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# Modeling and Optimization: Isomerization Reaction Rate using Response Surface Methodology with Two Kinetic Model Over Bi-Porous Catalysts

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**ABSTRACT**

A response surface methodology (RSM) with 3 levels and 4 variables was used to model and optimize the n-heptane isomerization kinetic process over Pt-HZSM-5/HMS catalysts in a fixed bed micro reactor. 30 sets of isomerization rate tests were performed at different conditions of $H_2$ flow rate (20-45 ccmin$^{-1}$), n-heptane flow rate (2-4.5 cch$^{-1}$), the temperatures (200-350 °C), and the weight percent of HZSM-5 (10-40%). It was observed that the amounts of HZSM-5 into Pt-HMS structure has the greatest effect on the rate of reaction. The surface and contour plots confirm that the rates do not considerably change versus temperature, n-heptane and $H_2$ flow rates. 0.24 molg$^{-1}$s$^{-1}$ is the highest reaction rate obtained in the 4.5 cch$^{-1}$ n-heptane and 45 cc min$^{-1}$ $H_2$ flow rate. The RSM was effective for predicting and optimizing this process. The modelling results also show both power-law and Langmuir–Hinshelwood models are in agreement with the experimental data.

## Introduction

The extensive use of petroleum has converted to a serious worry due to the poisonousness of the released pollutants from its combustion in the vehicle engine. Considerable amounts of these pollutants released into the environment will possibly reason detrimental health effects to organisms [1-5].

Isomerization reaction has received a renewed attention due to high quality petroleum without production of pollutants such as aromatics and also no a decrease in the octane number of gasoline, which is a measure to show its combustion. This reaction involves a catalytic reaction beginning with n-paraffins to produce a wide distribution of branched hydrocarbons [1-5].

In this process, the catalyst plays the main role in the progression of reaction. There are several reports about the application of different catalysts in this process. Among them and according to our previous researches [1, 6], hybrid systems, due to their interesting features, high activity and thermal stability in the various catalytic reactions have attracted our attention.

In our previous research [1], the activities of platinated catalysts supported on hexagonal mesoporous silica (HMS) were modified with HZSM-5 accomplished for the n-heptane (n-$C_7$) isomerization. A number of characterization analyses, including X-ray diffraction (XRD), X-ray

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fluorescence (XRF), temperature programmed desorption of $NH_3$ ($NH_3$-TPD), Fourier-transform infrared spectroscopy (FTIR), $H_2$ chemisorption, nitrogen sorption, and thermogravimetric analysis (TGA) have proceeded. Moreover, numerous catalytic performances for example activity and selectivity to various products, such as mono- and multi- branched iso-heptanes, cracking, hydrogenolysis and also research octane number at a range of temperature and time on the stream have been tested [1]. Continuing this work, the kinetics of this reaction over Pt-HZSM-5/HMS catalysts were studied.

The study of reported researches exposes that different parameters can be effected to improve the effectiveness of the kinetics of n-$C_7$ isomerization reaction: (a) catalytic structural properties; (b) reaction conditions such as temperature and pressure; (c) the flow rates of each reactant; (d) and so on [1, 6].

Because examining several variables simultaneously requires a lot of time and money [7], modelling tools were used in combination with experimental methods. One of these multivariate approaches is the Response Surface Method (RSM), which has been applied in experimental design, model building and optimization. This method is the mixture of statistical and mathematical methods and can analyze problems, where a connection between the response and the independent parameters through a response function [8-11]. In this research, to discover the maximum reaction rate, the optimal operation with RSM is used to find the best conditions.

In the present work, some effective parameters for example the $H_2$ and n-$C_7$ flow rates, temperature, and the weight percent of HZSM-5 were selected as important influences on the catalyst competence. Two models based on power law (PL) and Langmuir–Hinshelwood (LH) mechanism was used to study the kinetics of n-heptane.

According to reported literatures, the kinetic study of the aim reaction on the Pt-HZSM-5/HMS does not report earlier. This comprehensive method can suggest considerable development in the catalytic isomerization process.

## Experimental Section

### Catalyst Preparation

In this experiment, the preparation of Pt-HZSM-5/HMS catalysts refers to related literature [1]. The detailed steps are as follows: Dissolve 7 g ethanol in 5 g tetraethyl orthosilicate. After stirring, a solution of 1.2 g of dodecylamine and 0.5 cc of HCl (1 M) in 15 cc of distilled $H_2O$ with various zeolite amounts are slowly added to the previous solution. After stirring for 6 h, the precipitate is washed several times, filtered, and placed in an oven at 110 °C overnight. Finally, the Pt catalysts are calcined at 300 °C for 4 h. Pt amount in these catalysts is 0.6 wt%. Pt-HZSM-5/HMS catalysts were made by impregnating suitable amounts of HZSM-5 zeolite [1].

The weight percent of zeolite was varied from 10 to 40. These prepared catalysts with different HZSM-5 weights were named as PZH-10, PZH-20, PZH-30, and PZH-40, respectively.

### Kinetic Unit

The experiments were done in a continuous laboratory scale unit. The unit consists of feed injector, gas flow meters, fixed bed Pyrex micro reactor, two silica gel for drying the input gas, $H_2$ gas cylinder, thermometer and cooler with an appropriate control system for heating. The n-heptane as a feed was injected into a vaporizer by a syringe pump and blended with $H_2$ at different controlled temperatures.

The reaction operated under isothermal conditions. An on-line gas chromatograph (Agilent Technologies 7890A equipped with a flame ionization detector) was also connected to a micro reactor by a controller for analyzing the consumed gas during the reaction in the chosen time interval. The average accuracy of applied instruments and the uncertainties of measurements are ±0.0001. The reaction rate (Equation 1) for the isomerization process was defined as follows:

$$r\left(\frac{\text{mol}}{\text{g.s}}\right)=\frac{\text{n}-\text{C}_7\text{ flow rate}\times\text{n}-\text{C}_7\text{ density}\times\text{conversion}(\%)}{\text{n}-\text{C}_7\text{ molar weight}\times\text{weight of catalyst}\times\text{impregnated metal}} \qquad (1)$$

## Design of Experiments (DOE) and Response Surface Methodology (RSM)

DOE/RSM model of n-heptane isomerization was developed, for which the $H_2$ flow rate (A: cc $min^{-1}$), n–$C_7$ flow rate (B: cc $h^{-1}$), temperature (C: °C) and the weight of HZSM-5 (D: %) are central factors, influencing production. This model involves the mathematical and statistical methods, which optimize the experimental data by a response of the system (dependent variable) as a function of independent variables influencing the system [12]. The ranges of operating conditions (independent variable) were shown in Table 1. Three levels, including low level (−1), central value (0) and high level (+1) were measured for each factor. Central composite design was used as an experimental design for RSM. The responses of this design (by Design-Expert Software V.11) as the dependent variables were listed in Table 1.

**Table 1.** Input parameters and the experimental responses by the CCD design

| Parameters | Levels | | |
|---|---|---|---|
| | Low (-1) | Center (0) | High (+1) |
| A: $H_2$ flow rate (cc $min^{-1}$) | 20 | 32.5 | 45 |
| B: n-$C_7$ flow rate (cc $h^{-1}$) | 2 | 3.25 | 4.5 |
| C: Temperature (°C) | 200 | 275 | 350 |
| D: Weight of HZSM-5 (%) | 10 | 25 | 40 |

| RUN | Parameters | | | | Experimental Responses |
|---|---|---|---|---|---|
| - | A | B | C | D | rate (mol $g^{-1}s^{-1}$) |
| 1 | 32.5 | 3.25 | 125 | 25 | 0.14 |
| 2 | 45.0 | 2.00 | 350 | 40 | 0.02 |
| 3 | 32.5 | 3.25 | 275 | 25 | 0.10 |
| 4 | 32.5 | 0.75 | 275 | 25 | 0.01 |
| 5 | 45.0 | 4.50 | 200 | 40 | 0.24 |
| 6 | 32.5 | 3.25 | 275 | 25 | 0.10 |
| 7 | 32.5 | 3.25 | 275 | 55 | 0.22 |
| 8 | 32.5 | 3.25 | 425 | 25 | 0.12 |
| 9 | 32.5 | 3.25 | 275 | 25 | 0.10 |
| 10 | 20.0 | 4.50 | 350 | 40 | 0.12 |
| 11 | 32.5 | 3.25 | 275 | 25 | 0.10 |
| 12 | 32.5 | 3.25 | 275 | 25 | 0.10 |
| 13 | 32.5 | 3.25 | 275 | 25 | 0.10 |
| 14 | 45.0 | 2.00 | 350 | 10 | 0.05 |
| 15 | 45.0 | 4.50 | 350 | 40 | 0.04 |
| 16 | 20.0 | 2.00 | 350 | 40 | 0.08 |
| 17 | 7.5 | 3.25 | 275 | 25 | 0.09 |
| 18 | 45.0 | 2.00 | 200 | 40 | 0.13 |
| 19 | 45.0 | 2.00 | 200 | 10 | 0.16 |
| 20 | 20.0 | 2.00 | 350 | 10 | 0.09 |
| 21 | 20.0 | 2.00 | 200 | 40 | 0.15 |
| 22 | 20.0 | 4.50 | 200 | 10 | 0.03 |
| 23 | 32.5 | 3.25 | 275 | 5 | 0.02 |
| 24 | 20.0 | 4.50 | 350 | 10 | 0.01 |
| 25 | 57.5 | 3.25 | 275 | 25 | 0.18 |
| 26 | 45.0 | 4.50 | 200 | 10 | 0.06 |

| | | | | | |
|---|---|---|---|---|---|
| 27 | 32.5 | 5.75 | 275 | 25 | 0.17 |
| 28 | 20.0 | 4.50 | 200 | 40 | 0.10 |
| 29 | 20.0 | 2.00 | 200 | 10 | 0.15 |
| 30 | 45.0 | 4.50 | 350 | 10 | 0.04 |

The response surface plots are due to the fittings of empirical models to the experimental data. These responses are according to a second order polynomial function of codified factors (Table 2).

**Table 2.** Coefficients of the final equation versus actual parameters.

Actual Equation= $a + bA + cB + dC + eD + fAB + gAC + hAD + iBC + jBD + kCD + lA^2 + mB^2 + nC^2 + oD^2 + pABC + qABD + rACD + sBCD + tA^2B + uA^2C + vA^2D + wAB^2 + xAC^2 + yAD^2 + zB^2C + a\backprime B^2D + b\backprime BC^2 + c\backprime BD^2 + d\backprime C^2D + e\backprime CD^2 + f\backprime A^3 + g\backprime B^3 + h\backprime C^3 + i\backprime D^3$

A: $H_2$ flow rate (cc $min^{-1}$), B: n-$C_7$ flow rate (cc $h^{-1}$) C: Temperature (°C), D: Weight of HZSM-5 (%)

| | | | | | |
|---|---|---|---|---|---|
| Coefficient | *a* | *b* | *c* | *d* | *e* |
| rate | +0.1007 | +0.0230 | +0.0397 | -0.0049 | +0.0504 |
| Coefficient | *f* | *g* | *h* | *i* | *j* |
| rate | +0.0144 | -0.0186 | -0.0033 | +0.0076 | +0.0265 |
| Coefficient | *k* | *l* | *m* | *n* | *o* |
| rate | -0.0091 | +0.0037 | -0.0072 | +0.0027 | +0.0009 |
| Coefficient | *p* | *q* | *r* | *s* | *t* |
| rate | -0.0059 | +0.0028 | -0.0128 | -0.0085 | -0.0504 |
| Coefficient | *u* | *v* | *w* | *x* | *y* |
| rate | -0.0308 | -0.0327 | -0.0220 | +0.0000 | +0.0000 |
| Coefficient | *z* | $a\backprime$ | $b\backprime$ | $c\backprime$ | $d\backprime$ |
| rate | +0.0000 | +0.0000 | +0.0000 | +0.0000 | +0.0000 |
| Coefficient | $e\backprime$ | $f\backprime$ | $g\backprime$ | $h\backprime$ | $i\backprime$ |
| rate | +0.0000 | +0.0000 | +0.0000 | +0.0000 | +0.0000 |

The analysis of variance (ANOVA) was done to estimate the statistical importance of the parameters and interactions using Fisher's test, and its associated probability level (p-value). T-tests were also used to investigate the import of the coefficients measured for each model. The goodness of fit of the models to the experimental data was compared by the coefficient of determination ($R^2$) [12].

Two kinetic models based on power law (PL) and the Langmuir–Hinshelwood (LH) mechanism was used to obtain the kinetic parameters. A non-linear least-square regression was used to evaluation the kinetic parameters [6].

## Results and Discussion

### Regression Equation Development and ANOVA Analysis

A mathematical relationship between input variables and new experimental predicted responses was obtained for n-heptane in catalytic isomerization over Pt-ZH catalysts. The experiments were done in accordance with the designed matrix as shown in Table 1.

In the present work, the ANOVA analysis established cubic equations were developed in terms of the coded factors with the inclusion of both significant and insignificant terms for n-heptane isomerization under the use of the prepared catalysts as shown in Table 2.

Table 3 lists the linear effect of process variables coded A, B, C, and D, dual interactions as AB, AC, AD, BC, BD, and CD, square interactions as $A^2$, $B^2$, $C^2$, and $D^2$, triple interactions as ABC. ABD, ACD, etc., cubic interactions as $A^3$, $B^3$, $C^3$, and $D^3$ on the response variables.

**Table 3.** ANOVA of quadratic model for the surface response of suggested model.

| Source | Sum of Square | df[a] | Mean Square | F-Value | P-Value | |
|---|---|---|---|---|---|---|
| Model | 0.0939 | 22 | 0.0043 | 4.6500 | 0.0219 | significant |
| A: $H_2$ flow rate | 0.0042 | 1 | 0.0042 | 4.6000 | 0.0691 | - |
| B: n-$C_7$ flow rate | 0.0126 | 1 | 0.0126 | 13.7700 | 0.0075 | - |
| C: Temperature | 0.0002 | 1 | 0.0002 | 0.2130 | 0.6584 | - |
| D: Weight of HZSM-5 | 0.0203 | 1 | 0.0203 | 22.1200 | 0.0022 | - |
| AB | 0.0033 | 1 | 0.0033 | 3.6100 | 0.0993 | - |
| AC | 0.0056 | 1 | 0.0056 | 6.0500 | 0.0434 | - |
| AD | 0.0002 | 1 | 0.0002 | 0.1903 | 0.6758 | - |
| BC | 0.0009 | 1 | 0.0009 | 1.0000 | 0.3496 | - |
| BD | 0.0112 | 1 | 0.0112 | 12.2200 | 0.0101 | - |
| CD | 0.0013 | 1 | 0.0013 | 1.4500 | 0.2675 | - |
| $A^2$ | 0.0004 | 1 | 0.0004 | 0.4133 | 0.5408 | - |
| $B^2$ | 0.0014 | 1 | 0.0014 | 1.5400 | 0.2544 | - |
| $C^2$ | 0.0002 | 1 | 0.0002 | 0.2177 | 0.6550 | - |
| $D^2$ | 0.0000 | 1 | 0.0000 | 0.0225 | 0.8849 | - |
| ABC | 0.0006 | 1 | 0.0006 | 0.6136 | 0.4591 | - |
| ABD | 0.0001 | 1 | 0.0001 | 0.1332 | 0.7260 | - |
| ACD | 0.0026 | 1 | 0.0026 | 2.8500 | 0.1352 | - |
| BCD | 0.0012 | 1 | 0.0012 | 1.2700 | 0.2966 | - |
| $A^2B$ | 0.0136 | 1 | 0.0136 | 14.7800 | 0.0063 | - |
| $A^2C$ | 0.0050 | 1 | 0.0050 | 5.5000 | 0.0515 | - |
| $A^2D$ | 0.0057 | 1 | 0.0057 | 6.2000 | 0.0415 | - |
| $AB^2$ | 0.0026 | 1 | 0.0026 | 2.8100 | 0.1377 | - |
| $AC^2$, $AD^2$, $B^2C$, $B^2D$, $BC^2$, $BD^2$, $C^2D$, $CD^2$, $A^3$, $B^3$, $C^3$, $D^3$ | 0.0000 | 0 | - | - | - | - |
| Residual | 0.0064 | 7 | 0.0009 | - | - | - |
| Lack of Fit | 0.0064 | 2 | 0.0032 | - | - | - |
| Pure Error | 0.0000 | 5 | 0.0000 | - | - | - |
| Cor Total | 0.1003 | 29 | Sum of squares is Type III - Partial | | | |

[a] degree of freedom.

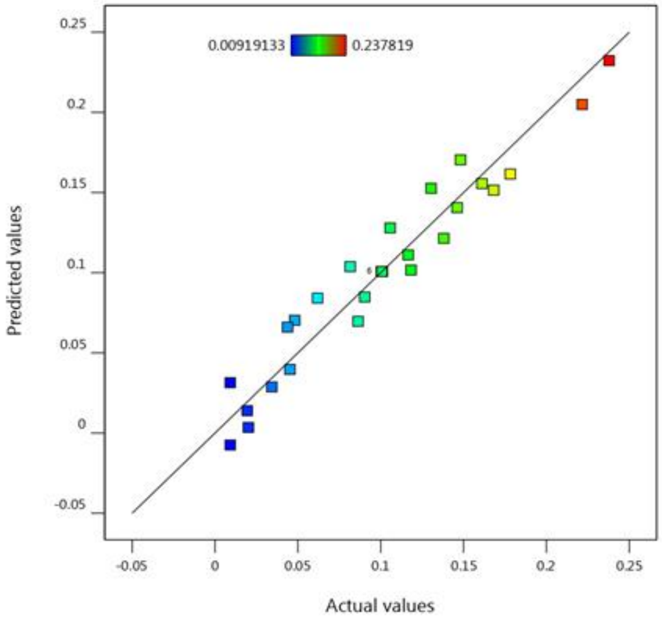

**Fig. 1**. Presentations of RSM for the reaction rates

Statistical analysis of variance (ANOVA) has been led to investigate the importance of model and variables for n-$C_7$ isomerization. The low P-value (0.0219) and high F-value (4.65) obtained for the used model, which confirm the fitness and the significance of the model response. There is only a 2.19% chance that an F-value this large could occur due to noise. Commonly, a significant level ($\alpha$) of 0.05 is well [12-16]. In this case B, D, AC, BD, $A^2B$, $A^2D$ are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

The model has the $R^2$ amount near to unity (0.94) that presents the model predicted data to approach the response data and the association of the model and the dependent parameters. A good correlation between predicted and actual experimental data of n-$C_7$ isomerization are presented in Fig. 1. Furthermore, the Root Mean Square Error (RMSE) that is the standard deviation of the residuals [13-16], obtained RMSE=0.03 for these data. The signal to noise ratio greater than 4 is another major factor for model evaluation. The results show the signal to noise ratios of 9.04 that indicates the used cubic model to be used to direct the design space. According to ANOVA data, the Lack of Fit is 0.0064 of the responses. Compared to the pure errors, the lack of fit is influential. However, the pure errors naturally eliminate and are not significant in this model.

Fig. 2 shows the model well fit the experimental data, because the points are in the constant range [17].

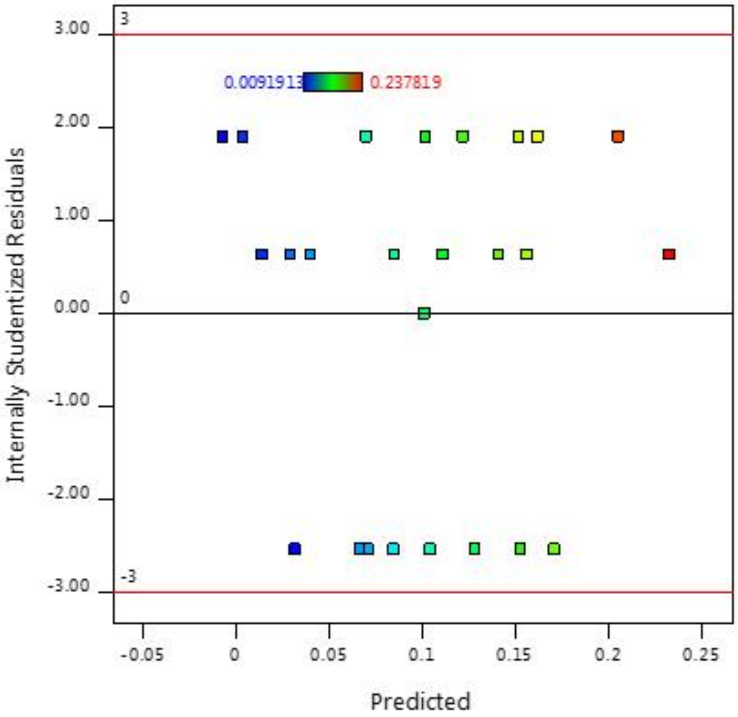

**Fig. 2**. The residuals versus predicted values plot for the model

To determine the most appropriate reaction rate according to the response data, Box-Cox plot is shown in Fig. 3. No specific transformation is recommended for this model, because the 95% confidence interval around the best lambda value (the minimum point of the curve= -0.16) is 1 [17].

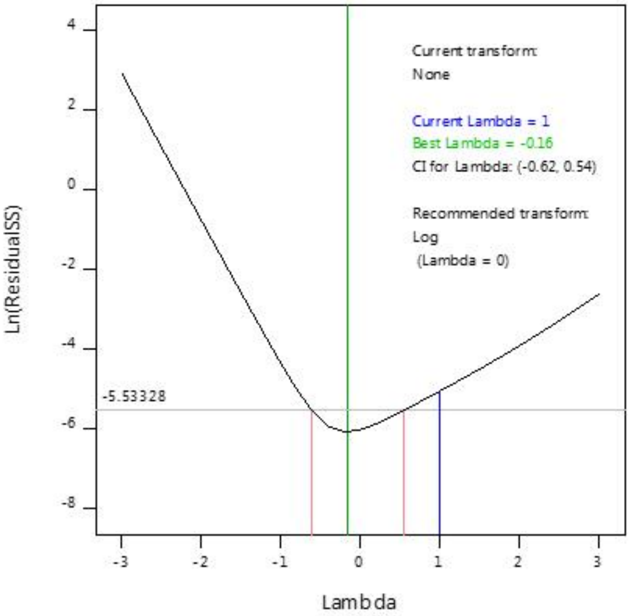

**Fig. 3**. Box-Cox plot for the model

Fig. 4 shows one-factor plots. The other parameters are constant at mean values. Increased n-$C_7$ flow rate and weight of HZSM-5 have significant influences on the reaction rate ($P < 0.05$).

The combined effect of operating parameters as $H_2$ flow rate (2-4.5, cc $h^{-1}$), n-$C_7$ flow rate (20-45 cc $min^{-1}$), temperature (200-350 °C), and weight of HZSM-5 (10-40%) on the isomerization reaction was studied by 3D response surface achieved from RSM as presented in Fig. 5. The contour graphs were also shown in Fig. 6. Between two variables, the third and fourth variables were fixed at the middle values (A: 32.5, B: 3.25, C: 275, and D: 25). The combined effect of $H_2$ flow rate and n-$C_7$ flow rate on this process in the constant temperature (275 °C) and weight of HZSM-5 (25%) as surface performances is shown in Fig. 5a. The rest of the parameter pairs are shown in other parts of this figure while the other parameter pairs are kept constant.

According to the surface response and contour plots, the maximum reaction rate (0.24 mol $g^{-1}$ $s^{-1}$) has obtained in the high flow rate of both n-$C_7$ (4.5 cc $h^{-1}$) and $H_2$ (45 cc $min^{-1}$). Increasing the $H_2$ flow rate to 45 cc $min^{-1}$ at a maximum constant flow rate of n-$C_7$ (4.5 cc $h^{-1}$) promotes the kinetic rate at around 200 °C for the PZH-40 catalyst, while this amount decreased to 0.13 mol $g^{-1}s^{-1}$ at n-$C_7$ flow rate (2.00 cc $h^{-1}$).

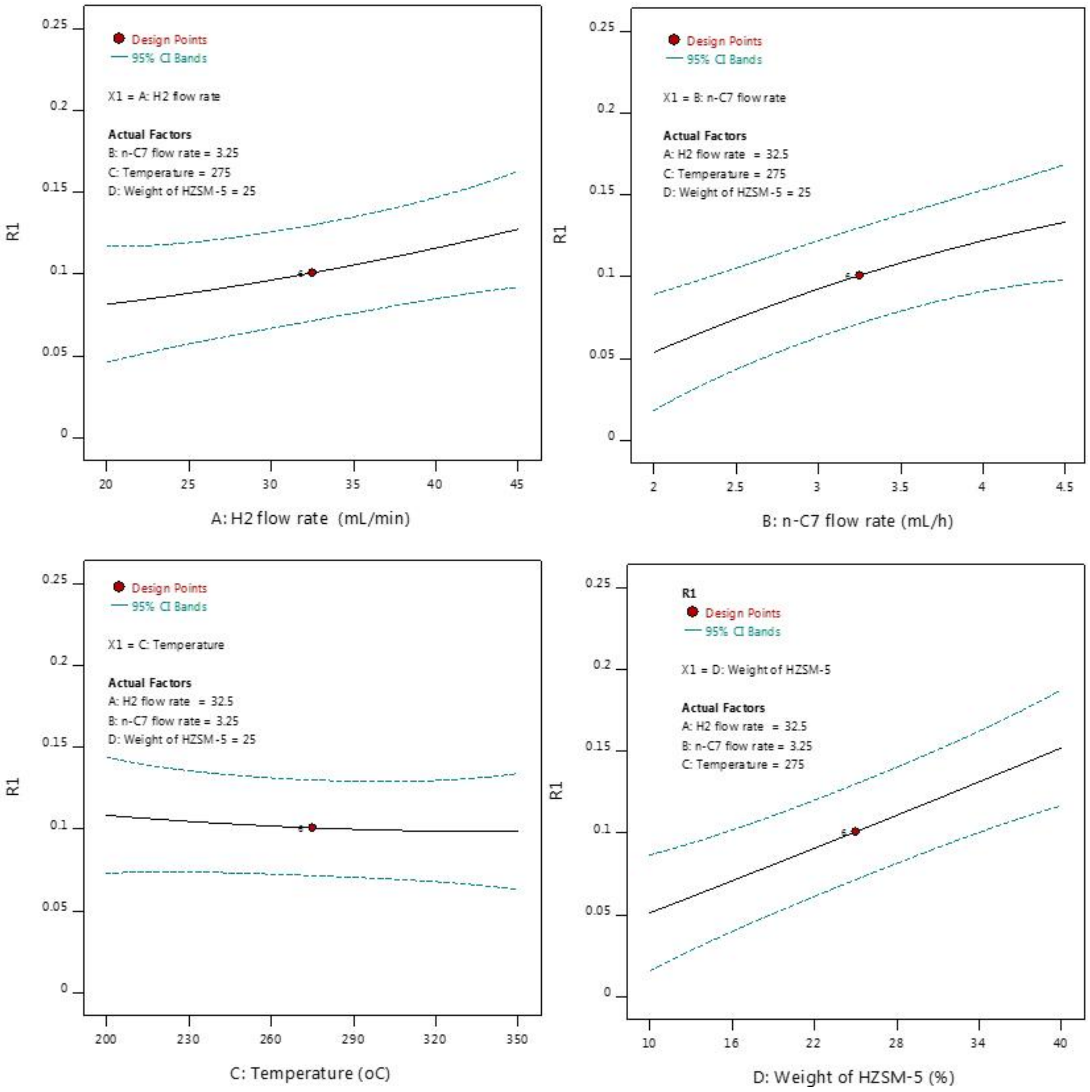

**Fig. 4**. One factor plots

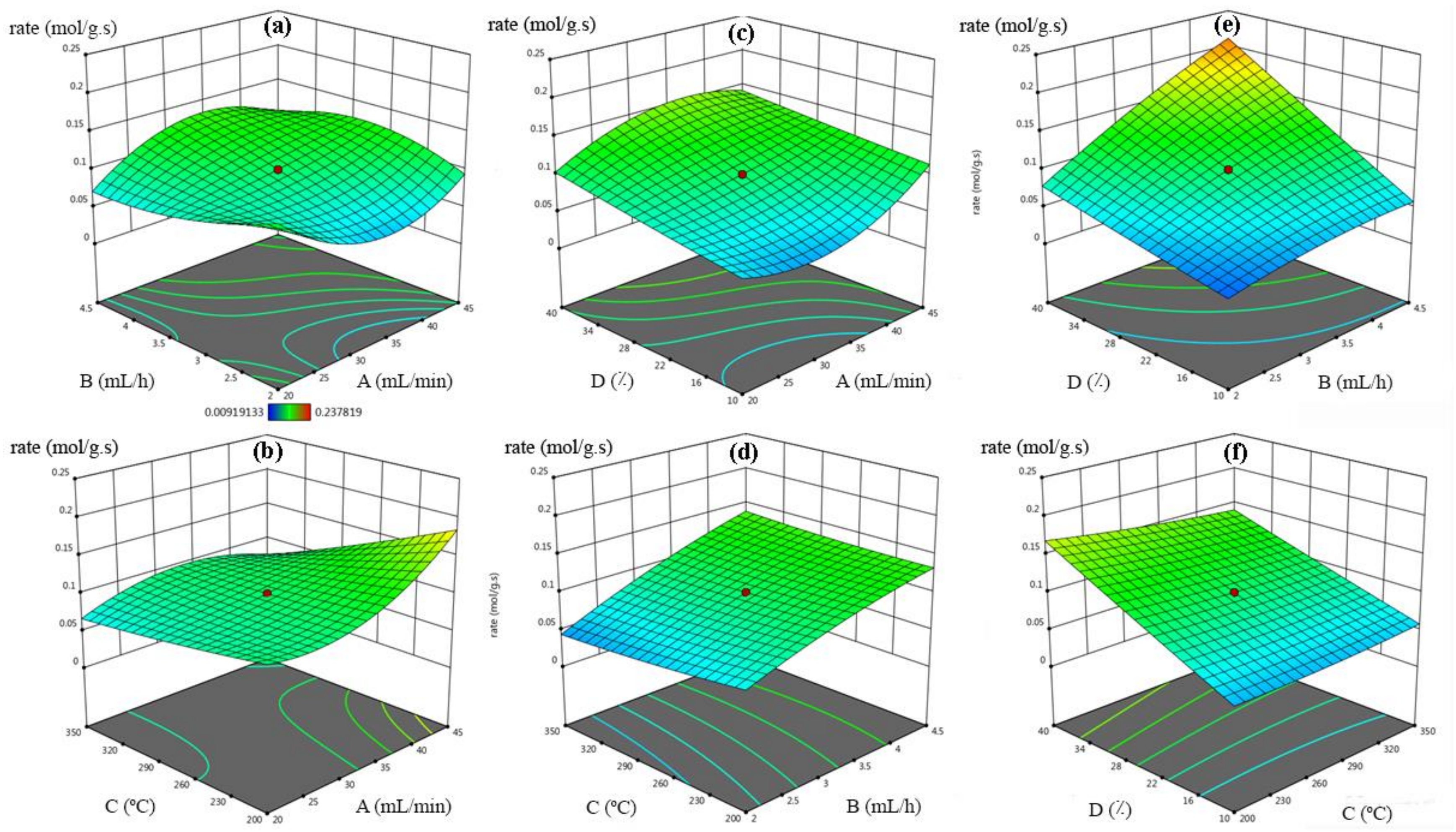

**Fig. 5**. 3-D response surface graphs for the reaction rates according to the combined effects of operating variables, (a) AB, (b) AC, (c) AD, (d) BC, (e) BD, and (f) CD at the middle values

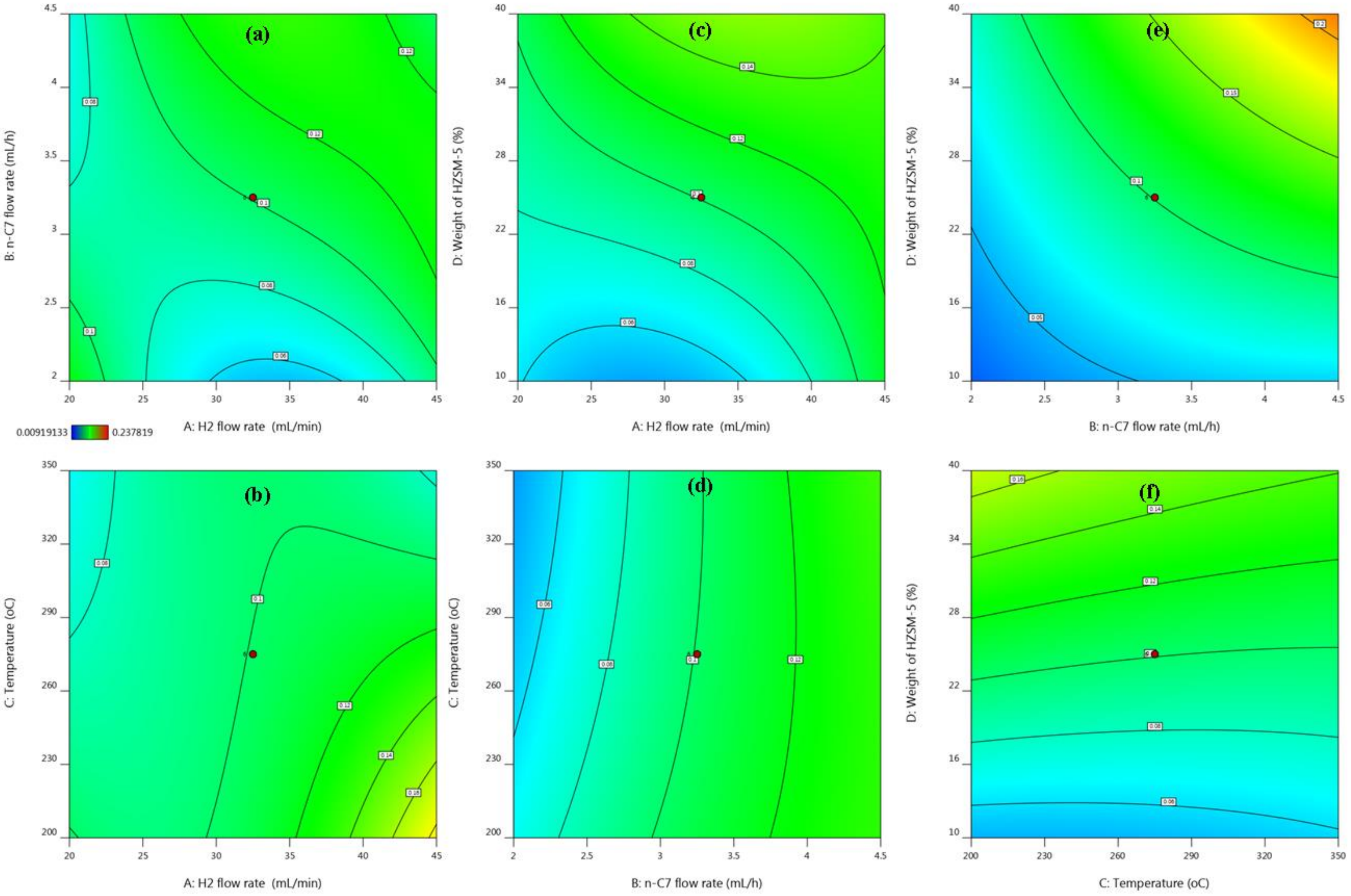

**Fig. 6**. Contour plots for the reaction rates according to the combined effects of operating variables, (a) AB, (b) AC, (c) AD, (d) BC, (e) BD, and (f) CD at the middle values

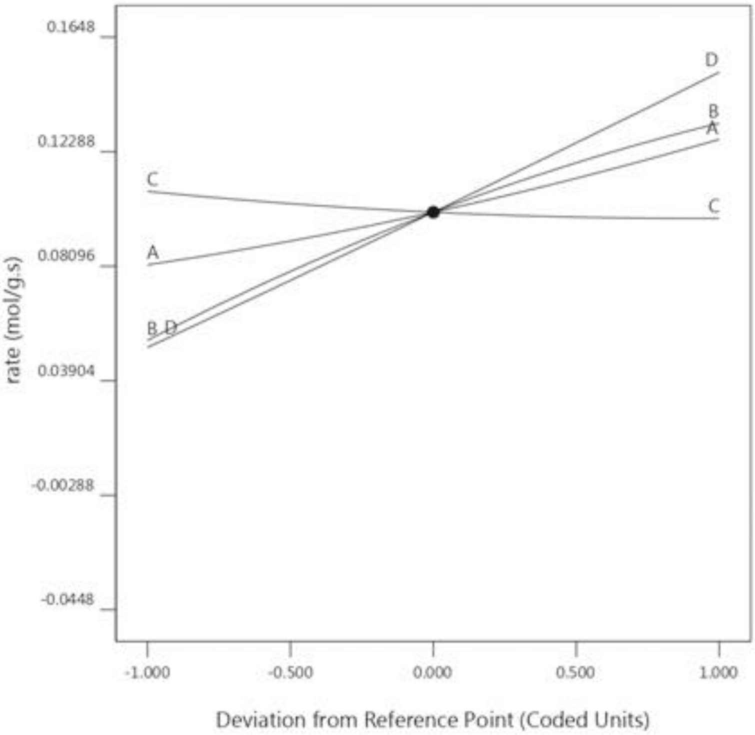

**Fig. 7**. Perturbation plot of model factors (A: $H_2$ flow rate, B: n-$C_7$ flow rate, C: Temperature, D: Weight of HZSM-5) for isomerization reaction

Among operating parameters of $H_2$ flow rate, n-$C_7$ flow rate, temperature, and weight of HZSM-5 perturbation plot show that temperature was a most influencing factor for isomerization reaction followed weight of HZSM-5 as shown in Fig. 7.

**Table 4**. Best conditions for the reaction rate of n-$C_7$ isomerization predicted by the CCD-surface response and experimental results

| | Reaction rate | n-$C_7$ flow rate | $H_2$ flow rate | Temperature | Weight of HZSM-5 |
|---|---|---|---|---|---|
| CCD surface | 0.24 | 4.50 | 43.25 | 200.00 | 40.00 |
| The real rate at the best point | 0.24 | 4.50 | 45.00 | 200.00 | 40.00 |

Table 4 presents the specific optimal conditions as the input variables and predicted responses by the Design-Expert 11. The experimental results under the optimum conditions of the CCD-surface response confirm the prediction of RSM is very well with a deviation of 0.03%.

A desirability function by numerical optimization was used to determine the optimum conditions for each factor combination. The objective of this work is to maximize the reaction rate as a response. Fig. 8 shows the optimal conditions for maximizing the reaction rate determined by the desirability function with numerical optimization. According to this, a temperature of 200.48 °C, an $H_2$ flow rate of 41.90 cc $min^{-1}$, an n-$C_7$ flow rate of 4.48 cc $h^{-1}$, and a weight of HZSM-5 of 39.74%, with a reaction rate of 0.238 mol $g^{-1}$ $s^{-1}$ are the optimal conditions. The desirability value was given as one.

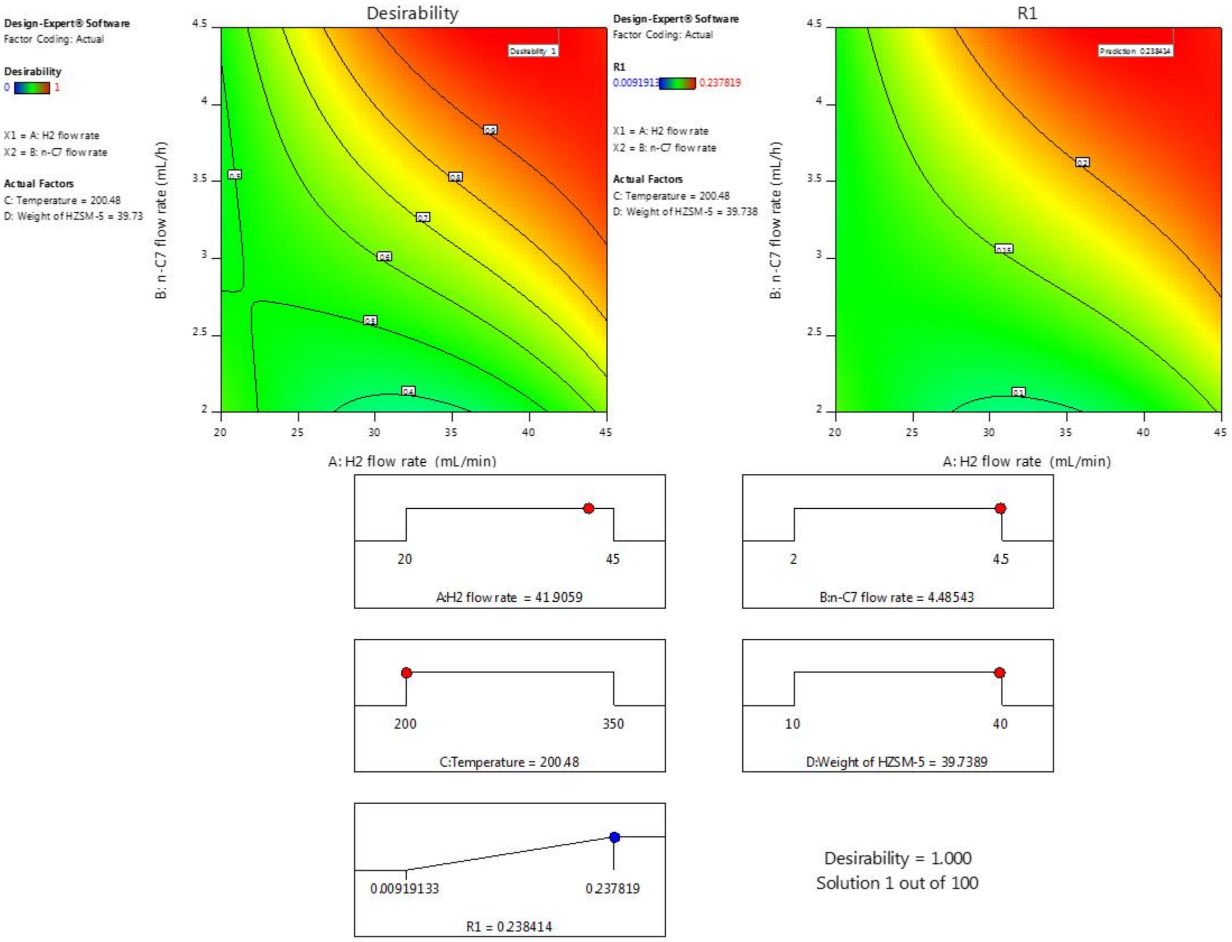

**Fig. 8**. Numerical optimization by desirability function

## PL and LH Models

PL and LH models over the conditions cited in the experimental section have been considered. The estimated parameters of these two models were summarized in Table 5. The Arrhenius plots (Fig. 9a) show the activation energies in the range of ~31 to ~99 kJ mol$^{-1}$ (Table 5) for this process.

According to the equation of PL model (Equation 2), the reaction order concerning hydrogen is -0.01 to -0.09 and the order kinetics for n-C$_7$ is 0.47-1.03 (see Table 5 and Fig. 9b).

$$r\left(\frac{\text{mol}}{\text{g}\cdot\text{s}}\right) = A\,e^{-\frac{E_{\text{app}}^{\text{act}}}{\text{RT}}} P_{H2}^{n} P_{C7}^{m} \qquad (2)$$

The H$_2$ reaction orders suggest low coverage of catalysts by H$_2$ and the dissociative and strong adsorption of n-C$_7$. According the results, the reaction rate declines with increasing P$_{\text{H2}}$.

To evaluate the performance of these models, regressions of the predicted and experimental data were drawn in Fig. 9c and 9d.

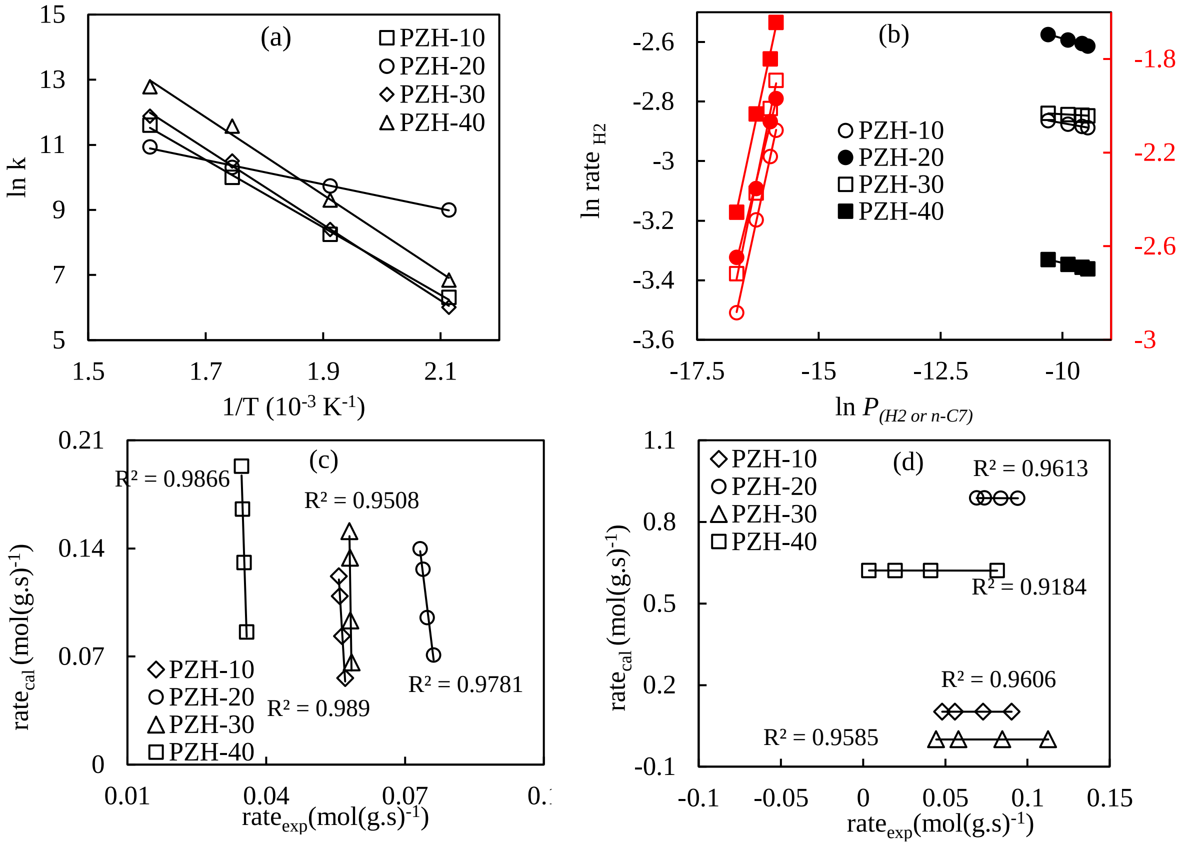

**Fig. 9**. (a) Arrhenius plots calculated from the experimental data, (b) double-log plots of the isomerization reaction rates versus the partial pressures of n-$C_7$ and $H_2$, (c) estimated data by PL and (d) estimated data LH models

**Table 5**. PL and PL parameters and activation energies

| T (°C) | Orders | PZH-10 | PZH-20 | PZH-30 | PZH-40 |
|---|---|---|---|---|---|
| PL model | | | | | |
| 200 | $n_{H2}$ | -0.07 | -0.08 | -0.02 | -0.09 |
| 250 | $n_{H2}$ | -0.06 | -0.06 | -0.03 | -0.06 |
| 300 | $n_{H2}$ | -0.03 | -0.05 | -0.01 | -0.05 |
| 350 | $n_{H2}$ | -0.03 | -0.05 | -0.01 | -0.04 |
| 200 | $m_{C7}$ | 0.47 | 0.67 | 0.60 | 0.57 |
| 250 | $m_{C7}$ | 0.60 | 0.71 | 0.62 | 0.93 |
| 300 | $m_{C7}$ | 0.77 | 0.72 | 0.80 | 0.96 |
| 350 | $m_{C7}$ | 0.96 | 0.84 | 1.03 | 0.98 |
| | $E_{app}^{act}$ (kJmol$^{-1}$) | 86.22 | 31.09 | 96.89 | 99.07 |
| LH model | | | | | |
| $K$ | $E_{app}^{act}$ (kJmol$^{-1}$) | 95.2 | 54.2 | 99.8 | 100.6 |
| | $A$ (mol(gs)$^{-1}$) | $1.1\times10^{-5}$ | $1.1\times10^{-9}$ | $2.7\times10^{-5}$ | $9.0\times10^{-7}$ |
| $K_{C7}$ | $-\Delta H_{ads-C7}$(kJmol$^{-1}$) | 27.2 | 15.6 | 87.5 | 52.6 |
| | $A_{C7}$ (atm$^{-1}$) | $1.2\times10^{-11}$ | $1.2\times10^{-12}$ | $2.7\times10^{-5}$ | $9.2\times10^{-9}$ |
| $K_{H2}$ | $-\Delta H_{ads-H2}$(kJmol$^{-1}$) | 4.5 | 7.1 | 7.1 | 7.1 |
| | $A_{H2}$(atm$^{-1}$) | $1.4\times10^{-2}$ | $2.7\times10^{-2}$ | $2.7\times10^{-2}$ | $2.7\times10^{-2}$ |

The correlation coefficients ($R^2$) were shown both models produce acceptable predicted results. However, the PL model is only a mathematical and unrealistic model, the Langmuir-Hinshelwood model can make better predictions by considering its mechanism (Eq. 3).

$$r = \frac{A\, e^{-\frac{E_{\text{app}}^{\text{act}}}{\text{RT}}} . P_{C7} . P_{H2}}{\left(\left(\frac{1}{A_{C7}\, e^{-\frac{\Delta H_{ads-C7}}{\text{RT}}}}\right)+P_{C7}\right).\left(\left(\frac{1}{A_{H2}\, e^{-\frac{\Delta H_{ads-H2}}{\text{RT}}}}\right)+P_{H2}\right)} \tag{3}$$

The correlation coefficients ($R^2$) valuations of this model (above 0.9) indicate the low error between experimental and predicted data (Fig. 9d). The activation energies obtained this model are in the range of ~54 to 100 kJ $mol^{-1}$, which is in accordance with the previous literatures [6].

According to Table 5, PZH-20 has the lowest activation energy that it confirms this catalyst fast reaction. The results show $A_{H2}$ (the pre-exponential factor of $H_2$ adsorption) is higher than $A_{C7}$. This presents faster adsorption of $H_2$ than n-$C_7$. Based on the strong adsorption of the n-$C_7$, the n-$C_7$ adsorption heat ($\Delta H_{ads-C7}$) is higher than $H_2$ ($\Delta H_{ads-H2}$).

## Conclusion

In this study, the effect of HZSM-5 amounts, temperature and n-C7 and H2 flow rates on the kinetics of this reaction were studied over platinated HZSM-5/HMS catalysts. To discover the relationships between these parameters and reaction rates, around 30 different runs of the surface response methodology were designed by Design-Expert software. Based on the predicted data, the below conclusions can be obtained:

1) In accordance with the obtained response, RSM can successfully predict the reaction rates.
2) The highest reaction rate (0.24 mol $g^{-1}$ $s^{-1}$) has occurred in the high flow rate of both n-$C_7$ (4.5 cc $h^{-1}$) and $H_2$ (45 cc $min^{-1}$).
3) The amount of HZSM-5 in the PZH-x structure is the most effective parameter on the isomerization kinetic rate.
4) Compared to the effect of zeolite content on the activity of catalysts, the other parameters, especially temperature, have not significantly affect on the rate response.

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## Compliance with Ethical Standards Section

- Disclosure of potential conflicts of interest: There is no conflicts of interest.
- Research involving Human Participants and/or Animals: Not applicable.
- Informed consent: There is informed consent in publishing this research.

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