# Mechanism Modeling and Optimization Design of Ethanol Coupling to Prepare C4 Olefins

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*Abstract: In view of the influence of different catalysts on the selectivity of C4 olefins and the yield of C4 olefins at different temperatures, based on the regression analysis method and the control variable method, the data were fitted and analyzed by MATLAB, and the principal component analysis method was established. Then, a nonlinear programming model was established and solved with the objective function of catalyst combination having the best performance, appropriate temperature, and C4 olefin yield as high as possible. Finally, the highest C4 olefin yield and the catalyst combination and temperature at this time were given.*

*Keywords: Regression analysis, control variable method, principal component analysis method, MATLAB*

## 1. Research Background

Since C4 olefins are widely used in the production of chemical products and medicines, the output of C4 olefins produced by traditional production methods has been unable to meet the needs of society, and ethanol has become the raw material for the production of C4 olefins [1]. However, in the preparation process, the catalyst combination and temperature are important factors that affect the selectivity of C4 olefins and the yield of C4 olefins. Therefore, we need to optimize the design of the catalyst combination and explore the process conditions of ethanol catalytic coupling to prepare C4 olefins. It is very important meaning and value.

Firstly, the data were analyzed by regression analysis method to study the relationship between ethanol conversion rate, C4 olefin selectivity and temperature under different catalyst combinations, and the regression equations between ethanol conversion rate, C4 olefin selectivity and temperature were obtained by using MATLAB. Function formula and image, and then each regression equation and image were analyzed for goodness of fit to obtain the relationship between ethanol conversion, C4 olefin selectivity and temperature under each catalyst combination. According to the test results of a given catalyst combination at 350 degrees at different times in an experiment, take time as the abscissa and other indicators as the ordinate, and use MATLAB to build a relationship diagram to reflect the difference of each index at different times in an experiment.

Secondly, the effects of different catalyst combinations and temperatures on ethanol conversion and C4 olefin selectivity were discussed. Further, the catalyst combination and temperature are selected so that the yield of C4 olefins is as high as possible under the same experimental conditions, and the fitting is performed according to the analyzed results. Select the catalyst combination and temperature with the highest overall score.

Finally, with the goal of maximizing the yield of C4 olefins, an experimental design was carried out based on temperature considerations. On this basis, additional experiments are designed to verify the correctness and rationality of the experimental design. Starting from the charging method, adjacent proportions, different catalysts, and adjacent temperatures, in order to ensure the rationality of the design, data explanation is required. By substituting the design data into the problem-one model for comparison, the feasibility and rationality of the model are ensured.

## 2. Model Establishment and Solution

### 2.1. Regression Analysis

For each catalyst combination, the relationship between ethanol conversion, C4 olefin selectivity and temperature was studied separately. Using regression analysis, the temperature was taken as the abscissa, and the ethanol conversion and C4 olefin selectivity were taken as the ordinate, and plotted with MATLAB. The image of the regression equation [2] was obtained, and the regression equations between the ethanol conversion rate, C4 olefin selectivity and temperature were obtained respectively, so as to reflect the relationship between ethanol conversion rate, C4 olefin selectivity and temperature. The goodness of fit of the regression equation between groups is shown in table 1.

*Table 1: Goodness of fit of regression equation*

| $A_i$ | $R^2$ | $A_i$ | $R^2$ | $B_i$ | $R^2$ |
|---|---|---|---|---|---|
| A1 | $R_1^2=0.9797$ $R_2^2=0.9160$ | A8 | $R_1^2=0.9991$ $R_2^2=0.9995$ | B1 | $R_1^2=0.9989$ $R_2^2=0.9972$ |
| A2 | $R_1^2=0.9911$ $R_2^2=0.9803$ | A9 | $R_1^2=0.9905$ $R_2^2=0.9949$ | B2 | $R_1^2=0.9915$ $R_2^2=0.9977$ |
| A3 | $R_1^2=0.9663$ $R_2^2=0.9980$ | A10 | $R_1^2=0.9939$ $R_2^2=0.9785$ | B3 | $R_1^2=0.9916$ $R_2^2=0.9763$ |
| A4 | $R_1^2=0.9959$ $R_2^2=0.9765$ | A11 | $R_1^2=0.9871$ $R_2^2=0.9994$ | B4 | $R_1^2=0.9867$ $R_2^2=0.9737$ |
| A5 | $R_1^2=0.9940$ $R_2^2=0.9905$ | A12 | $R_1^2=0.9990$ $R_2^2=0.9993$ | B5 | $R_1^2=0.9916$ $R_2^2=0.9982$ |
| A6 | $R_1^2=0.9859$ $R_2^2=0.9454$ | A13 | $R_1^2=0.9963$ $R_2^2=0.9817$ | B6 | $R_1^2=0.9904$ $R_2^2=0.9709$ |
| A7 | $R_1^2=0.9997$ $R_2^2=0.9997$ | A14 | $R_1^2=0.9971$ $R_2^2=0.9995$ | B7 | $R_1^2=0.9966$ $R_2^2=0.9971$ |

According to the test results of a given catalyst combination at 350 degrees at different times in one experiment, the relationship between each index and time was solved by MATLAB, as shown in Fig. 1.

Fig.1 shows the changes of each index at different times in one experiment: when the reaction time of the catalyst in the ethanol atmosphere continued to increase, the ethanol conversion rate continued to decrease, and the selectivity of C4 olefins in the product did not increase significantly. , on the contrary, the selectivity of the remaining products (ethylene, acetaldehyde, methyl benzaldehyde and methyl benzyl alcohol and others) increased with increasing reaction time.
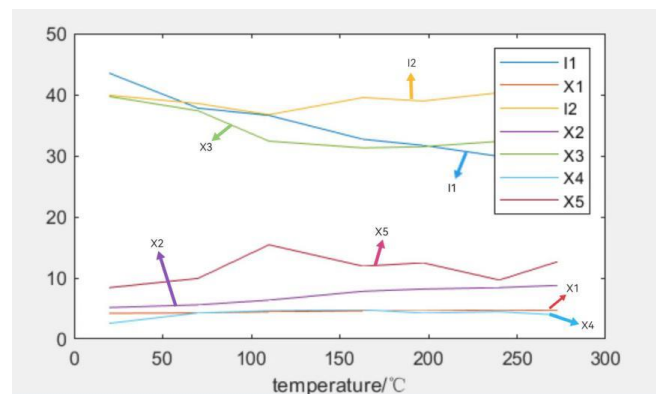


*Figure 1: The relationship between indicators and time*

### 2.2. Control Variable Method

In order to explore the effect of different catalyst combinations and temperatures on the ethanol conversion and C4 olefin selectivity, the method of controlling variables was used to study respectively, and one variable was changed, and the other variables remained unchanged, and MATLAB was used to make different catalyst combinations for each group, and temperature to ethanol conversion and C4 olefin selectivity histogram, the histogram was analyzed to obtain the results, as shown in Fig. 2 to Fig.19.
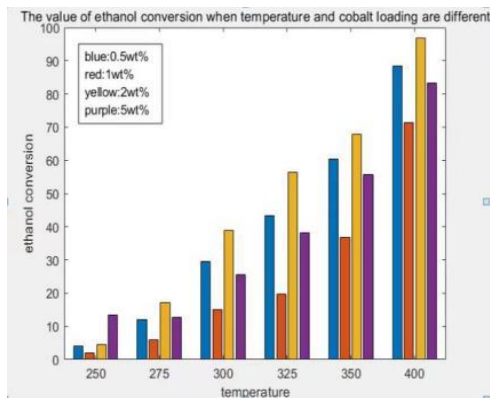
*Figure 2: The value of ehanol conversion when temperature and cobalt loading are different*
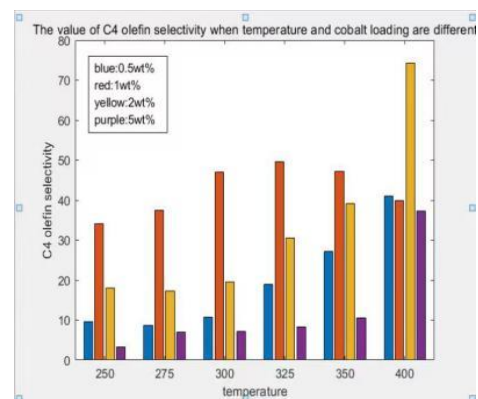


*Figure 3: The value of C4 olefin selectivity when temperature and cobalt loading are different*

Fig. 2 and Fig.3 show that the catalyst combinations A1, A2, A4, and A6 increase the ethanol conversion rate with the increase of Co loading and temperature, and the maximum value is 96.872% when the catalyst combination A2 and the temperature are 400 ℃; The selectivity of C4 olefins increases continuously, and the maximum value is also 74.38% when the catalyst combination A2 and the temperature are 400℃.
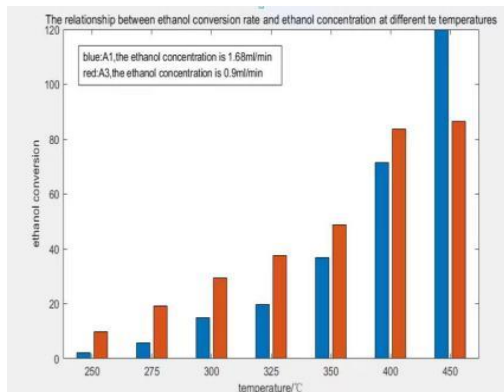


*Figure 4: The relationship between ethanol conversion rate and ethanol concentration at different temperatures*
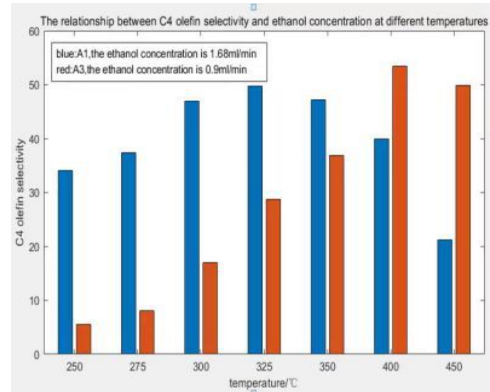


*Figure 5: The relationship between C4 olefin selectivity and ethanol concentration at different temperatures*

Fig.4 and Fig.5 show that the ethanol conversion rate of catalyst combinations A1 and A3 increases continuously with the decrease of ethanol concentration and the increase of temperature. The maximum value is shown in catalyst combination A3 and the temperature is 400 ℃, and the value is 83.7%, C4 olefin selectivity first decreased and then increased, and the maximum value was also shown in the catalyst combination A3, when the temperature was 400 ℃, the value was 53.43%.
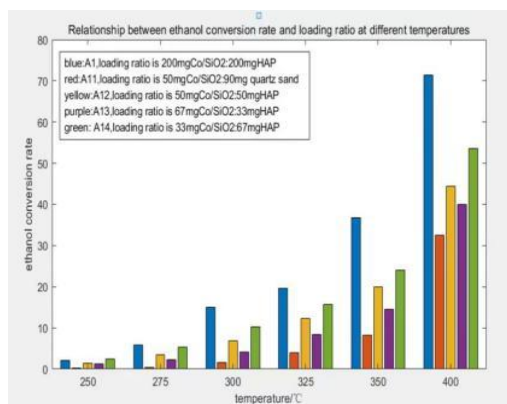


*Figure 6: Relationship between ethanol conversion rate and loading ratio at different temperatures*
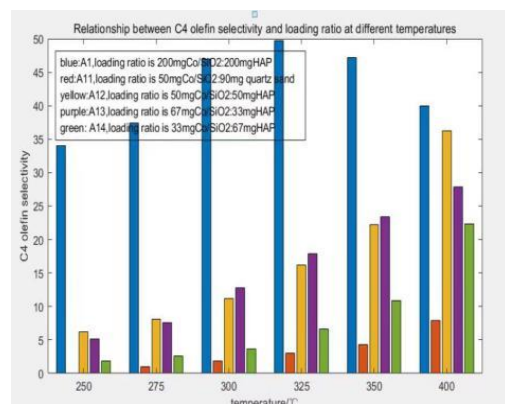


*Figure 7: Relationship between C4 olefin selectivity and loading ratio at different temperatures*

Fig. 6 and Fig.7 show that the catalyst combinations A1, A11, A12, A13, and A14 decrease with the decrease of the mass of the charge and the increase of the temperature. The ethanol conversion rate

decreases continuously. The maximum value is shown in the catalyst combination A1 and the temperature of 400℃, the value is 71.4%, the C4 olefin selectivity increases first and then decreases, and its maximum value is 49.7% when the catalyst combination A1 and the temperature are 325℃.
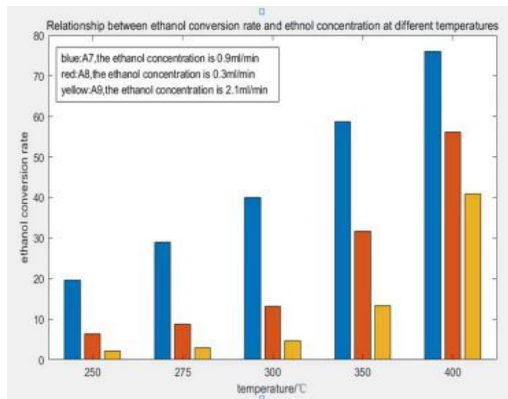


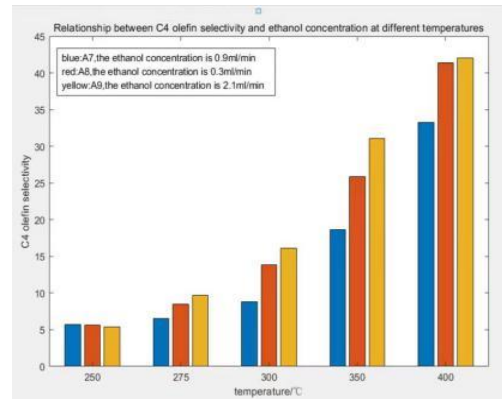*Figure 8: Relationship between ethanol conversion rate and ethnol concentration at different temperatures*



*Figure 9: Relationship between C4 olefin selectivity and ethanol concentration at different temperatures*

Fig. 8 and Fig. 9 show that the ethanol conversion rate of catalyst combinations A7, A8, and A9 increases continuously with the increase of ethanol concentration and temperature, and the maximum value is 76% when the catalyst combination A7 and the temperature are 400 ℃, C4 The olefin selectivity also increases continuously, and its maximum value is 42.04% when the catalyst combination A9 is at a temperature of 400 ℃.
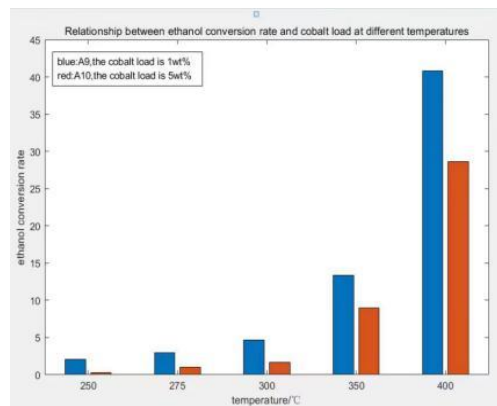


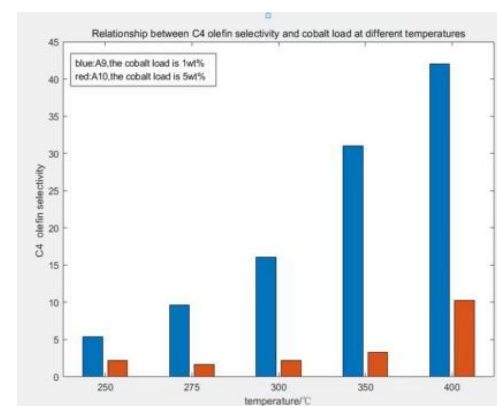*Figure 10: Relationship between ethanol conversion rate and cobalt load at different temperatures*



*Figure 11: Relationship between C4 olefin selectivity and cobalt load at different temperatures*

Fig. 10 and Fig. 11 show that the ethanol conversion of catalyst combinations A9 and A10 increases with the increase of Co loading and temperature, and the maximum value is 40.8% for catalyst combination A9 and 400℃, C4 olefins The selectivity also increases continuously, and its maximum value is 42.04% when the catalyst combination A9 and the temperature are 400°C.
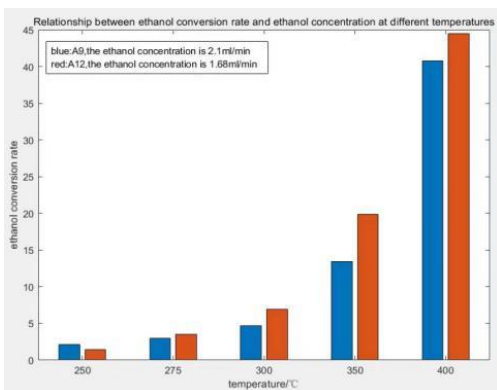


*Figure 12: Relationship between ethanol conversion rate and ethanol concentration at different temperatures*
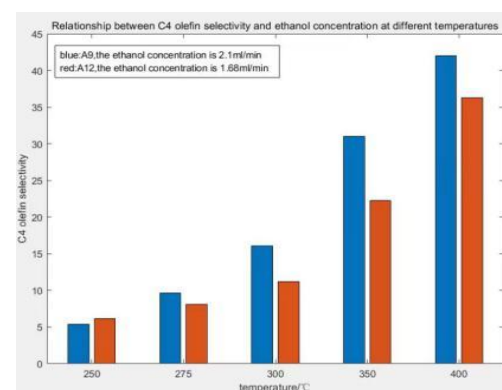


*Figure 13: Relationship between C4 olefin selectivity and ethanol concentration at different temperatures*

Fig.12 and Fig. 13 show that the ethanol conversion rate of catalyst combinations A9 and A12 increases with the increase of ethanol concentration and temperature, and the maximum value is 44.5% when the catalyst combination A12 and temperature are 400 ℃, C4 olefin selection The performance is also increasing, and its maximum value is 42.04% when the catalyst combination A9 and the temperature are 400°C.
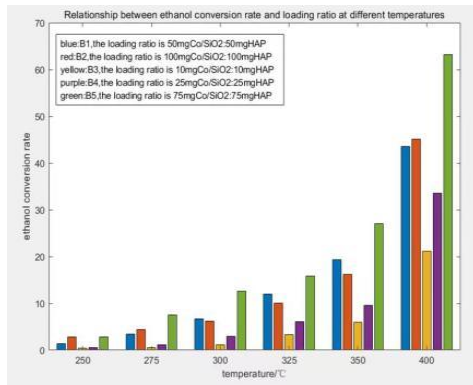


*Figure 14: Relationship between ethanol conversion rate and loading ratio at different temperatures*
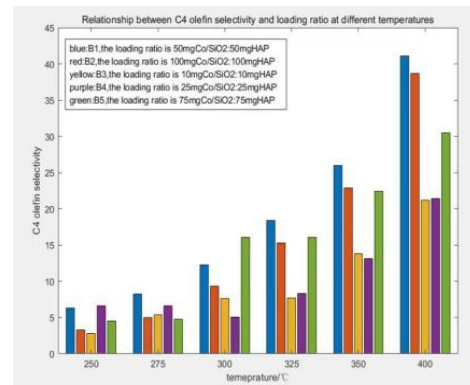


*Figure 15: Relationship between C4 olefin selectivity and loading ratio at different temperatures*

Fig. 14 and Fig. 15 show that the ethanol conversion rate of catalyst combinations B1, B2, B3, B4, and B6 increases continuously with the increase of charging ratio and temperature. The maximum value is shown in catalyst combination B6 and the temperature is 400°C, and the value is 63.2%, the C4 olefin selectivity increases first and then decreases, and its maximum value is 41.08% when the catalyst combination B1 and the temperature are 400°C.
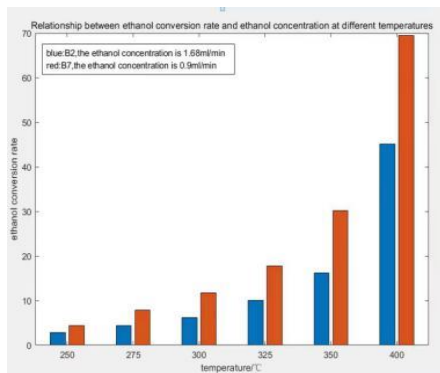


*Figure 16: Relationship between ethanol conversion rate and ethanol concentration at different temperatures*
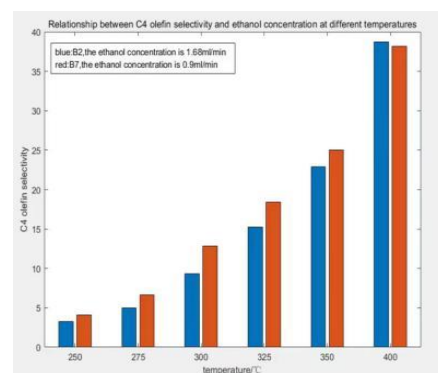


*Figure 17: Relationship between C4 olefin selectivity and ethanol concentration at different temperatures*

Fig. 16 and Fig. 17 show that the ethanol conversion rate of catalyst combinations B2 and B7 increases continuously with the decrease of ethanol concentration and the increase of temperature. The maximum value is shown in catalyst combination B7 and the temperature is 400°C, and the value is 69.4%, C4 The olefin selectivity also increases continuously, and its maximum value is 38.7% when the catalyst combination B2 and the temperature are 400°C.
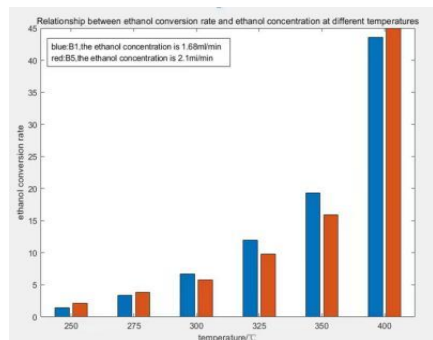


*Figure 18: Relationship between ethanol conversion rate and ethanol concentration at different temperatures*
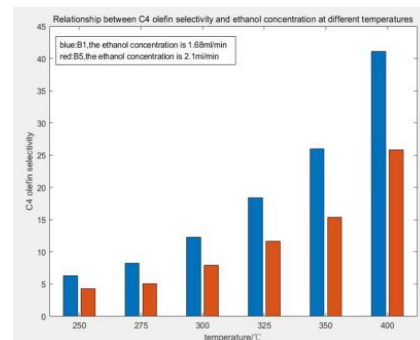


*Figure 19: Relationship between C4 olefin selectivity and ethanol concentration at different temperatures*

Fig. 18 and Fig. 19 show that the ethanol conversion rate of catalyst combination B1 and B5 increases with the increase of ethanol concentration and temperature, and the maximum value is 45% in catalyst combination B5 and temperature 400 ℃, C4 olefin selection The performance also increases continuously, and its maximum value is 41.08% in catalyst combination B1 and temperature 400℃.

According to the above conclusions, it can be concluded that the catalyst has better performance at 400 ℃. According to the relationship between the ethanol conversion rate, C4 olefin selectivity and temperature under each catalyst combination, the catalyst combinations A1 and A2 can be obtained at 400 ℃. Ethanol conversion and C4 olefin selectivity at 325℃ and catalyst combinations A6, A7, A8, A9, A10, A11, A12, A13, A14, B1, B2 at 325℃ using MATLAB The principal component analysis method [3] was carried out on the data, and it was found that the C4 olefin yield was the highest when the A2 catalyst was combined at 400 ℃, with a value of 96.87%*74.38%=72.05%. When the temperature is lower than 350℃, the principal component analysis method is also used to perform the data on the A2 catalyst combination, and the C4 olefin yield is the highest at 325℃, and its value is 56.38%*30.62%=17.26%.

According to the relationship between ethanol conversion, C4 olefin selectivity and temperature under each catalyst combination, it can be seen that the A7 catalyst combination has the highest goodness of fit and the closest variance to 0, so the A7 catalyst combination is selected as the new experiment 5 experiments were designed with temperature as the independent variable, and the values were 225 ℃, 375 ℃, 425 ℃, 450 ℃, and 475 ℃, respectively, and the dependent variables were calculated for the ethanol conversion rate I1 and the C4 olefin selectivity I2. The specific values are shown in table 2.

*Table 2: Numerical results at different temperatures*

| Temperatures (T/°C) | Ethanol conversion rate (I1/%) | C4 olefin selectivity (I2/%) | C4 olefin yield (I1*I2/%) |
|---|---|---|---|
| 225 | 8.79 | 6.05 | 0.53 |
| 375 | 67.5 | 25.15 | 16.98 |
| 425 | 84.34 | 43.05 | 36.31 |
| 450 | 92.25 | 54.17 | 49.97 |
| 475 | 99.82 | 66.73 | 66.61 |

The differences in the performance of the two catalysts were compared, and the effect of the mixing method on the catalyst was investigated. The test results are shown in Fig. 20. It can be seen that under the same reaction conditions, the two catalysts have similar ethanol conversion and C4 olefin selectivity, indicating that the charging method has no effect on the performance of the catalyst [4].
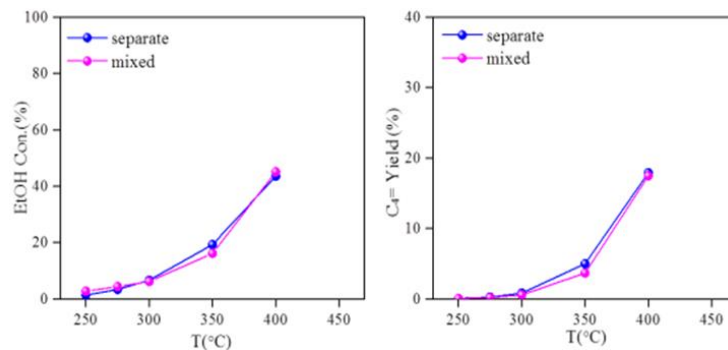


*Figure 20: Effect of charging method on the catalytic performance of 1Co/SiO2-HAP for ethanol*

## 3. Conclusion

In this paper, we study the relationship between ethanol conversion, C4 olefin selectivity and temperature for each catalyst combination separately, and quantitatively analyze the test results of a given catalyst combination at 350 ℃ at different times in one experiment. In addition, the effects of different catalyst combinations and temperatures on ethanol conversion and C4 olefin selectivity were discussed. Further, the C4 olefin yield can be as high as possible under the same experimental conditions by selecting the appropriate catalyst combination and temperature. At the same time, if the temperature is lower than 350 ℃, how to choose the appropriate catalyst combination and temperature to make the C4 olefin yield as high as possible. Finally, five sets of experiments are designed to make the yield of C4 olefins higher, and detailed rational reasons are given.

**References**

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