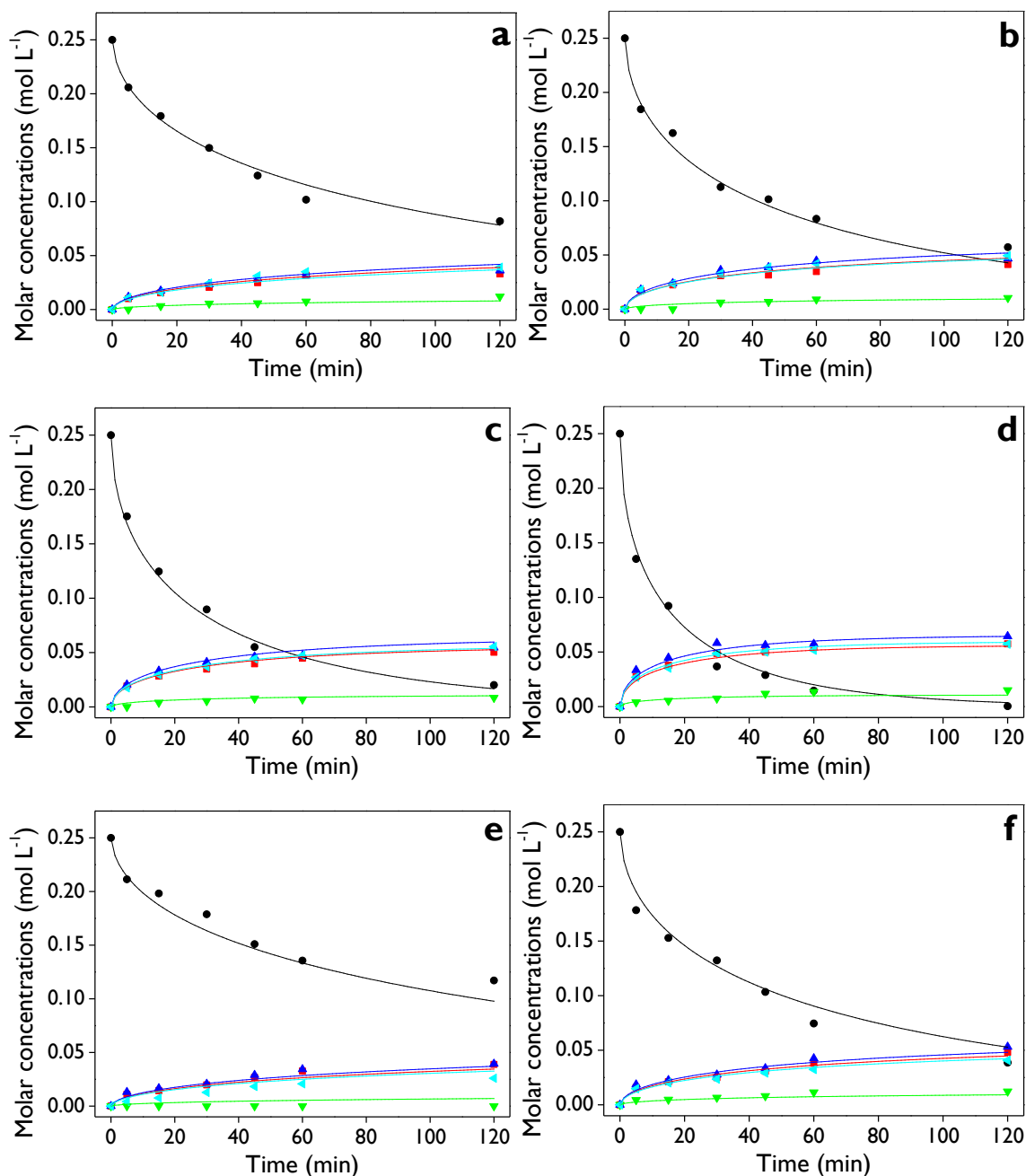
## 8.2. Isomerization of $\beta$ -pinene epoxide

**Table S7.** Optimized kinetic parameters for the kinetic model for  $\beta$ -pinene epoxide, considering unimolecular surface reactions.

Parameter	Value	Units	Standard error (%)
$k_1$	$8.41 \times 10^{-3}$	$\text{mL mg}^{-1} \text{ min}^{-1}$	56.0
$k_2$	$9.53 \times 10^{-3}$	$\text{mL mg}^{-1} \text{ min}^{-1}$	55.9
$k_3$	$1.63 \times 10^{-3}$	$\text{mL mg}^{-1} \text{ min}^{-1}$	57.3
$k_4$	$8.61 \times 10^{-3}$	$\text{mL mg}^{-1} \text{ min}^{-1}$	55.9
$k_5$	$9.08 \times 10^{-3}$	$\text{mL mg}^{-1} \text{ min}^{-1}$	55.8
$E_{a1}$	55.8	$\text{kJ mol}^{-1}$	6.0
$E_{a2}$	58.1	$\text{kJ mol}^{-1}$	4.0
$E_{a3}$	53.4	$\text{kJ mol}^{-1}$	16.1
$E_{a4}$	59.3	$\text{kJ mol}^{-1}$	4.1
$E_{a5}$	51.9	$\text{kJ mol}^{-1}$	6.3
$K_{\text{CMAL}}$	$8.69 \times 10^2$	$\text{L mol}^{-1}$	59.0

$k_i$  values were estimated at 60 °C.





**Figure S10.** Concentration profiles of the species ( $C_{\text{BPO}}$  (—, ●),  $C_{\text{CMAL}}$  (—, ■),  $C_{\text{TMAL}}$  (—, ▲),  $C_{\text{MOL}}$  (—, ▼),  $C_{\text{PA}}$  (—, ◀) involved in the isomerization of  $\beta$ -pinene epoxide over d-ZSM-5/7d catalyst, with experimental values (symbols) and modeled values (solid lines), considering unimolecular surface reactions. Reaction conditions:  $0.25 \text{ mol L}^{-1}$  epoxide. (a)  $40^\circ\text{C}$  and 10 mg of catalyst, (b)  $50^\circ\text{C}$  and 10 mg of catalyst, (c)  $60^\circ\text{C}$  and 10 mg of catalyst, (d)  $70^\circ\text{C}$  and 10 mg of catalyst, (e)  $40^\circ\text{C}$  and 7 mg of catalyst, (f)  $40^\circ\text{C}$  and 16 mg of catalyst.

## 9. Green metrics

**Table S8.** Summary of green metrics for the isomerization of  $\alpha$ - and  $\beta$ -pinene epoxides.

<b><math>\alpha</math>-Pinene epoxide</b>								
<b>Catalyst</b>	<b>Scenario</b>	<b>AE</b>	<b><math>\epsilon</math></b>	<b>1/SF</b>	<b>MRP</b>	<b>RME</b>	<b>E-factor</b>	<b>PMI</b>
h-ZSM-5	Recovery	1.00	0.56	1.00	0.97	0.54	0.85	1.85
	No recovery	1.00	0.56	1.00	0.04	0.02	43.97	44.97
d-ZSM-5/4d	Partial recovery	1.00	0.61	1.00	0.97	0.59	0.69	1.69
	No recovery	1.00	0.61	1.00	0.04	0.02	40.07	41.07
d-ZSM-5/7d	Partial recovery	1.00	0.64	1.00	0.97	0.62	0.62	1.62
	No recovery	1.00	0.64	1.00	0.04	0.03	38.24	39.24
<b><math>\beta</math>-Pinene epoxide</b>								
<b>Catalyst</b>	<b>Scenario</b>	<b>AE</b>	<b><math>\epsilon</math></b>	<b>1/SF</b>	<b>MRP</b>	<b>RME</b>	<b>E-factor</b>	<b>PMI</b>
h-ZSM-5	Recovery	1.00	0.34	1.00	0.97	0.33	2.01	3.01
	No recovery	1.00	0.34	1.00	0.04	0.01	72.72	73.72
d-ZSM-5/4d	Partial recovery	1.00	0.44	1.00	0.97	0.43	1.34	2.34
	No recovery	1.00	0.44	1.00	0.04	0.02	56.31	57.31
d-ZSM-5/7d	Partial recovery	1.00	0.43	1.00	0.97	0.41	1.41	2.41
	No recovery	1.00	0.43	1.00	0.04	0.02	58.07	59.07

**AE:** Atom economy,  **$\epsilon$ :** Reaction yield, **SF:** Stoichiometric factor, **MRP:** Material recovery parameter, **RME:** Reaction mass efficiency, **E-factor:** Environmental factor, **PMI:** Process mass intensity.

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