

Article

Application of kinetics and computational fluid dynamics in pinene isomerization

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ABSTRACT

A reliable kinetic model to describe the effects of various factors on the reaction rate and selectivity of pinene isomerization is developed. Furthermore, computational fluid dynamics (CFD) is applied to simulate the solid–liquid dispersion in reactor. The catalyst TiM is obtained by improving the composition and structure of hydrated titanium dioxide. The kinetic equation of pinene isomerization is deduced based on reaction mechanism and catalyst deactivation model. The kinetic equation of pinene isomerization reaction is fitted, and the results show that the fitted equation is correlated with the experimental data. The rate and selectivity of pinene isomerization reaction are affected by the amount of catalyst, deactivation of catalyst, structure of catalyst, reaction temperature and water content of catalyst. The solid–liquid distribution of the reactor is calculated by computational fluid dynamics numerical simulation, and the solid–liquid dispersion in commercial scale reactor is more uniform than that in lab-scale reactor.

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1. Introduction

Pinene is the primary constituent of turpentine. As the important intermediates, camphene and tricyclene are mainly obtained by isomerization of pinene. Camphene and tricyclene are widely used in perfume synthesis such as camphor, drug synthesis, food additive for flavoring and other fields. The overall reaction network of the pinene isomerization is shown in Fig. 1 [1,2]. The isomerization process is very complicated. The product of the isomerization is usually a mixture containing various chemicals, such as camphene, tricyclene, p-cymene, terpinolene, terpinenes and limonene. In practical applications, the selectivity and rate of the reaction is the most concerned issues.

In order to solve the problem of pinene isomerization reaction selectivity, the main solution is to screen and improve the catalyst. The pinene isomerization is carried out on acidic catalysts, and the research of catalysts is mainly focused on clay [3], bentonite [4], montmorillonite [5], kaolinite [6], vermiculite [7], aluminosilicate [8], titanium oxide [9], heteropoly acid [10,11], ferrierite type zeolite [12–15], clinoptilolite [16,17], sulfated ZrO₂ [18–21], and ion exchange resin [22,23]. Then, more and more kinds of catalysts were studied, including mesoporous acid catalyst [24–28], ionic liquids [29], nano solid acid [30], MOF catalyst [31] and so on. However, due to its high selectivity, acidic titanium oxide is still the main catalyst for industrial applications.

The reaction selectivity and rate has an effect on the industrial application of pinene isomerization. The reaction selectivity and rate are influenced by the reaction conditions and catalyst properties, reaction temperature, catalyst concentration, catalyst deactivation and so on. It is found in Fujian Green Pine Co., Ltd. that the reaction rate decreases with the enlargement of reaction scale in industrial application and the pinene isomerization reaction is carried out in a stirred tank reactor. Stirred tank reactor with solid–liquid system is widely used in chemical industry. Computational fluid dynamics (CFD) makes multiphase flow visualization in stirred reactor [32,33]. Wadnerkar [33] and Tamburian [34] used CFD to predict hydrodynamics of solid–liquid interaction in stirred tank. CFD is widely used to investigate the hydrodynamics of catalyst particles in stirred reactor [35]. The CFD simulation of stirred reactor could be helpful to the practical application of pinene isomerization. In order to improve the selectivity and rate of the reaction, it is necessary to improve the composition and structure of catalysts, optimize the reaction conditions, and investigate the kinetics and the CFD reactor simulation.

In this study, the kinetic equations of pinene isomerization were deduced based on reaction mechanism and catalyst deactivation model. The acidic titanium oxide catalyst used in industry was improved by adding auxiliaries MnSO₄, and its catalytic performance was tested. The activity of catalysts prepared in the lab-scale and industrial scale was compared, and the solid–liquid dispersion in the lab-scale and commercial scale was compared by using the numerical simulation method of CFD. CFD simulation was also carried out for commercial scale reactor with different position and number of impellers.

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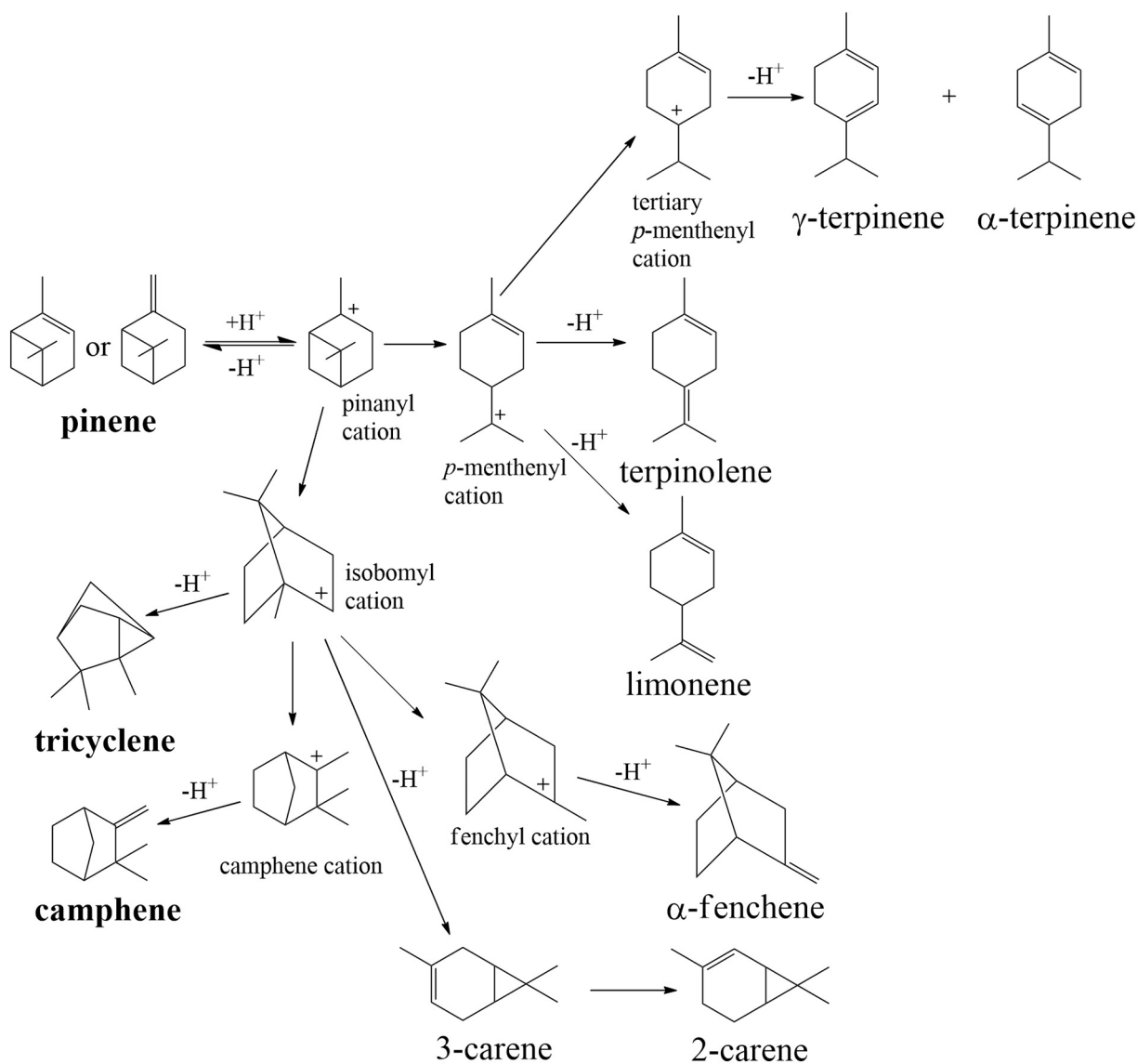


Fig. 1. Mechanism of isomerization reaction of pinene.

2. Methods

2.1. The derivation of kinetic equations

The products of the pinene isomerization are divided into target product and by-product, and the reaction mechanism was simplified as follows:



2.2. Catalyst preparation and characterization

The raw materials of hydrated titanium dioxide (Fujian Green Pine Co., Ltd.) and manganese sulfate were acidified in a certain proportion (the content of manganese sulfate is 5%–10%) and then filtered and washed. The composite catalyst denoted by TiM was obtained after drying at 100 °C. The surface area of the catalyst was calculated from absorption isotherms by the BET method,

in a Micromeritics Tristar 3020 equipment, and the pore size distribution was calculated from the adsorption isotherm by BJH method.

2.3. Catalytic test

The reaction was carried out in a three necked round bottom flask fitted with a thermometer, a reflux condenser, and an impeller. Usually 100 g of turpentine was charged in the flask. The turpentine of different batches was analyzed before the isomerization reaction started. The reaction mixture was stirred vigorously to eliminate the external diffusion. The pinene isomerization reaction was investigated including the reaction temperature and the amount of catalyst. The samples were taken during the course of the reaction. They were cooled to room temperature rapidly and filtered to remove the catalyst. The products were analyzed by flame ionization detector (FID) gas chromatography (Varian CP-3800 with 30 m $\times$ 0.25 μm $\times$ 0.3 μm SE-54 capillary column). Temperature programming (increase at a rate of 6 $^{\circ}\text{C} \cdot \text{min}^{-1}$ from 75 $^{\circ}\text{C}$ to 120 $^{\circ}\text{C}$, hold for 2 min, then increase at a rate of 20 $^{\circ}\text{C} \cdot \text{min}^{-1}$ until 240 $^{\circ}\text{C}$, hold for 5 min) was applied for separation at 1 $\text{ml} \cdot \text{min}^{-1}$ N_2 flow.

The conversion of pinene and selectivity to any product was determined in the following ways:

$$\text{Conversion} = \frac{\text{moles of isomerized pinene}}{\text{moles of initial pinene}} \quad (1)$$

$$\text{Selectivity} = \frac{\text{moles of product} - \text{moles of initial product}}{\text{moles of isomerized pinene}} \quad (2)$$

2.4. Simulation details

The CFD was adopted to simulate the flow field and volume fraction distribution of catalyst in reactor. All simulations were carried out in 3D STR. Standard $k - \varepsilon$ turbulence model was used for turbulence transport equation. Eulerian model was adopted in multiphase model. The motion of each phase was governed by the respective mass and momentum conservation equations without considering mass transfer. The continuity and momentum conservation equations can be written as follows:

$$\frac{\partial \rho_i \alpha_i}{\partial t} + \nabla \cdot (\rho_i \alpha_i \mathbf{U}_i) = 0 \quad (3)$$

$$\frac{\partial (\rho_i \alpha_i \mathbf{U}_i)}{\partial t} + \nabla \cdot (\rho_i \alpha_i \mathbf{U}_i \mathbf{U}_i) = -\alpha_i \nabla p + \nabla (\alpha_i \tau_i) + \mathbf{F}_{i,j} + \alpha_i \rho_i \mathbf{g} \quad (4)$$

where i represents different phases (i.e. $i = s$ for the solid phase and l for the liquid phase). ρ_i is the phase density. $\mathbf{U}_i$ is the velocity vector which has three orthogonal components in Cartesian coordinate system. α_i is the volume fraction of i th phase. τ_i is the viscous stress tensor and $\mathbf{F}_{i,j}$ represents interface momentum exchange term.

In order to reduce the calculation cost, the multiple reference frame (MRF) technique was adopted for the impeller rotation. The rotating stirring speed of lab-scale and commercial scale was $300 \text{ r} \cdot \text{min}^{-1}$ and $200 \text{ r} \cdot \text{min}^{-1}$ respectively. The sketches of lab-scale and commercial scale reactor system were depicted in Fig. 2 and Fig. 3 respectively. The meshes of the STR were unstructured. The finite volume method was adopted in the discretization for continuity and momentum equations. The grid sensitivity analysis was investigated by cases. Velocity

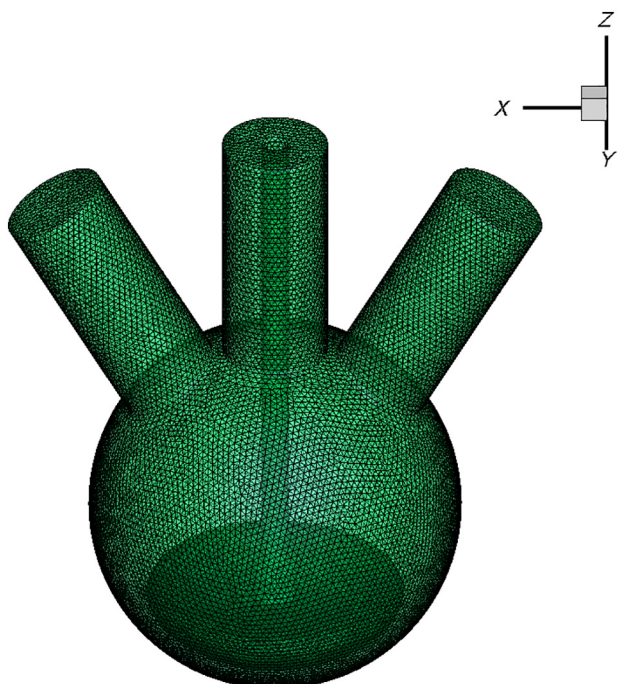


Fig. 2. The sketch of lab-scale reactor.

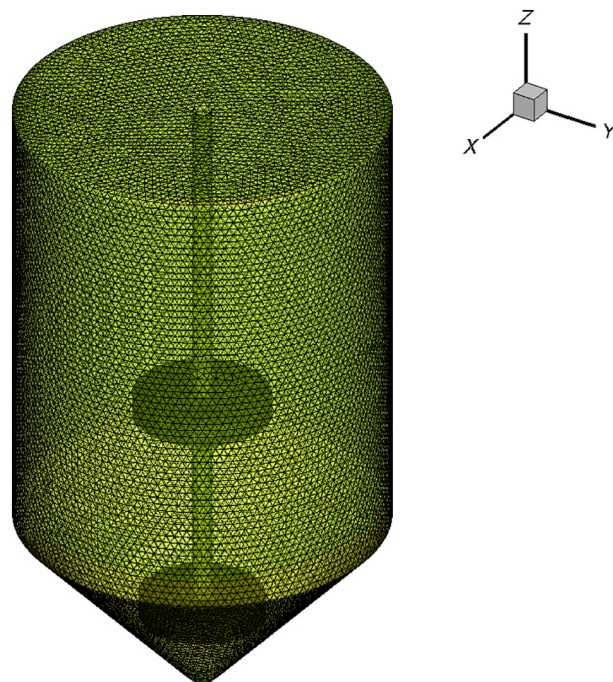


Fig. 3. The sketch of commercial scale reactor.

and pressure fields were obtained by SIMPLE algorithm. Governing equations were discrete with second order upwind scheme. The convergence criterion of the residual was 1×10^{-3} , and all calculations were carried out in steady state. The reactor was investigated by CFD numerical calculation of solid–liquid dispersion.

3. Results and Discussion

3.1. Derivation of kinetic equations

The pinene isomerization was stirred vigorously, thus the external diffusion resistance between the bulk liquid and the catalyst surface can be eliminated. The volume mean diameter of the TiM catalyst is $13.45 \mu\text{m}$ [36], so the internal diffusion resistance can also be negligible due to the small size of the catalyst particles.

Therefore, the rate of reaction could be expressed as follows:

$$r_A = -\frac{dC_A}{dt} = (k_2 + k_3)C_{[ATiM]} \quad (5)$$

According to the complex concentration equilibrium hypothesis:

$$k_1 C_A C_{TiM} = k_{-1} C_{[ATiM]} \quad (6)$$

In fact, the catalyst was deactivated after a long period of use. The catalyst deactivation could be assumed as follows:



where D denotes the deactivated catalyst. The deactivation rate of the catalyst could be described as follows:

$$r_d = -\frac{dC_{TiM}}{dt} = k_d C_{TiM} \quad (7)$$

$$C_{TiM} = C_0 \exp(-k_d t) \quad (8)$$

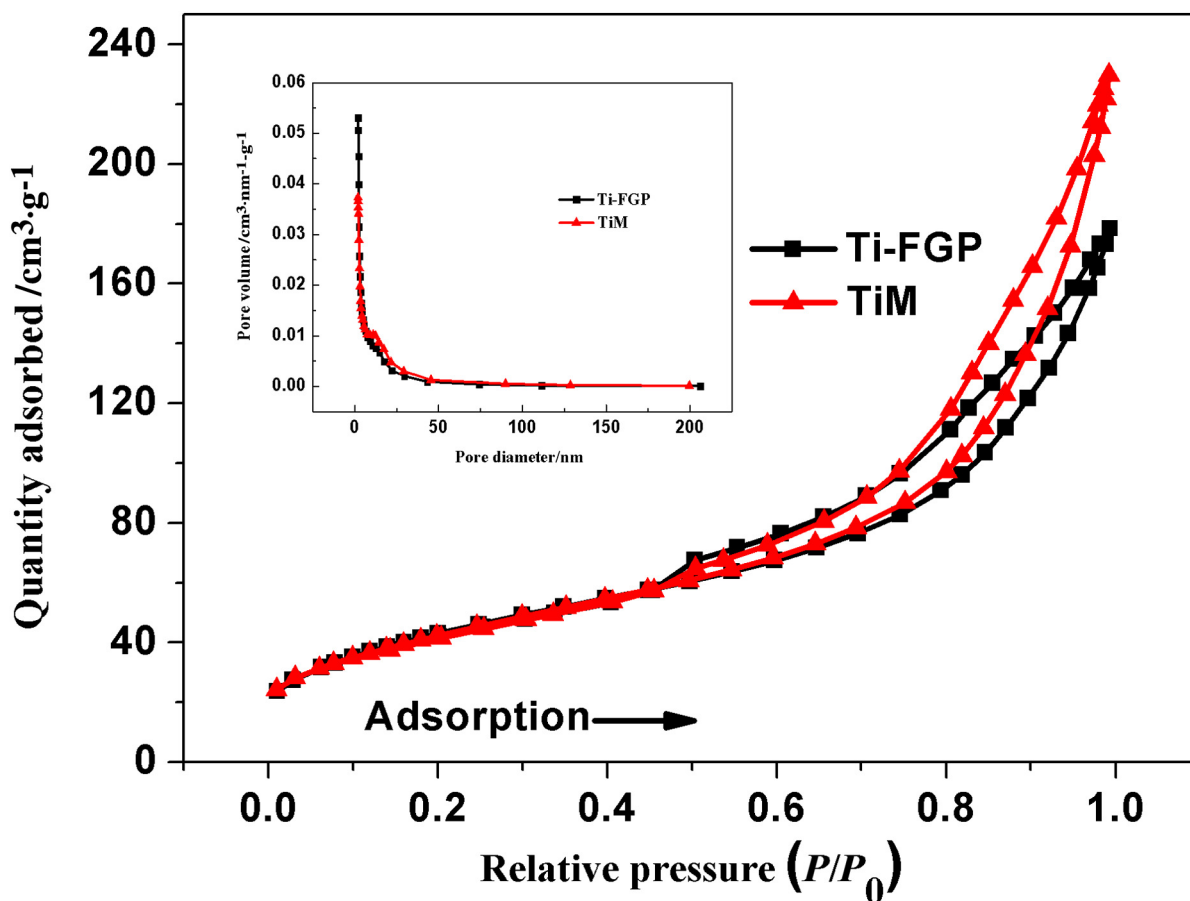


Fig. 4. The N₂ adsorption-desorption isotherm and the pore size distribution of TiM and Ti-FGP.

where C_0 denotes the initial effective concentration of catalyst.

$$C_P - C_{P0} = S(C_{A0} - C_A) \quad (17)$$

$$C_{[ATiM]} = \frac{k_1 C_A C_{TiM}}{k_{-1}} = \frac{k_1 C_A C_0 \exp(-k_d t)}{k_{-1}}$$

$$C_P = C_{P0} + S \left[C_{A0} - C_{A0} \exp \left(- \left(\frac{K}{k_d} - \frac{K}{k_d} \exp(-k_d t) \right) \right) \right] \quad (18)$$

$$r_A = -\frac{dC_A}{dt} = (k_2 + k_3) C_{[ATiM]} = \frac{(k_2 + k_3) k_1 C_A C_0 \exp(-k_d t)}{k_{-1}} \quad (10)$$

$$K = (k_2 + k_3) \frac{k_1}{k_{-1}} C_0 \quad (11)$$

$$r_A = -\frac{dC_A}{dt} = K C_A \exp(-k_d t) \quad (12)$$

$$\ln \frac{C_{A0}}{C_A} = \frac{K}{k_d} [1 - \exp(-k_d t)] \quad (13)$$

In the same way, the kinetic equation of the product could be shown as follows:

$$r_P = \frac{dC_P}{dt} = k_2 C_{[ATiM]} = \frac{k_2}{k_2} + k_3 \times r_A \quad (14)$$

$$S = \frac{k_2}{k_2} + k_3 \quad (15)$$

where, S denotes the selectivity of the target product.

$$r_P = \frac{dC_P}{dt} = S r_A = -\frac{dC_A}{dt} \times S \quad (16)$$

3.2. Characterization

The catalyst TiM prepared in laboratory and the catalyst Ti-FGP prepared in industrial production (Fujian Green Pine Co., Ltd.) were compared by BET method. Fig. 4 shows the N₂ adsorption-desorption isotherm and the pore size distribution of catalysts Ti-FGP and TiM, respectively. The textural properties of TiM and Ti-FGP are summarized in Table 1. The specific surface area of TiM is close to that of Ti-FGP, and the pore size of TiM is larger than that of Ti-FGP. The other characterization of TiM can be found in previous research [36]. Compared with the reaction results of TiM and Ti-FGP [36], the BET test results show that the pore structure of the catalyst has an effect on the selectivity.

3.3. Catalytic test and kinetic model verification

According to the production process of the Fujian Green Pine Co., Ltd., the amount of the catalyst was investigated at 2.5%, 3.5% and

Table 1
Textural properties of TiM and Ti-FGP

	BET surface area /m ² ·g ⁻¹	Average pore diameter /nm
Ti-FGP	159.3114	6.8489
TiM	154.9131	8.6420

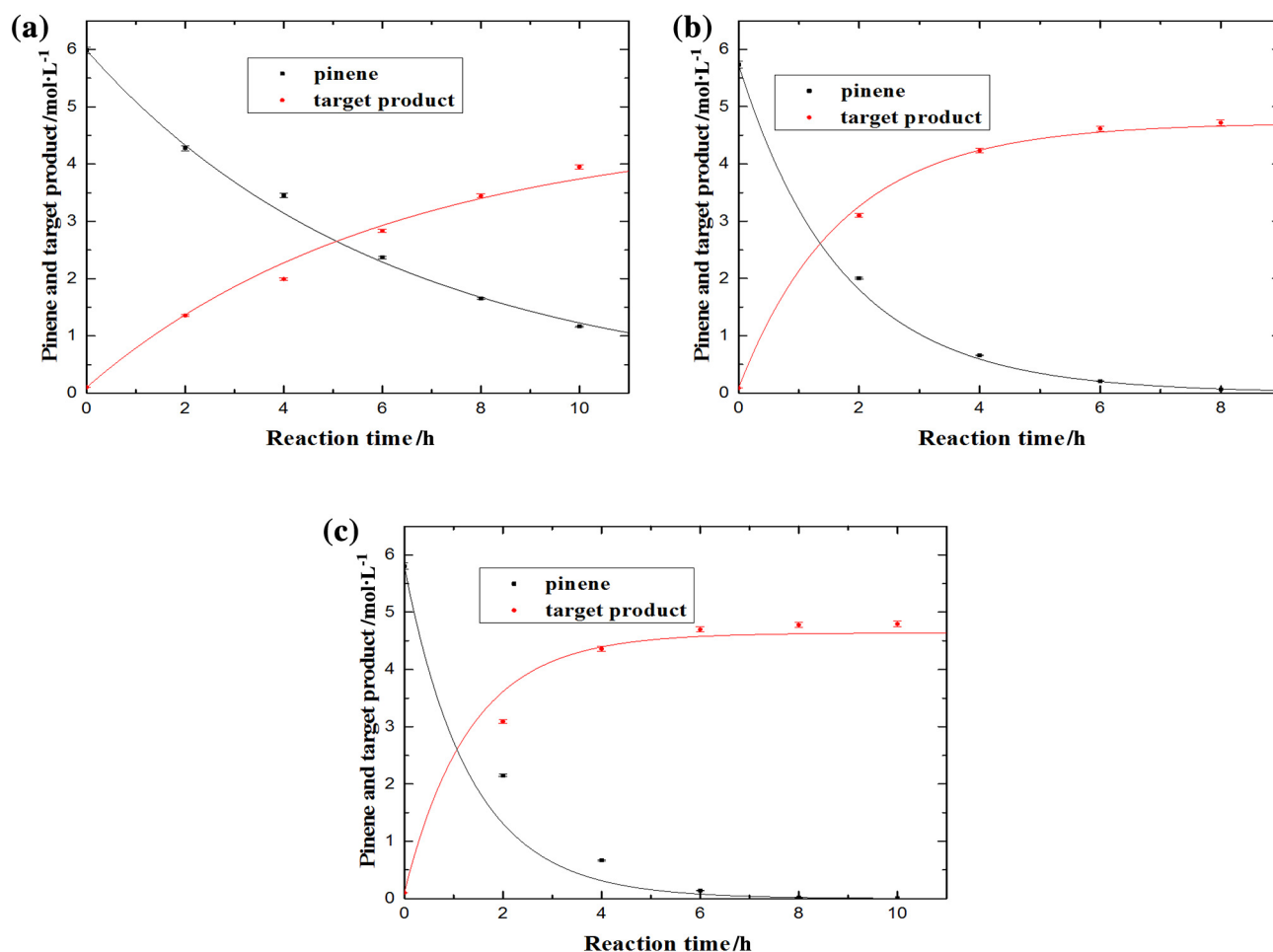


Fig. 5. (a) The kinetic curves for 2.5% catalyst TiM at 120 °C. (b) The kinetic curves for 3.5% catalyst TiM at 120 °C. (c) The kinetic curves for 4.5% catalyst TiM at 120 °C.

4.5%, and the reaction temperature was set at 120 °C. The experimental data is fitted according to the above mentioned models, and the least squares method is used to fit the model parameters of Eqs. (13) and (18). The results are shown in Fig. 5. As shown in the figure, the pinene concentration decreases with time, while the target product concentration increases. In addition, the amount of catalyst is large, and the reaction rate is fast, but the difference between 3.5% and 4.5% is not significant.

Next, another two reaction temperatures, *i.e.* 116 °C and 124 °C, was investigated with the amount of the catalyst of 3.5%. The results are shown in Fig. 6. As shown in the figures, the reaction rate increases with the increase of reaction temperature. However, the selectivity of the target product decreases at 124 °C. It is caused by the occurrences of the side reactions. Some of the reported catalysts [14,24] have a very high initial reactivity and a fast reaction rate, but the final conversion rate pinene is low. It is possible that the reaction is too fast and

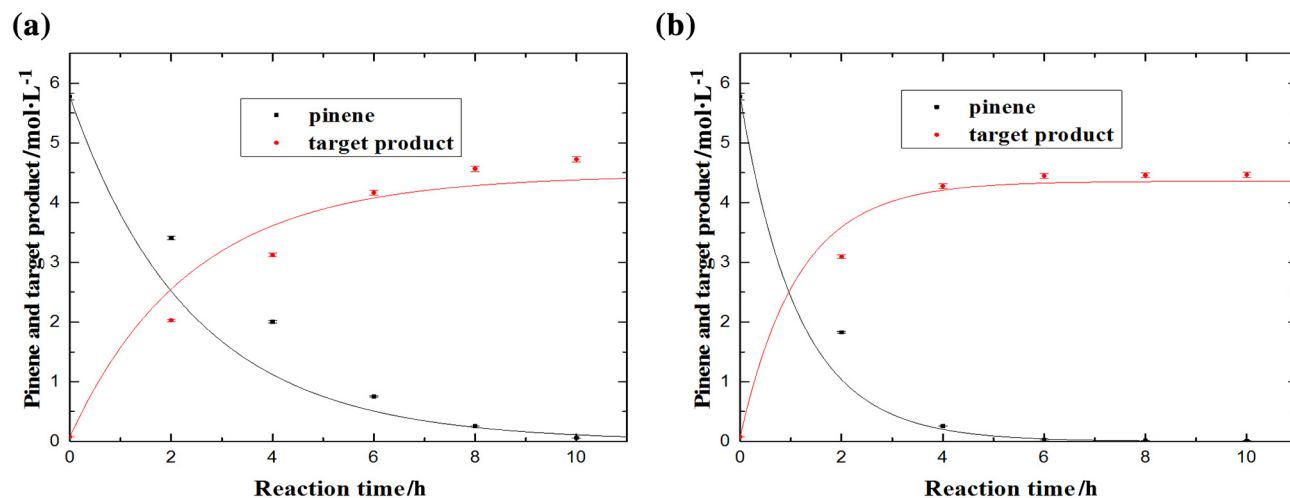


Fig. 6. (a) The kinetic curves for 3.5% catalyst TiM at 116 °C. (b) The kinetic curves for 3.5% catalyst TiM at 124 °C.

there are many by-products, which results in the blockage of the catalyst active sites.

The results show that the kinetic model is consistent with the experimental data. The fitted parameters of the reaction temperature investigation are shown in Table 2. According to the reaction rate corresponding to the reaction temperature in the table, the activation energy of the reaction was calculated by using the Arrhenius equation. The results are shown in Fig. 7. The activation energy of the reaction is 118.97 kJ·mol⁻¹.

Through the investigation of the catalyst amount and the reaction temperature, the optimum reaction conditions are obtained as follows, *i.e.* reaction temperature: 120 °C, catalyst amount: 3.5%. After 8 h of the reaction, the conversion of the pinene is as high as 98.86%, and the selectivity of the target products (camphene and tricyclene) is 81.79%. The experimental data is fitted by the kinetic equations, and the results show that the fitted equations are correlated with the experimental data. At the optimum reaction condition, the function graph can be expressed as follows:

$$C_A = 5.735 / \exp(31.35 \times (1 - \exp(-0.01878 \times t))) \quad (19)$$

$$C_P = 0.08702 + 0.8078 \times (5.735 - 5.735 \exp(-31.35 + 31.35 \exp(-0.01878t))) \quad (20)$$

$$k_d = 0.01878 h^{-1} \quad (21)$$

$$K = 0.5887 h^{-1} \quad (22)$$

$$S = 0.8078 \quad (23)$$

The reaction selectivity obtained by the fitted equation is 80.78%, and the experimental result is 81.79%.

3.4. Kinetic fitting of catalyst reuse

The reusability of the TiM catalyst was investigated at 120 °C with the 3.5% catalyst. When the pinene concentration was less than 1%, the reaction was terminated. At the end of each reaction, the catalyst was separated by centrifugation. The kinetic fitting results of catalyst reuse are shown in Fig. 8. The fitted parameters of the reusability investigation are shown in Table 3. As can be seen from the figures, the fitted equations are correlated with the experimental data, and the activity of TiM catalyst decreases with the increase of reuse times, but the selectivity of the target product remains almost unchanged.

The deactivation of the catalyst is usually neglected in constructing the kinetic models [37,38]. In this study, the isomerization kinetics model including catalyst deactivation was established. The reaction time can be calculated by the kinetic Eq. (19). When catalyst is reused, the *K* value is different.

$$K_i = K_{i-1} \exp\left(-k_d \sum_{j=0}^{i-1} t_j\right) \quad (24)$$

$$K_0 = 0.5887 h^{-1}, t_0 = 0 \quad (25)$$

The calculated reaction time is 10.07 h, 12.95 h and 17.55 h respectively.

3.5. Investigation on activity of industrial scale catalyst TiM

Industrial scale catalyst TiM was prepared by industrial experiments. The water content of industrial scale catalyst TiM was 12.5%. Part of the industrial catalyst TiM was dried in an oven at

Table 2
The fitted parameter of the temperature investigation

<i>T</i> /°C	<i>K</i> /h ⁻¹	<i>k_d</i> /h ⁻¹	<i>S</i>	Correlation coefficient
116	0.4203	0.01274	0.7598	0.98
120	0.5887	0.01878	0.8078	0.99
124	0.8818	0.02622	0.7414	0.99

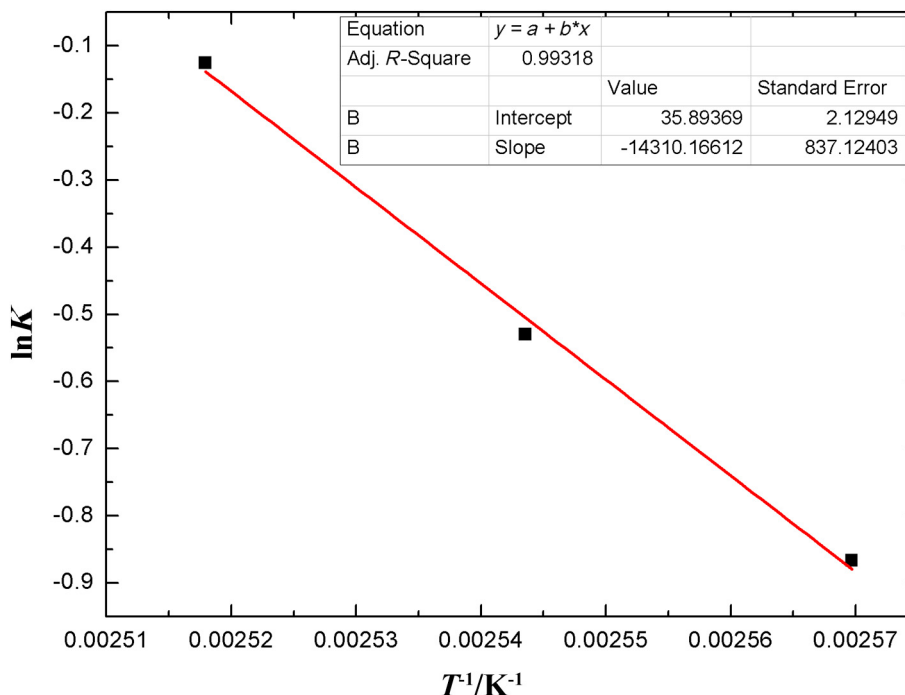


Fig. 7. Arrhenius plot for rate constant of target product.

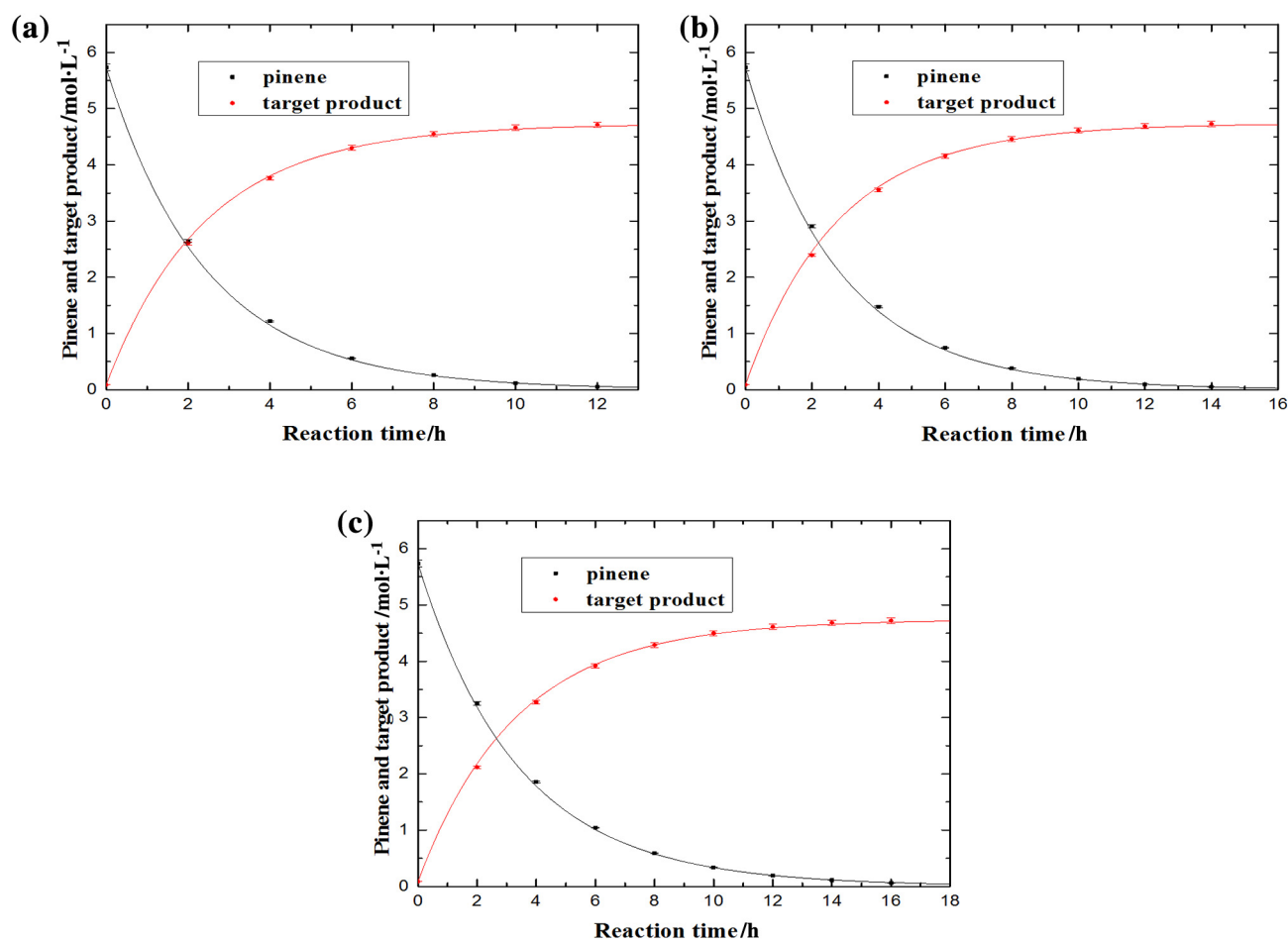


Fig. 8. (a) The kinetic curves for the first reused of 3.5% catalyst TiM at 120 °C. (b) The kinetic curves for the second reused of 3.5% catalyst TiM at 120 °C. (c) The kinetic curves for the third reused of 3.5% catalyst TiM at 120 °C.

100 °C, till constant weight. Then the activity of industrial scale catalyst TiM before and after drying was compared. The result is shown in Fig. 9. The experimental results show that the activity of catalyst TiM after drying is higher than that before drying, and the selectivity is almost unchanged. It can be inferred that water affects the contact between pinene and catalyst, and the reaction rate is decreased. The drying process of industrial scale needs to be improved.

3.6. CFD simulation

The stirring speed of commercial scale reactor was limited to 200 r·min⁻¹, and that of lab-scale reactor was set to 300 r·min⁻¹. There are three different grid sizes in CFD simulation. Fig. 10(a) illustrates the volume fraction of catalyst along the lab-scale reactor height at a constant radial position ($X = 0.035$ m) close to the edge of agitating vane. Fig. 10(b) illustrates the volume fraction of catalyst along the commercial scale reactor at a constant radial

position ($X = 0.3$ m) close to the agitating vane. The results show that the volume fractions of catalyst calculated by different grid sizes are similar.

The volume fraction of catalyst in the whole reactor is 0.02, and the mean volume fraction of catalyst in different height sections of

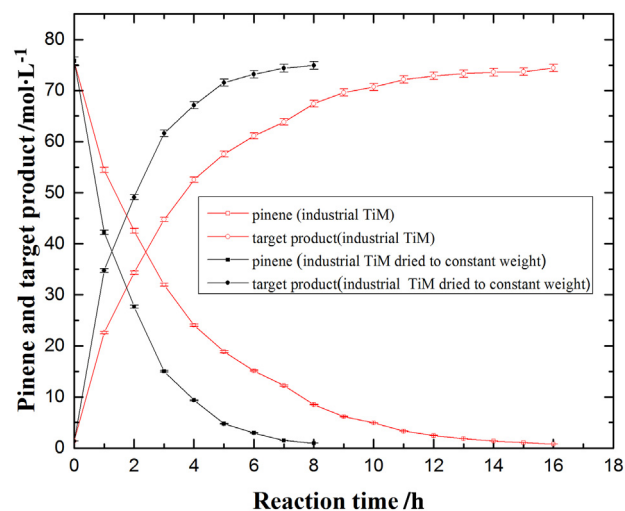


Fig. 9. The catalytic activity of industrial catalyst TiM before and after drying.

Table 3
The fitted parameter of the catalyst TiM reuse (120 °C, TiM3.5%)

	K/h^{-1}	k_d/h^{-1}	S	Correlation coefficient
the first reuse	0.4128	0.01357	0.8103	0.99
the second reuse	0.3622	0.01194	0.8118	0.99
the third reuse	0.3018	0.00999	0.8128	0.99

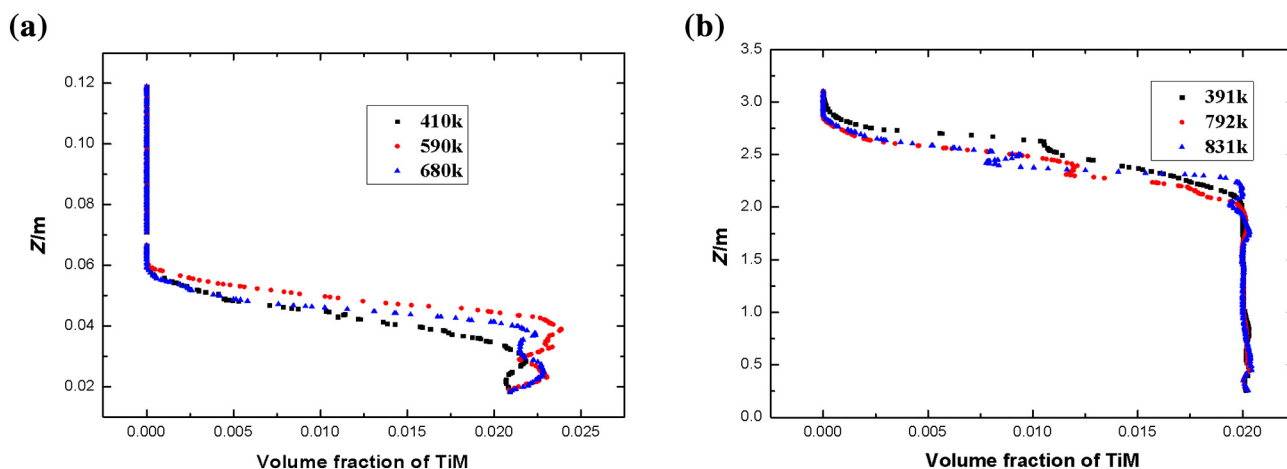


Fig. 10. (a) The volume fraction of catalyst along the lab-scale reactor height at $X = 0.035$ m. (b) The volume fraction of catalyst along the commercial scale reactor height at $X = 0.3$ m.

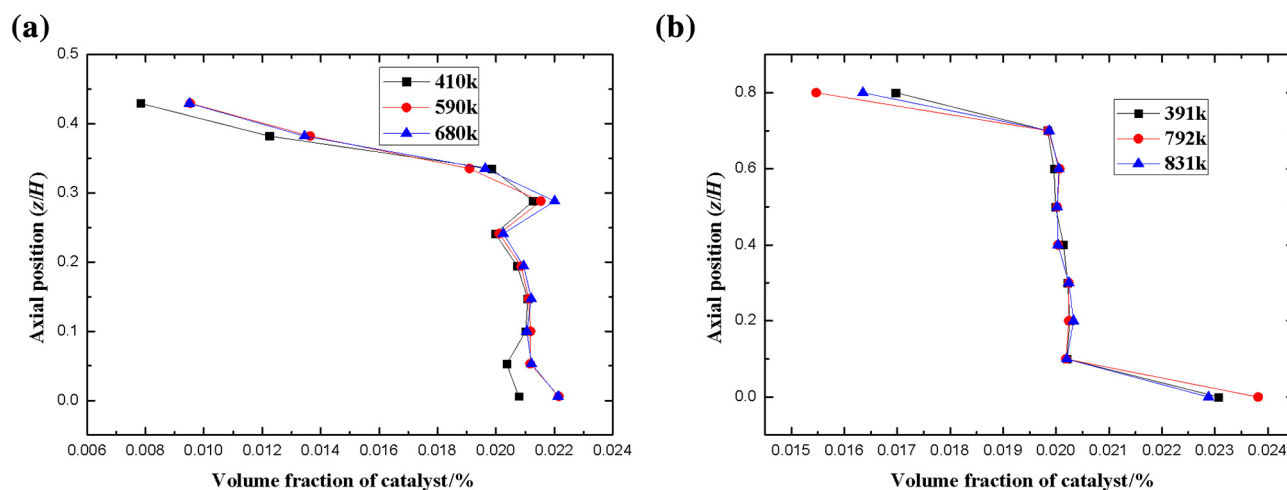


Fig. 11. (a) The mean volume fraction of catalyst in different height sections of the lab-scale reactor. (b) The mean volume fraction of catalyst in different height sections of the commercial scale reactor.

the reactor are shown in Fig. 11. It can be seen from Fig. 11(a) that the volume fraction of catalyst in the upper part of the lab-scale reactor is less than 0.02 and the volume fraction of catalyst at the bottom is close to 0.02. As can be seen from Fig. 11(b), the volume fraction of catalyst in the upper part of the commercial scale reactor is less than 0.02 in commercial scale, and the volume fraction of catalyst at the bottom is more than 0.02.

The above results show that the simulation results of different grid sizes are similar. In order to obtain higher accuracy, the grid sizes used in the subsequent calculation are 831 k (commercial scale) and 680 k (lab-scale), respectively.

The axial catalyst volume fraction contours of lab-scale and commercial scale reactor are shown in Fig. 12 and Fig. 13. By statistical analysis, the standard deviation of catalyst volume fraction in the axial direction of lab-scale and commercial scale is 0.0095 and 0.0075 respectively. The standard deviation of catalyst volume fraction in commercial scale reactor is smaller than that in lab-scale reactor.

The down-press agitating vane was added to the upper part of the commercial scale reactor. The mean volume fraction of catalyst in different height sections of the reactor is shown in Fig. 14. The axial catalyst volume fraction contours of the reactor are shown in Fig. 15. By statistical analysis, the standard deviation of catalyst volume fraction in the axial direction is 0.0054.

The results of CFD numerical simulation show that the catalyst distribution in industrial scale reactor is more uniform than that in laboratory scale reactor. However, the commercial scale reactor

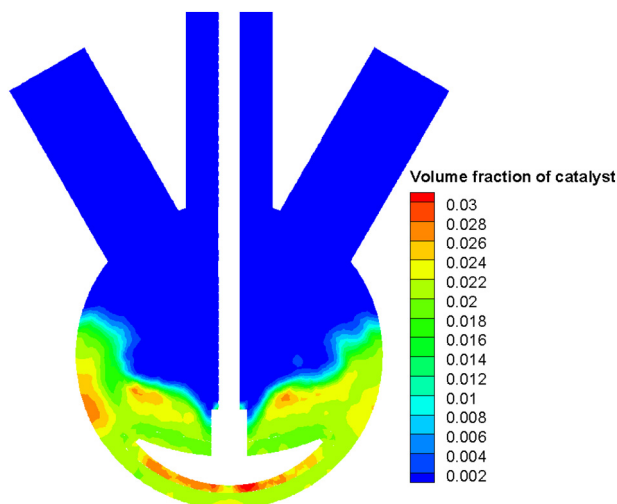


Fig. 12. The axial catalyst volume fraction contours of lab-scale reactor.

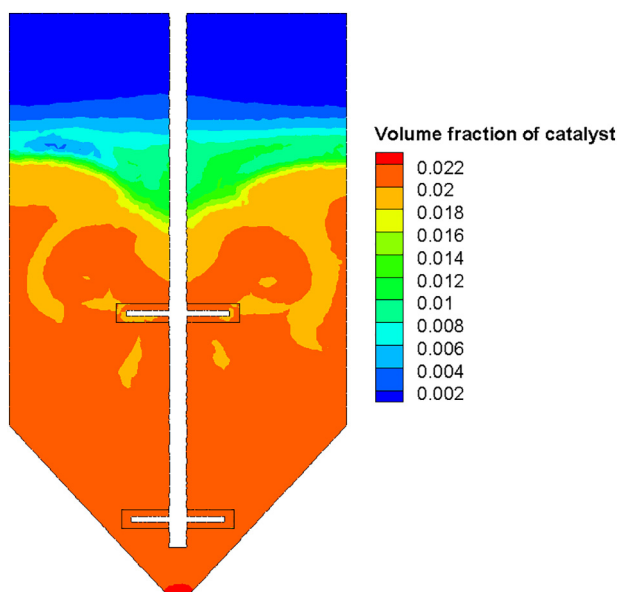


Fig. 13. The axial catalyst volume fraction contours of commercial scale reactor.

can still be optimized, such as the improvement of the bottom structure of the reactor, the length, width, position and quantity of the agitator.

4. Conclusions

In summary, TiM catalyst has high activity and selectivity for the pinene isomerization reaction. In addition, TiM catalyst can be used repeatedly. The pore structure of the catalyst has an effect on the selectivity of pinene isomerization reaction. A kinetic model considering the catalyst deactivation is developed in our present work for the pinene isomerization. The results derived from the kinetic model correlate with the experimental data. The reaction selectivity obtained by the kinetic equation is close to the experimental data. When TiM catalyst is reused, the reaction time calculated by the derived kinetic equation is close to the experimental data. The derived kinetic equation is more applicable than the simple first-order kinetic model for pinene isomerization. Catalysts prepared in industry scale have high water content, which leads to the decrease of catalyst activity. The results of CFD numerical simulation show that the stirring effect of commercial scale

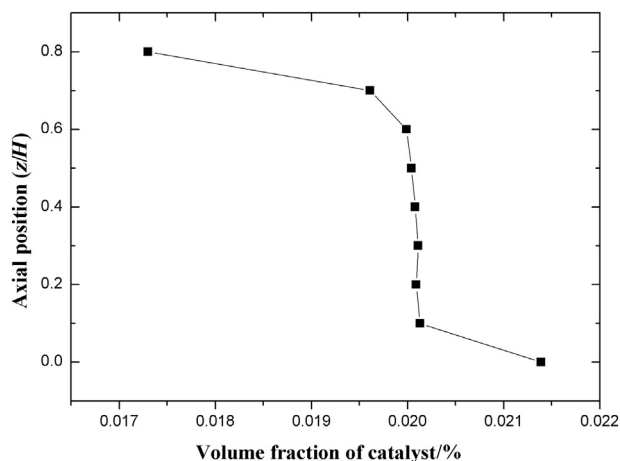


Fig. 14. The mean volume fraction of catalyst in different height sections of the improved commercial scale reactor.

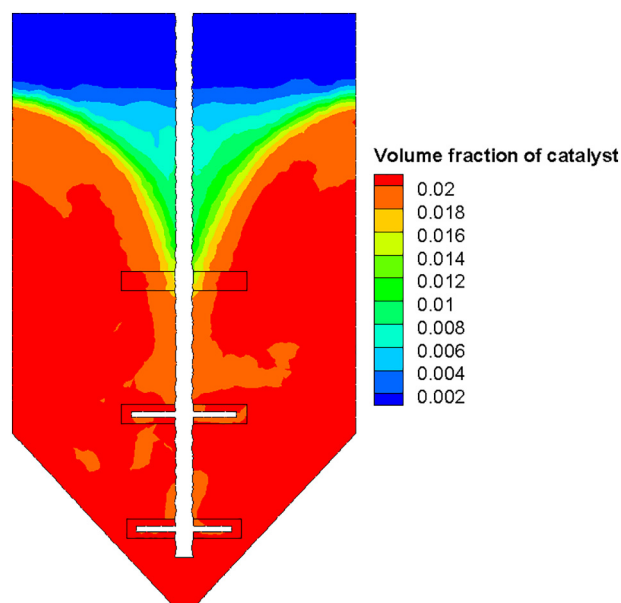


Fig. 15. The axial catalyst volume fraction contours of the improved commercial scale reactor.

reactor is better than that of lab-scale reactor, and the stirring effect of commercial scale reactor can be optimized.

Nomenclature

C_A	concentration of pinene, $\text{mol} \cdot \text{L}^{-1}$
C_{A0}	initial concentration of pinene, $\text{mol} \cdot \text{L}^{-1}$
C_p	concentration of target product, $\text{mol} \cdot \text{L}^{-1}$
C_{p0}	initial concentration of target product, $\text{mol} \cdot \text{L}^{-1}$
K_i	rate constant of step i

Subscripts

A	pinene
D	deactivation catalyst
P	target product
Q	by-product
$[ATiM]$	the complex of pinene and catalyst

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