Mechanism explanation for SO_2 oxidation rate of Cs-Rb-V series sulfuric acid catalyst at low temperature[①]

CHEN Zhen-xing(陈振兴), YE Hua(叶　华), LIU Jin(刘　今), LI Hong-gui(李洪桂)

(Institute of Chemistry and Chemical Engineering, Central South University,

Changsha 410083, P. R. China)

[**Abstract**] The reaction kinetics of SO_2 oxidation on Cs-Rb-V series sulfuric acid catalyst promoted by alkali salts such as cesium and rubidium was studied. A three-step reaction mechanism of SO_2 oxidation was proposed, in which it was assumed that oxidation of quadrivalent vanadium complex was a controlling step. Then, a mechanism model equation was concluded according to the three-step reaction mechanism. The SO_2 oxidation rate was measured with a non-gradient reactor under the conditions of temperature of 380~ 520 ℃ and space velocity of 3 600~ 7 200 h^{-1}. Through calculating with Powell nonlinear regression method, the parameters of model equation were obtained: $K_1 = 0. 152 \exp(- 62 073/(RT))$, $K_2 = 8. 18 \exp(- 2 384/(RT))$, $K_3 = 0. 221 \exp(- 18 949/(RT))$. It was found that the model equation could fit with all the experimental reaction rate data very well.

[**Key words**] reaction mechanism; low temperature catalyst; sulfur dioxide; sulfuric acid

[**CLC number**] O 643. 36　　　　　　　　　　　　　[**Document code**] A

1 INTRODUCTION

Cs-Rb-V series catalyst is a newly developed sulfuric acid catalyst used under low temperature. Its initial combustion temperature is 30 ~ 50 ℃ lower than common sulfuric acid catalyst, that is to say that its initial combustion temperature could be reduced to about 370 ℃ and its normal operation temperature is 380~ 520 ℃. Furthermore, its preparation process is simple and its preparation cost is cheaper compared with other cesium-containing low temperature catalyst[1, 2]. In order to produce sulfuric acid with low concentration or high concentration metallurgical fume and increase total conversion, we should study the reaction mechanism and reaction kinetics of SO_2 oxidation on Cs-Rb-V catalyst, by which we could provide basis for the design of industrial reactors.

2 MECHANISM MODEL

Many researchers had done a lot of investigation about the SO_2 oxidation over vanadium catalysts used in sulfuric acid industry. However, there still exist many problems about the reaction mechanism and so far most of kinetic equations are empirical models. Since last several years, a great progress had been made in physical-chemistry properties of fusing salt systems, which were made up of divanadium pentoxide and alkali metal salts[1~ 6]. Especially, we have recently done a lot of basical research work around Cs-Rb-V series low temperature catalyst[1, 2]. Com-bining the results about the physical-chemistry properties of fusing salt systems, physical phases and catalytic reaction kinetic behaviors over Cs-Rb-V catalysts[1, 2] with many former investigation[3~ 13], it could be concluded that the oxidizing reaction of SO_2 over Cs-Rb-V catalyst at 380~ 520 ℃ is a three-step catalytic reaction. During the process of catalytic reaction, SO_2 dissolves into fusing salts, then combines with complex X made up of pentavalent vanadium and becomes X•SO_2. After being internally oxidized, X•SO_2 gradually becomes Y•SO_3. Then, Y•SO_3 releases SO_3 and produces chemical compound Z (quadrivalent vanadium). Z is oxidized by oxygen dissolved in fusing salts, then becomes chemical compound X (pentavalent vanadium) and SO_3 is released from fusing salts. As molar ratio of alkali metal and vanadium in the Cs-Rb-V catalyst is in the range of 3~ 5, X is mainly composed of pentavalent vanadium complex $(VO_2SO_4)_2S_2O_7^{4-}$, and Z is mainly composed of quadrivalent vanadium complex $(VOSO_4)_2(SO_4)_2^{4-}$. Three-step reaction mechanism is as:

$$X+ SO_2 \rightleftharpoons Y•SO_3 \tag{1}$$

$$Y•SO_3 \rightleftharpoons Z+ SO_3 \tag{2}$$

$$Z+ \frac{1}{2}O_2 \rightleftharpoons X \tag{3}$$

Many experiments[1~ 5] demonstrated that oxidation of quadrivalent vanadium complex was the controlling step, i. e. reaction (3) was the controlling step, whereas reactions (1) and (2) could reach equilibrium quickly. Assuming that $\overrightarrow{k_i}$ stands for positive reaction rate ($i = 1, 2, 3$) of reaction (i), K_{Pi}

stands for the equilibrium constant of reaction (i), c_j stands for the concentration of component j (j = X, Y·SO_3, Z, SO_2, SO_3, O_2), then the SO_2 oxidation rate over Cs-Rb-V catalyst could be expressed by

$$r = \overrightarrow{k_3}[c(Z) c^{1/2}(O_2) - c(X)/K_{P3}] \quad (4)$$

where $K_{P1} = \dfrac{c(Y \cdot SO_3)}{c(X) c(SO_2)}$, $K_{P2} = \dfrac{c(Z) c(SO_3)}{c(Y \cdot SO_3)}$,

$K_{P3} = \dfrac{c(X)}{c(Z) c^{1/2}(O_2)}$; besides, the total quantity of vanadium in fusing salts is as: $c_t = c(X) + c(Y \cdot SO_3) + c(Z)$. Put above relationships into formula (4), following formula is attained:

$$r = \dfrac{\overrightarrow{k_3}K_{P1}K_{P2}c_t c^{1/2}(O_2)\left[1 - \dfrac{c(SO_3)}{K_{P1}K_{P2}K_{P3}c(SO_2) c^{1/2}(O_2)}\right]}{\dfrac{K_{P1}K_{P2}}{K_{P3}} + K_{P1}c(SO_3) + \dfrac{c(SO_3)}{c(SO_2)}} \quad (5)$$

The dissolution of SO_2 and O_2 in active fusing salts is much faster than its reaction, gas phase and liquid phase may reach quasi-equilibrium under the reaction conditions[7]. Thus, given that SO_2, O_2 and SO_3 in the solution and gas phase reaches gas-liquid equilibrium respectively, and meet Henry's rule, i.e. $c(SO_2) = H(SO_2) p(SO_2)$, $c(SO_3) = H(SO_3) p(SO_3)$, $c(O_2) = H(O_2) p(O_2)$. Here, H_j is the dissolvability coefficient of component j. p_j is the partial pressure of component j in gas phase, which reaches equilibrium. Put above relationships into formula (5), mechanism model equation of three-step catalytic reaction can be obtained:

$$r = \dfrac{K_1 p^{1/2}(O_2)}{K_2 + K_3 p(SO_3) + \dfrac{p(SO_3)}{p(SO_2)}} \cdot$$
$$\left(1 - \dfrac{p(SO_3)}{p(SO_2) p^{1/2}(O_2) K_P}\right) \quad (6)$$

where $K_1 = \overrightarrow{k_3}K_{P1}K_{P2}c_t H^{1/2} \cdot (O_2) \dfrac{H(SO_2)}{H(SO_3)}$, $K_2 = \dfrac{K_{P1}K_{P2}H(SO_2)}{H(SO_3)}$, $K_3 = K_{P1} \cdot H(SO_2)$. K_β could be represented with $K_\beta = k_\beta \exp(-E_\beta/RT)$ ($\beta = 1, 2, 3$), where T is the reaction temperature, K_P is the total equilibrium constant of SO_2 oxidation reaction and it can be calculated by

$$K_P = \exp[2.3026(48\ 123/T - 2.825\ 4gT) +$$
$$2.284 \times 10^{-3}T - 7.012 \times 10^{-7}T^2 +$$
$$1.197 \times 10^{-10}T^3 + 2.23] \quad (7)$$

3　EXPERIMENTAL

The experimental apparatus are shown in Fig. 1. CD-2 type internal-circle non-gradient reactor, which could reach 2 800 r/min, was adopted during the experiment. The experimental condition was chosen by orthogonal design method and the condition factors are shown in Table 1, where d_0 and m represent the average article size and mass of catalyst respectively,

$y(SO_2)$ and $y(O_2)$ represent the mole fraction of SO_2 and O_2 respectively, T is the reaction temperature, ζ represents space velocity. Concentrations of SO_2 and O_2 were divided into two levels as well as space velocity, and the reaction temperature was divided into seven levels. By means of test and analysis, it was found that the influence of internal and external diffusion was so little under experimental conditions that it could be ignored.
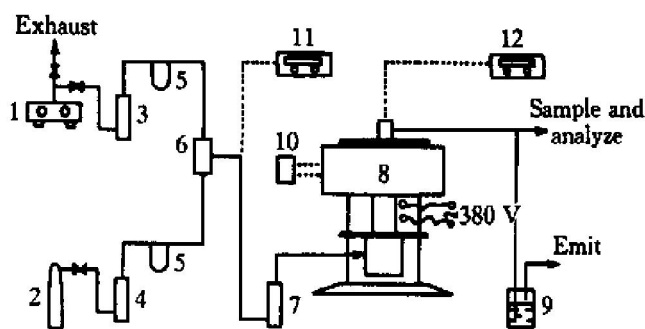

Fig. 1　Experiment apparatus
1 —Air compressor; 2 —SO_2 steel cylinder;
3 —Drying bottle of silica gel and concentrated sulfuric acid;
4 —Drying bottle of concentrated sulfuric acid and molecular sieve; 5 —Capillary flow meter; 6 —Gas mixer; 7 —Drying bottle of phosphorus pentoxide; 8 —Internal-circle non-gradient reactor; 9 —Lye absorption bottle;
10 —Temperature controller; 11 —CM type oxygen indicator;
12 —U J36 type direct current potential difference meter

Table 1　Experimental conditions

d_0 /mm	m/g	$y(SO_2)$ /%	$y(O_2)$ /%	t/℃	ζ/h^{-1}
0.5	1.125	8~13	7~18	380~520	3 600~7 200

Stuff gas was a mixture of SO_2 and air. Air was dried first by silica gel and then by concentrated sulfuric acid. SO_2 was dried first by concentrated sulfuric acid and then by molecular sieve. After being deeply dried by particulate phosphorus pentoxide, mixed gas was put into CD-2 type non-gradient reactor. Reaction temperature was controlled by TDW type temperature-controlling instrument and measured by U J36 potential meter. Concentration of SO_2 at reactor inlet and outlet was analyzed by iodimetric analysis. Partial pressure of O_2 was measured by CM type oxygen-measuring instrument. All of the related experimental data are shown in Table 2 in which $x(SO_2)$ and r represent the conversion and reaction rate of SO_2 respectively.

4　DATA TREATMENT AND RESULT ANALYSIS

To compare with three-step catalytic reaction mechanism model, we chose typical equations, such as Balzhinimaev equation[9], Mars and Maessen equation[4], Boreskov equation[7], as competitive models.

Then, we selected residual quadratic sum as objective

Table 2 Kinetic experimental data

t /℃	ζ /h^{-1}	$p(SO_2)$ /kPa	$p(O_2)$ /kPa	$p(SO_3)$ /kPa	$x(SO_2)$ /%	$r/(10^6 \cdot mol \cdot g^{-1} \cdot s^{-1})$
380	3 664	10. 65	17. 62	1. 74	14. 1	1. 34
380	7 312	8. 77	18. 50	0. 94	9. 7	1. 45
380	7 504	11. 30	9. 20	0. 74	6. 2	1. 17
380	3 930	12. 29	9. 33	1. 04	7. 8	0. 85
380	3 795	8. 87	10. 11	2. 69	23. 3	2. 12
380	7 472	9. 66	10. 27	1. 09	10. 1	1. 70
380	7 427	8. 33	18. 02	1. 88	18. 4	2. 93
380	3 981	10. 41	16. 14	4. 27	29. 1	3. 52
420	3 926	7. 42	14. 79	7. 54	50. 4	6. 03
420	7 270	5. 10	17. 33	4. 14	44. 8	6. 23
420	7 565	9. 52	9. 26	3. 33	25. 9	5. 24
420	3 776	5. 95	8. 32	5. 30	47. 1	4. 12
450	3 776	4. 24	7. 33	7. 50	63. 9	5. 77
450	7 584	8. 57	8. 64	4. 73	35. 6	7. 40
450	7 267	3. 72	16. 77	5. 54	59. 8	8. 28
450	3 587	3. 25	15. 84	7. 24	69. 0	5. 30
470	3 901	3. 06	8. 02	7. 26	70. 3	5. 77
470	7 280	6. 58	9. 32	2. 72	29. 2	4. 12
470	7 658	6. 43	15. 92	6. 02	48. 3	9. 45
470	3 862	2. 54	16. 28	6. 77	72. 7	5. 34
490	3 574	2. 23	15. 89	7. 52	77. 2	5. 47
490	7 443	4. 73	15. 76	6. 87	59. 2	10. 46
490	7 456	4. 96	12. 03	6. 84	58. 0	10. 42
490	3 926	2. 65	9. 77	7. 92	74. 9	6. 32
505	3 840	2. 94	15. 62	7. 72	72. 4	6. 03
505	7 360	4. 32	16. 12	6. 41	59. 8	9. 67
505	3 914	6. 53	5. 78	6. 95	51. 5	5. 55
505	7 360	6. 06	6. 91	4. 38	42. 0	6. 66
520	3 862	2. 48	16. 25	6. 83	73. 3	5. 39
520	7 459	4. 46	16. 55	5. 65	55. 9	8. 67
520	7 475	6. 58	7. 32	5. 32	44. 7	8. 19
520	4 195	3. 85	8. 43	6. 57	63. 0	5. 64

function S:

$$S = \sum_{\mu=1}^{N}\left(\frac{r_\mu - r_{c,\ \mu}}{r_\mu}\right)^2 \qquad (8)$$

where r_μ is the experimental rate of μth experimental point, $r_{c,\ \mu}$ is the calculated rate of μth experiential point according to reaction mechanism model, N is the sum of experimental points. Adopt Powell nonlinear optimization method to fit the experimental rate data. The residual quadratic sums S and standard deviation σ of different kinetic models are shown in Table 3. It may be concluded that three-step reaction mechanism model best fits the experimental rate data, and its residual quadratic sums S and standard deviation σ are 0. 181 and 0. 242 respectively.

The model parameters value calculating from the three-step reaction model are $k_1 = 0. 152$, $E_1 =$

62 073; $k_2 = 8. 18$, $E_2 = 2 384$, $k_3 = -0. 221$, $E_3 = -18 949$.

Table 3 Residual quadratic sum and standard deviation

Model equation	S	σ
Three-step catalytic model	1. 81	0. 242
Balzhinimaev equation	2. 82	0. 302
Mars-Maessen equation	3. 61	0. 341
Boreskov equation	4. 89	0. 397

Therefore, kinetic model equations are obtained:

$$r = \frac{0. 152 \exp(-62 073/RT)p^{1/2}(O_2)}{8. 18 \exp(-2 384/RT) -} \cdot$$
$$\frac{0. 152 \exp(-62 073/RT)p^{1/2}(O_2)}{0. 221 \exp(18 949/RT)p(SO_3) + \dfrac{p(SO_3)}{p(SO_2)}} \cdot$$
$$\left(1 - \frac{p(SO_3)}{p(SO_2)p^{1/2}(O_2)K_P}\right) \qquad (9)$$

Adopt variance analysis to analyze the effect of which three-step reaction mechanism model fits the experimental data. Assuming that, O_1 is the residual quadratic sum, Q_2 is the regression quadratic sum, Q_3 is the total quadratic sum, F is the statistical quantity, then $Q_1 = \sum_{\mu=1}^{N}(r_\mu,\ r_{c,\ \mu})^2$, $Q_2 = \sum_{\mu=1}^{N}(r_{c,\ \mu},\ \overline{r})^2$, $Q_3 = \sum_{\mu=1}^{N}(r_{c,\ \mu},\ \overline{r})^2$, $F = \frac{Q_2/M}{Q_1/(N-M-1)} \sim F_a(M,\ N-M-1)$. Among them, $\overline{r}$ is the experimental average value of reaction rate, N is the sum of experimental points; M is the sum of unknown parameters in model equation, α is the confidence level. The results of variance analysis are shown in Table 4. Because $F > F_{0.01}$, it could be concluded that three-step reaction model equation fits the experimental data very well under significance level of 0. 01.

Table 4 Variance analysis

$Q/10^{14}$	Degree of freedom	Mean square error	F	$F_{0.01}$
$Q_1 = 2. 041$	6	34. 02		
$Q_2 = 0. 712$	25	2. 85	11. 9	3. 63
$Q_3 = 2. 251$	31	7. 26		

5　CONCLUSIONS

1) The oxidation of SO_2 on Cs-Rb-V series low temperature catalyst is a three-step reaction. The mechanism model equation is

$$r = \frac{K_1 p^{1/2}(O_2)}{K_2 + K_3 p(SO_3) + \dfrac{p(SO_3)}{p(SO_2)}} \cdot$$

$$\left(1- \frac{p(SO_3)}{p(SO_2)\, p^{1/2}(O_2)\, K_P}\right)$$

2) The rate data of SO_2 oxidation on Cs-Rb-V series catalyst at $380 \sim 520\,°C$ have been measured with a non-gradient reactor, experiment data fit with Powell nonlinear regression method and a kinetic model equations is obtained:

$$r = \frac{0.152\exp(-62\,073/RT)\, p^{1/2}(O_2)}{8.18\exp(-2\,384/RT)-} \cdot$$

$$\frac{0.152\exp(-62\,073/RT)\, p^{1/2}(O_2)}{0.221\exp(18\,949/RT)\, p(SO_3)+ \frac{p(SO_3)}{p(SO_2)}} \cdot$$

$$\left(1- \frac{p(SO_3)}{p(SO_2)\, p^{1/2}(O_2)\, K_P}\right)$$

3) Variance analysis shows that three-step reaction mechanism model fits the experimental rate data very well and it could be used to design industrial reactors.

[REFERENCES]

[1]   YE Hua. Preparation of low temperature vanadium catalyst used for sulfur dioxide oxidation [D], (in Chinese). Changsha: Central South University of Technology, 1999.

[2]   CHEN Zhen-xing, YE Hua, FANG Zhong-he, et al. Preparation of Cs-Rb-V series sulfuric acid catalyst used under low temperature [J]. Journal of Catalysis, (in Chinese), 2000, 21(4): 384– 386.

[3]   Villandsen J, Livbjerg H. Supported liquid-phase catalysts [J]. Catalyst Review-Science and Engineering, 1979, 17(2): 203– 272.

[4]   Urbanek A. Catalytic oxidation of sulfur dioxide [J]. Catalyst Review-Science and Engineering, 1980, 21(1): 73– 133.

[5]   Eriksen K M, Karydis D A, Boghosian S, et al. Deactivation and compound formation in sulfuric acid catalysts and model systems [J]. Journal of Catalysis, 1995, 155(1): 32– 42.

[6]   Boghosian S, Fehramann R, Bjerrum N J, et al. Formation of crystalline compounds and catalyst deactivation during SO_2 oxidation in V_2O_5-$M_2S_2O_7$(M = Na, K, Cs) melts [J]. Journal of Catalysis, 1989, 119(1): 121– 134.

[7]   Balzhinimaev B S, Ponomarev V E, Boreskov G K. Studies of adsorption-desorption processes in SO_2 oxidation on the active component of vanadium catalysts [J]. Kinetics and Catalysis, 1985, 28(1): 81– 88.

[8]   Doering F J, Unland M L, Berkel K A. Modeling of SO_2 oxidation rates based on kinetic data of a Cs/V catalyst at high pressures and conversion [J]. Chemical Engineering Science, 1988, 43(2): 221– 226

[9]   Balzhinimaev B S, Ponomarev V E, Belyaeva N P, et al. Steady state kinetic equation for SO_2 oxidation on vanadium catalysts [J]. Reaction Kinetics and Catalysis Letters, 1986, 30(1): 23– 32.

[10]   Adlkofer J, Dieckmann E, Winkler E. Catalysts for high-concentration SO_2 gases [J]. Sulphur, 1993, 229: 50– 52.

[11]   Doering F J, Berkel D A. Comparison of kinetic data for K/V and Cs/V sulfuric acid catalysts [J]. Journal of Catalysis, 1987, 103(1): 126– 139.

[12]   Doering F J, Yuen H K, Berger P A, et al. Investigation of the SO_2 oxidation rate limiting factors for K/V and Cs/V catalysts at low temperature [J]. Journal of Catalysis, 1987, 104(1): 186– 201.

[13]   Folkmann G E, Hatem G, Fehrmann R, et al. Conductivity, thermal analysis, and phase diagram of the system $Cs_2S_2O_7$-V_2O_5 ——Spectroscopic characterization of $Cs_4(VO_2)_2(SO_4)_2S_2O_7$ [J]. Inorganic Chemistry, 1991, 30(21): 4057– 4061.

(Edited by LONG Huai-zhong)