Study on surface reaction kinetics of SO\textsubscript{2} temperature programmed on sulphur tail gas hydrogenation catalyst

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Abstract. This study is aimed to investigate the reaction energy of hydrodesulphurization catalyst for SO\textsubscript{2} to H\textsubscript{2}S and the desorption energy of H\textsubscript{2}S. We use polymath software to fit the experiment data. The result of the fitting shows that the reaction energy is about 96 kJ/mol. In addition, a series of experiments with different heating rate was carried out to get the desorption energy of H\textsubscript{2}S on the catalyst. The obtained value is about 169.85 kJ/mol.

1. Introduction

Stricter environmental regulations on the sulphur emission standards place greater demands on the desulphurization of sulphur-containing tail gas. In China, according to the regulations of the environmental protection department in 2015, SO\textsubscript{2} emissions for general areas should not exceed 50 mg/m\textsuperscript{3}. Most industrial hydrodesulphurization catalysts are alumina-supported CoMo and NiMo metal sulphides [1]. It is believed that the sulphur vacancies at the edges of the MoS\textsubscript{2} crystallites are very important for catalytic activity [2, 3] and that the catalytic properties of these sites are strongly enhanced by the close presence of a promoter atom (Co or Ni) in the so-called Co(Ni)-Mo-S structures [4, 5].

Sulphur hydrogenation for sulphur tail gas is a strong exothermic reaction with reduced number of molecules. Both higher pressure and lower temperature are beneficial to the conversion of sulphide to H\textsubscript{2}S, which is recovered and treated, such as SO\textsubscript{2} hydrogenation reaction:

\[ \text{SO}_2 + 3\text{H}_2 = \text{H}_2\text{S} + 2\text{H}_2\text{O} \Delta H_{298K} = -207.436 \text{ kJ/mol} \] (1)

Lower operating temperature leads to the better reaction performance of the catalyst. The operating temperature of commercial catalysts such as C-234 and C-537 developed by Shell are generally between 250°C and 270°C. In this paper, commercial catalyst named LS-03A was studied, with the operating temperature of about 220°C. The reaction kinetic parameters and equations were studied by temperature-programmed surface reaction.

2. Methods

H\textsubscript{2}/Ar is a self-mixing gas and it contains 10.24 % of H\textsubscript{2}. The purity of SO\textsubscript{2} raw material gas used in the experiment was 99.99 %, produced by Dalian Date Gas Co., Ltd. The product gas was detected by Pfeiffer Prisma Plus QMG 220 quadrupole mass spectrometer from Pfeiffer, Germany. The
commercial catalyst (LS-03A) used in the experiment was provided by Qilu Petrochemical Research Institute. The kinetic parameters and equations were fitted using the L-M nonlinear regression of Polymath 6.1.

The SO₂ temperature programmed surface reaction (SO₂-TPSR) was carried out with the in-situ pretreating LS-03A using a mixture of SO₂ and H₂/Ar gases at different flow rates. The loading of catalyst was 0.050 g, reaction temperature was raised from 40°C to 500°C with a heating rate of 20 °C/min.

The H₂S temperature programmed desorption (H₂S-TPD) was carried out with a high heating rate. H₂S was adsorbed on the catalyst at 25°C. And then the catalyst was heated to 500°C to desorb the adsorbed H₂S.

3. Results

It can be seen from the Figure 1 that the hydrogeneration reaction of SO₂ has already been observed at less than 200°C. From 200°C to 320°C, the signals of H₂ and SO₂ decrease continuously, indicating that the hydrogeneration reaction rate of SO₂ on the catalyst increases continuously. These parameters were fitted by Polymath in the range of 230-290°C according to the Arrhenius formula:

\[
\frac{dp_{SO_2}}{dt} = Ae^{\frac{E_a}{RT}}p_{SO_2}^m p_{H_2}^n
\]

The results of fitting are shown in Table 1.

| Variable | A   | m    | n    | E_a (J/mol) |
|----------|-----|------|------|-------------|
| Value    | 1.69E+11 | 1.33 | 1.25 | 9.60E+04    |
| 95% confidence | 4.78E+09 | 0.14 | 0.023 | 1216.91     |

Regression correlation coefficient \( R^2 = 0.991 \). The reaction energy is about 96 kJ/mol. The regression kinetic equation is as follows:

\[
r = 1.69 \times 10^{11} \times e^{\frac{96000}{RT}}p_{H_2}^{1.33}p_{SO_2}^{1.25}
\]
Figure 2 shows H$_2$S desorption signal for the catalyst. It can be seen that there are two major peaks at around 125°C and 350°C. The peak at low temperature is desorption due to physical and weak desorption of H$_2$S on the catalyst. The desorption energy was calculated according to the formula:

$$2\lg T_m - \lg \beta = \frac{E_d}{2.303 R T_m} + \lg \left( \frac{E_d}{v R n g_h^2} - 1 \right)$$

We can draw a straight line about $2\lg T_m - \lg \beta$ to $1/T_m$, and $E_d$ can be calculated from the slope of this line (Fig. 3). The fitting results are shown in Table 2. So the desorption energy of H$_2$S by fitting is 169.85 kJ/mol.

![Figure 2. H$_2$S response signal of H$_2$S-TPD in different heating rate.](image1)

![Figure 3. Fitting results of desorption energy of H$_2$S.](image2)
Table 2. Fitting parameters of desorption energy of H$_2$S.

| Fitting results | Intercept | Slope | Statistics |
|-----------------|-----------|-------|------------|
| Value           | Standard error | Value | Standard error | R-square |
| $2\lg T_m - \lg \beta$ | -8.384 | 8923.503 | 1085.307 | 0.957 |

4. Conclusion

We investigated the reaction energy of hydrodesulphurization catalyst for SO$_2$ to H$_2$S and the desorption energy of H$_2$S. We used polymath software to fit the experiment data. The result of the fitting shows that the reaction energy is about 96 kJ/mol. In addition, a series of experiments with different heating rates was carried out to get the desorption energy of H$_2$S on the catalyst. The obtained value is about 169.85 kJ/mol.

Acknowledgements

I would like to acknowledge everybody who has contributed to the results of this paper, in particular my tutors Changchun Yu, Ranjia Li, Xiaosheng Wang and my girlfriend Liya Zhang who gives me a lot of help. I also want to acknowledge Anna Zapotoczna and other staff member of the ASRTU forum.

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