Kinetic Modelling of the Hydrolysis of COS Catalyzed by Titania Based CT6-8

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Abstract. The carbonyl sulfide (COS) hydrolys is kinetic over titania based sulfur recovery catalyst CT6-8 was studied. Kinetic data were obtained by orthogonal experimental design under the conditions of 280-350 ^{o}C, contact time 3.5×10^{-6}-10^{-5} h, COS concentration 0.1-1%, H_2O concentration 5-30%, H_2S concentration 2-5%, SO_2 concentration 1-2.5%, without both internal and external diffusion limitation. The relationship between the reaction rate and the experimental conditions was fitted by power function model and the COS hydrolysis reaction kinetic equation was obtained as $-r_{COS} = 1.77\times10^7 e^{-65100/RT} P_{H_2S}^{-0.11} P_{SO_2}^{-0.67} P_{COS}^{0.96} P_{H_2O}^{-0.17}$.

1. Introduction

The Claus process works well for gas streams containing greater than 20% H_2S and less than 5% hydrocarbons in the world. The first stage of the Claus process is the thermal oxidation of 1/3 of the initial H_2S concentration at high temperature condition. The formation of COS and CS_2 is inevitable for the present of hydrocarbon in the combustion step. The efficient hydrolysis of COS and CS_2 is helpful to achieve the high levels of sulfur recovery rate. In the first reactor, the conversion of COS and CS_2 is limited to 75% for COS and 50% for CS_2 by alumina catalyst while titania-based catalysts, such as CRS-31 & CT6-8, are regarded as a more efficient way for COS and CS_2 hydrolysis [1].

CS_2 and COS are two problem compounds that often appear together in the first Claus converter. The kinetic of CS_2 and COS hydrolysis have been studied in numerous research papers [2-5]. Tong studied the hydrolysis of CS_2 and COS for a titania catalyst and found that the hydrolysis of CS_2 can be best described by an Eley-Rideal model over the ranges of temperature from 270 to 330°C. In this study, the feed gas contains only CS_2 or COS, H_2O and N_2[6,7]. In the first Claus converter, H_2S and SO_2 with high concentration, can strongly influence the hydrolysis of CS_2 or COS. We have reported the hydrolysis of CS_2 in the presents of H_2S and SO_2, and got great different results compared with the previous reports [8].

In this research, the kinetic measurements for the hydrolysis of COS using titania-based CT6-8 catalyst was obtained under controlled condition using a continuous flow fixed bed reactor. The

reaction temperature varied from 280 to 350°C. The feed gas contains COS, H_2O, H_2S, SO_2 and N_2 to simulate the gases encountered within the first Claus converter.

2. Experimental section

2.1. Catalyst
CT6-8 catalyst was produced by Research Institute of Natural Gas Technology, Petro China Southwest Oil and Gas Field Company.

2.2. Experimental apparatus
A fixed-bed reactor used for this study was constructed with a stainless steel tube 12 mm ID and 300 mm in length. The concentration of water in the feed was controlled by a microscale water pump. The flow rates of H_2S, SO_2, COS and N_2 were controlled by mass flow controller. In each experiment, 0.20 g catalyst was in use. The inlet and outlet gas were measured by Agilent 7890 gas chromatograph with thermal conductivity cell detector. The conversion rate of COS was calculated as Equation (1):

$$\eta_{COS}=(1-Kv\times\varphi/\varphi_0)\times100\% \tag{1}$$

Where φ_0 = COS concentration without water in the inlet gas, φ = COS concentration without water in the outlet gas, Kv = volume adjusting factor [4], calculated as Equation (2) [8]:

$$Kv = [100 - (\varphi_{H_2S} + \varphi_{SO_2})]\big/[100 - (\varphi'_{H_2S} + \varphi'_{SO_2})] \tag{2}$$

3. Results and discussion

3.1. Blank test
Prior to the measurement of the reaction test, blank runs using an empty reactor or reactor filled with ceramic balls showed no detectable conversion of COS.

### 3.2. The effect of internal and external diffusion
For the purpose of kinetic study, it is important to ensure that the rate data obtained are under the kinetic regime.

To eliminate the external diffusion effect, two group COS conversion rate test (with catalyst loading amount of 0.20 g and 0.25 g) were carried out. As shown in Figure 1, when the contact time is less than 1×10^{-5} h, the COS conversion rate is almost the same. This shows that the conversion rate is uncorrelated with the gas flow rate. Then, it can be supposed that the external diffusion effect has been eliminated.
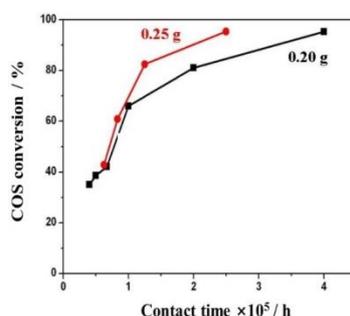
Figure 1. Variation of the COS conversion rate with the contact time (reaction condition: 5.5% H_2S, 2.5% SO_2, 1% COS, 30% H_2O, N_2 as balance gas, the reaction temperature was 350°C and the size of the catalyst was 30-40 mesh)

The catalysts were crushed to different size to test the effect of particle size on internal diffusion effect. As shown in Figure 2, when the catalyst size was smaller than 0.6mm (30-40mesh), the COS conversion rate remain unchanged with different size, which showed that the reaction was free of internal diffusion with particles size.
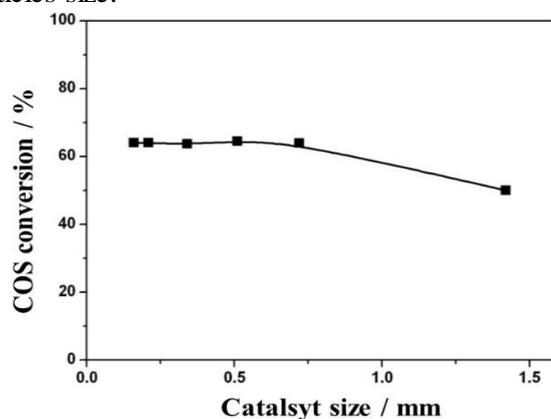
Figure 2. Variation of the COS conversion rate with the catalyst size (reaction condition: 5.5% H_2S, 2.5% SO_2, 1% COS, 30% H_2O, N_2 as balance gas, the reaction temperature was 350°C and GHSV was 10,000h^{-1})

3.3. Kinetic data results

Orthogonal table ($L_{16}(4^5)$) was applied to arrange the experiments with the aim to reduce the experimental trials. Considered the actual situation in the first Claus converter, the reaction conditions were selected as follows: temperature range 280-350°C, COS concentration 0.1-1%, H_2O concentration 5-30%, H_2S concentration 2-5% and SO_2 concentration 1-2.5%.

Kinetic data were collected after the reaction system reached a stable condition. Parallel samples were taken at least 3 times for each experimental point. H_2S, SO_2 and COS partial pressure were calculated according to the results of chromatographic data, atmospheric pressure and internal pressure of the kinetic experiment apparatus. The partial pressure of H_2O was calculated by the flow rate of micro-metering pump and the total pressure. The kinetic data were shown in Table 1.

Table 1. COS kinetic data

T/°C	H_2O /kPa	H_2S /kPa	SO_2 /kPa	COS /kPa	$-r_{exp}$ /mol/h.L
350	13.30	2.28	2.19	0.12	5.20
350	4.75	2.00	2.59	0.70	21.99
350	28.50	5.13	1.33	0.52	20.00
350	19.95	6.27	2.15	0.12	3.62
320	19.95	3.42	1.26	1.21	21.93
320	28.50	2.95	2.38	0.93	11.03
320	4.75	4.66	2.47	0.41	8.22
320	13.30	4.56	2.38	0.11	1.16
300	4.75	4.18	1.43	1.02	11.11
300	13.30	4.94	1.52	0.76	8.10
300	19.95	2.66	3.23	0.47	1.35
300	28.50	4.18	2.57	0.13	0.75
280	28.50	6.56	3.33	1.28	4.10
280	4.75	4.75	2.38	0.81	5.85
280	13.30	3.33	1.52	0.48	2.21
280	4.75	2.00	1.24	0.11	0.51

3.4. Kinetic model and parameter analysis

In this study, we selected power function model as shown in Equation (3) due to the complexity of the experimental conditions, easier data processing and parameter estimation.

$$-r_{COS} = k_1 e^{-E_1/RT} P_{H_2S}^a P_{SO_2}^b P_{COS}^c P_{H_2O}^d \tag{3}$$

The proposed model for the hydrolysis of COS is a non-linear functions of the parameters. Microsoft excel was used to search for best values of the model parameters. The best fitting values of the parameters were shown in Table 2. The value of k_1 and E were all greater than zero, which compliance with the physics-chemistry rule.

Table 2. Best fitting values of the parameters in Equation (3)

Parameters	Values
k1	1.77×107
E / kJ/mol	65.1
a	-0.11
b	-0.67
c	0.96
d	-0.17

The reaction series of COS is 0.96, which is close to 1, indicating that the reaction order of COS is 1. The reaction order of H_2S, SO_2 and H_2O were -0.11, -0.67 and -0.17, indicating H_2S, SO_2 and H_2O inhibit the reaction of COS due to the competitive adsorption with COS on surface active position. Because of the strongest adsorption capacity of SO_2, the greater hindrance of SO_2 to the hydrolysis of COS.

The reaction rate comparison of the experimental value (-r_{exp}, as shown in Table 1) and the calculated value (-r_{cal}, calculated by Equation (3) and the values in Table 2) was shown in Figure 3. The points evenly distributed on both sides of the diagonal, indicating that the deviation between the calculated values and the experimental values is smaller to meet kinetic experiments requirement.
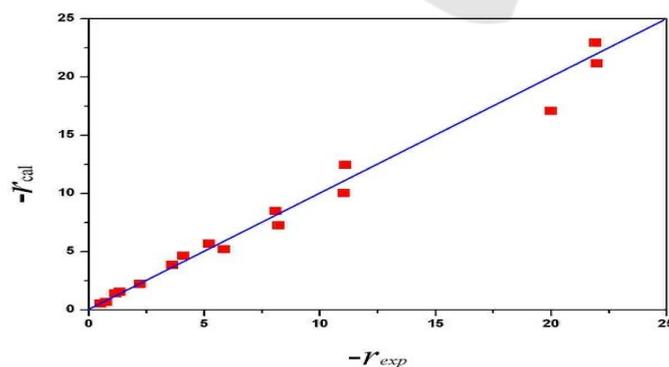
Figure 3. The reaction rate comparison of the experimental value and the calculated value

4. Conclusions

COS hydrolysis kinetic have been studied in the simulated first Claus converter condition and the kinetic equation has been obtained as:

$$-r_{COS} = 1.77 \times 10^7 e^{-65100/RT} P_{H_2S}^{-0.11} P_{SO_2}^{-0.67} P_{COS}^{0.96} P_{H_2O}^{-0.17} . \tag{4}$$

This study lays the foundation for optimization of the Claus reactor design and titania-based catalysts improvements.

Acknowledgments

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