Research of the Pore Structure Model of Low-temperature Claus Catalyst

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Abstract. This paper simulated and calculated the process of low temperature reaction. Using the principle of response surface method (RSM) Box-Behnken and central composite design, the paper studied the effects of macroporous, mesoporous and microporous in the catalyst on conversion rate of reaction process; it also created the relationship between the pore structure of the catalyst and the efficiency of low temperature Claus reaction, and determined the optimal pore structure parameters of low temperature Claus catalyst.

Low-temperature Claus technology [1-3], also known as sub-dew point (SDP) sulfur recovery technology is one of the widely used sulfur recovery and tail gas treatment technology, and the process characteristic of the technology is that the Claus reaction is carried out below the temperature of SPD [4-6]. Currently, active alumina is the catalyst used in low-temperature Claus process, and a number of studies in recent years have demonstrated that the efficiency of SPD Claus reaction is closely related to the pore structure of active alumina catalyst, especially the large pore volume or the porosity of macroporous which has been determined as an important parameter for measuring the transforming activity of the catalyst [5-8].

1. Typical calculating process

The catalyst used for low-temperature Claus reaction has a large number of pores which are widely distributed. Based on experimental data, the catalyst can be considered as a massive accumulation of all kinds of single pores in the actual reaction process. Therefore, the conversion amount of H2S can be calculated by the formula as follows:

$$x = \frac{C}{C_0} \tag{1}$$

$$C = N_1 c_1 + N_2 c_2 + N_3 c_3 \tag{2}$$

N1, N2 and N3 represent the quantities of macroporous, mesoporous and microporous respectively; c1, c2 and c3 represent the conversion amount of sulfur in macroporous, mesoporous and microporous respectively; N1, N2 and N3 can be calculated as follows:

$$N_i = \frac{V_i}{V_{si}} \tag{3}$$

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Vi represents the total porous volume of a certain type of pore, and Vsi is single pore volume of a certain type of pore; the volume of pore is approximated to a sphere, and can be calculated using the formula of sphere as follows:

$$V_{si} = \frac{4}{3}\pi r^3 \tag{4}$$

The total conversion amount of H2S under different pore-size distribution conditions can be determined by solving the three simultaneous equations. Normalizing the above results with the total amount of H2S involved in the reaction, the actual conversion rate of H2S can be obtained.

According to the experimental conditions, the concentration of H2S is 42%, SO2 is 2.1%, and the other one is nitrogen in the reactant gas at constant pressure. The actual concentration of H2S is about 1.875mol/m3 and SO2 is about 0.9375mol/m3. Therefore, according to the previous simulation, if the concentrations of H2S and SO2 are assigned as 2mol/m3 and 1mol/m3 respectively, the process of reaction is calculated as follows:

The radius of micropore, mesopore and macropore are assigned as r1, r2 and r3 respectively, and the typical values of which are as follows:

$$r_1 = 40\text{nm}, r_2 = 40\ \text{nm}, r_3 = 100\ \text{nm} \tag{5}$$

The single pore volume with different corresponding pore diameter can be calculated according to formula (4).

Thus, the total conversion amount and conversion rate can be obtained. Based on the experimental results, putting the previous calculation results into the former formula, the results of the comparison are displayed, as shown in Figure 1:

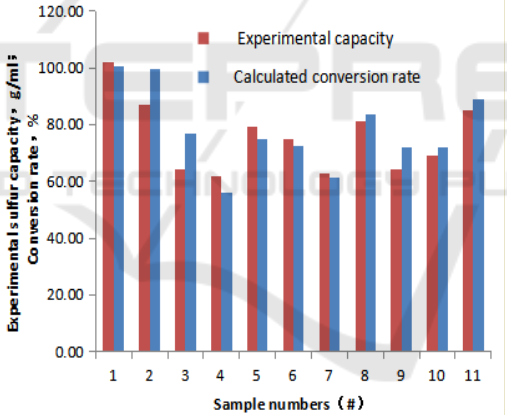

Figure 1. Results comparisons of experimental sulphur capacity and calculated conversion rate.

Based on the experimental data and simulation results, it shows that the sulfur capacity obtained by experiments and the conversion rate gotten by simulation have a similar tendency.

2. Contributions of different pare diameter

The contribution of pores with different pore diameter of the different catalysts to the reaction process can be calculated using formula as follows:

$$\gamma = \frac{N_i c_i}{N_1 c_1 + N_2 c_2 + N_3 c_3} \tag{6}$$

The comparisons of the previous results and conversion rate data are shown in Figure 2:

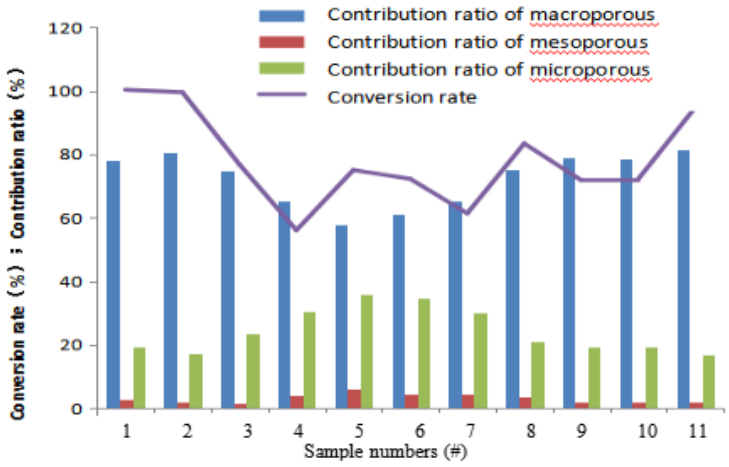

Figure 2. The calculated conversion rate and contribution ratios of macroporous, mesoporous and microporous.

The results show that the macroporous with total volume ratio of 10%-30% in the catalyst contribute conversion rate of 60%-80% to the reaction process, the microporous with total volume ratio of 25%-35% contribute conversion rate of 20%-35%, and the role of mesoporous with volume ratio of 5%-15% contributing conversion rate of 1%-6% can be ignored. The conversion rate of sample 5# which has the maximum mesoporous volume ratio of 13.15% is only 72.26%.

3. Pore diameter optimization

The effects of macroporous, mesoporous and microporous in the catalyst on the conversion rate of reaction process were studied using the principle of RSM Box-Behnken and central composite design. Based on experimental data range, the optimal value is finally determined by means of 3 factors and 3 levels RSM, as shown in Table 1.

Table 1. Levels table of response surface method experimental factors

Factors	Levels		
	-1	0	+1
The total volume of macroporous	0.05	0.11	0.18
The total volume of mesoporous	0.03	0.05	0.07
The total volume of microporous	0.34	0.37	0.40

Taking the conversion rate as dependent variable Y, using letters A, B, and C standing for volume ratios of macroporous, mesoporous and microporous respectively, the calculation scheme and result of RSM can be obtained. Analyzing the various factors by RSM, the following equation can be obtained:

$$Y = 5.55207+380.07101\times A \ +50\times B \ +50\times C \ +617.75148\times A2 \quad (7)$$

The response surface plots have been obtained by solving the model equation, as shown in Figure 3. and Figure 4. The graphs visually represent the effect of the other 2 variables and the interaction of them on the response of conversion rate, when one of the variables gets to mid-point of the test. The graphs also show that the volume ratio of macroporous plays a crucial role on the conversion rate of the catalyst. When the volume ratio of macroporous is constant, the effect of changing the volume ratio of mesoporous and microporous on the conversion rate of the catalyst can be ignored. Through variance analysis of all factors, the results indicate that the model is significant ($P<0.0001$), the lack

of fit is not significant P=0, and the multi-correlation coefficient R^2 =0.9999, all of which illustrate that the model is very useful for simulating the conversion rate of the catalyst. Therefore, the model can be used for analysis and prediction of the reaction results.

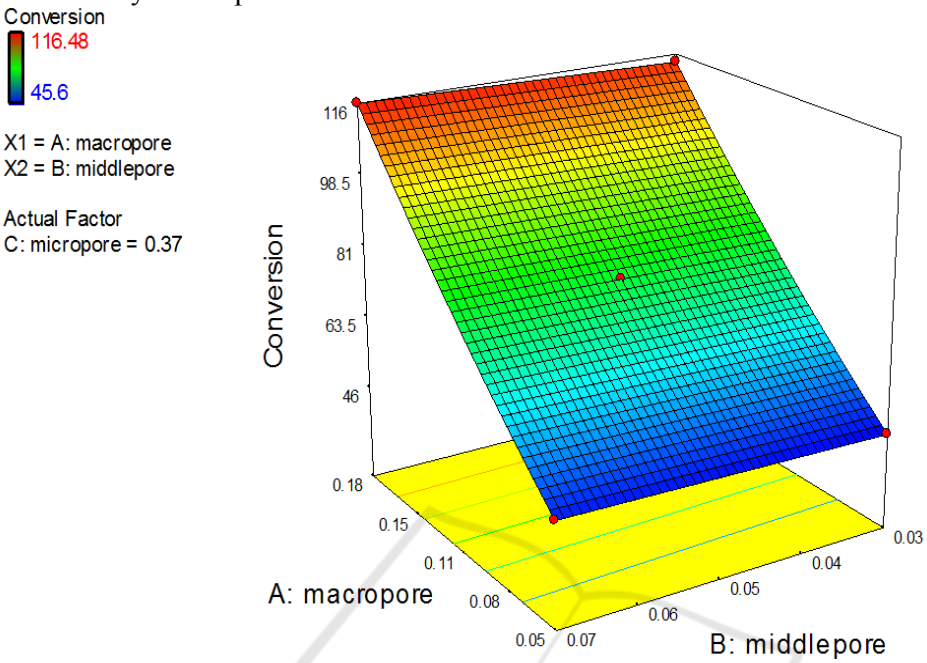

Figure 3. The effects of interaction between macroporous and mesoporous on the conversion rate.

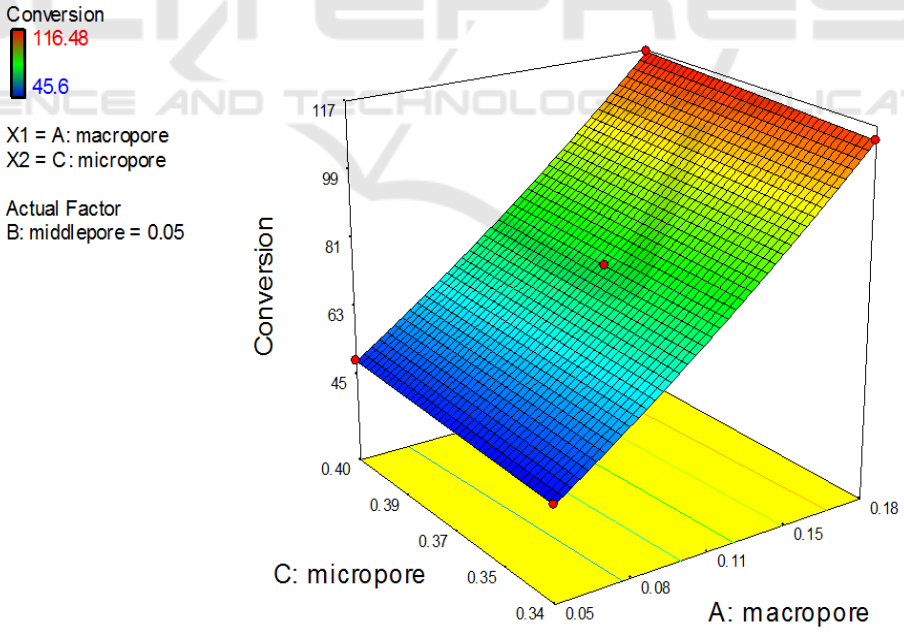

Figure 4. The effects of interaction between macroporous and microporous on the conversion rate.

Optimizing experimental conditions with the above-mentioned model, the graphs showing the relationships between expected values and other influencing factors are plotted, and the results are shown in Figure 5 and Figure 6.

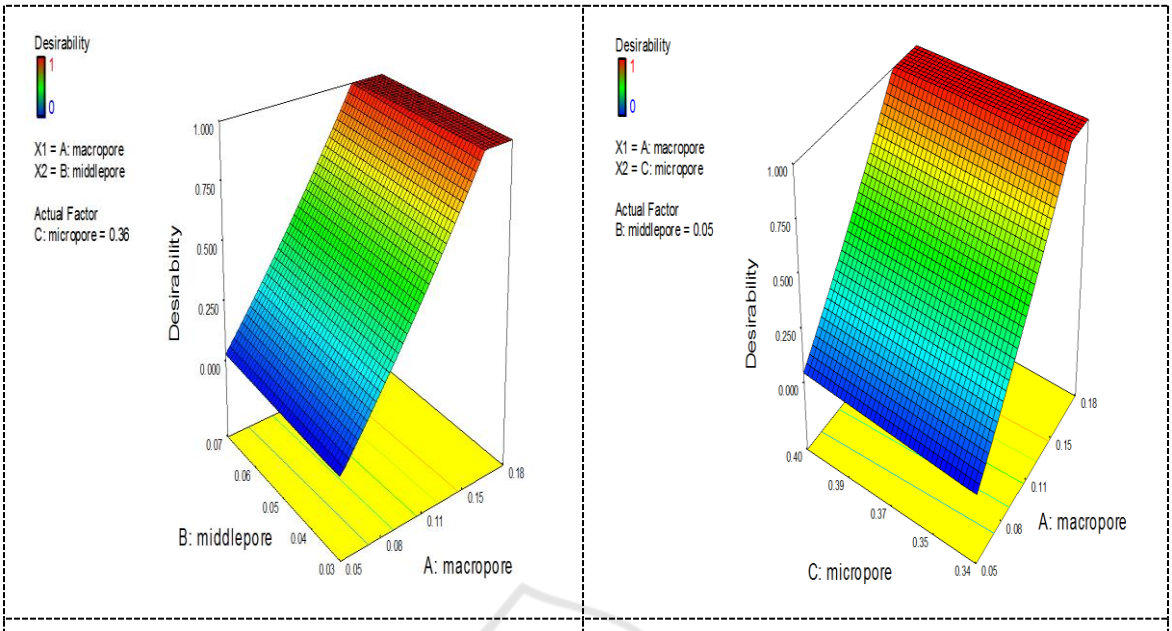

Figure 5. The effects of interaction between macroporous and mesoporous on the expected values.

Figure 6. The effects of interaction between macroporous and microporous on the expected values.

Based on the optimal conversion rate expectation determined by the expected value model, the effects of macroporous, mesoporous and microporous are shown in Figure 7 and Figure 8:

Through calculation, the optimal results are that the volume ratios of macroporous, mesoporous and microporous are 0.16 ml/g, 0.06 ml/g, and 0.36 ml/g respectively. According to the formula calculation, the conversion rate can reach to 103.17%.

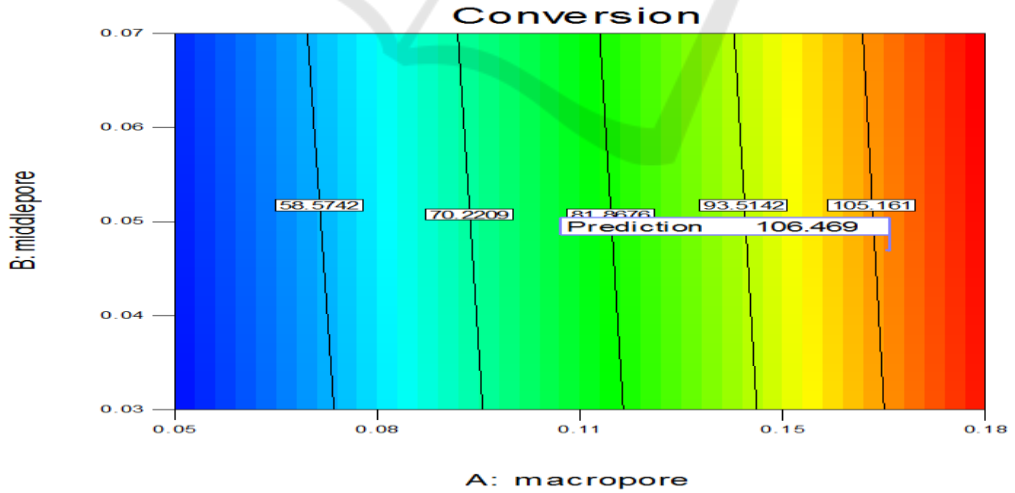

Figure 7. The optimization results of macroporous and mesoporous.

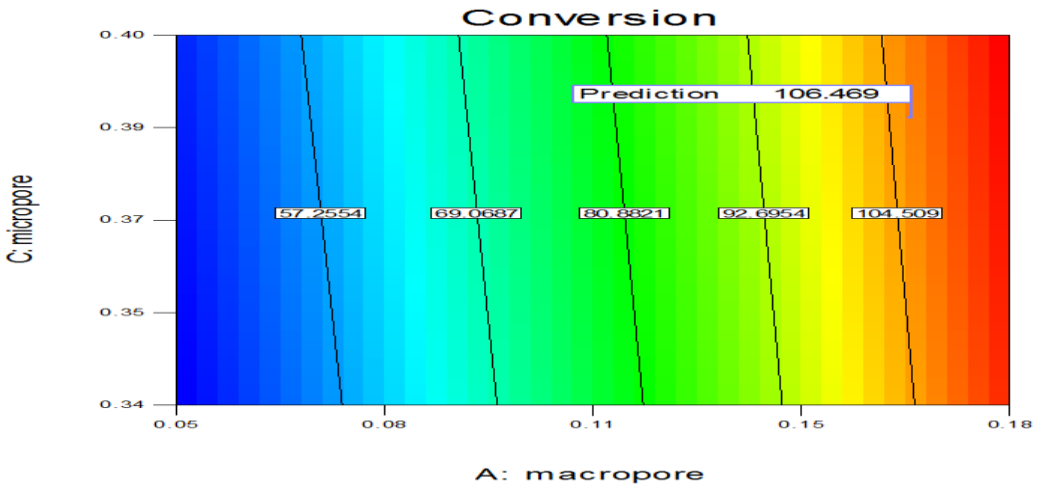

Figure 8. The optimization results of macroporous and microporous.

4. Conclusions

The effect of pore distribution in the catalyst on the conversion rate can be simulated by the equation Y = 5.55207+380.07101×A +50×B +50×C +617.75148×A2. According to the optimization of the equation, the optimal pore distribution is that the volume ratios of macroporous, mesoporous and microporous are 0.16 ml/g, 0.06 ml/g, and 0.36 ml/g respectively. According to the formula calculation, the conversion rate can reach to 103.17%.

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