Vol. 11 № 4 **Trans. Nonferrous Met. Soc. China** Aug. 2001

[Article ID] 1003- 6326(2001)04- 0595- 04

Preparation of Cs-Rb-V series sulphuric acid catalyst ①

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[Abstract] Cs-Rb-V series low temperature sulphuric acid catalyst was prepared for the first time by using carbonized mother liquor containing alkali-metal salts. The results show that the conversion of SO_2 on catalyst prepared directly with carbonized mother liquor could reach to 24.8% at 410 ℃. If $n(\mathrm{Na})/n(\mathrm{V})$ was adjusted properly, the conversion of SO_2 could be increased to 35.6% at 410 ℃. Refined carbonized mother liquor could make the catalytic activity even higher at low temperature, the conversion of SO_2 could be increased to 36.65% at 410 ℃. The catalyst was examined with differential thermal analysis. It was found that both endothermic peaks and exothermic peaks of catalyst shifted forward obviously and the catalyst possessed higher activity at low temperature.

[Key words] sulphuric acid catalyst; sulphur dioxide; alkali-metal element; low temperature activity; promoter
[CLC number] O 643.36 **[Document code]** A

1 INTRODUCTION

Low temperature sulphuric acid catalyst is made of active composition (generally vanadium pentoxide), promoter and diatomite. Because of its low ignition temperature, low temperature catalyst can make the temperature of inlet and outlet gas of reactor decrease, reduce the equilibrium concentration of sulphur dioxide in the off-gas and make it possible to use low concentration or high concentration metallurgical fume to produce sulphuric acid. Besides, low temperature catalyst can shorten startup time, decrease capital investment and operating cost in the conversion process. Alkali metals, lanthanide metals, phosphorous pentoxide, boron sesquioxide, manganese dioxide, tungsten trioxide and rare-earth metal have already been used as promoters. It has been found that both Rb and Li have promoter action, but the activity of catalyst containing Cs is much higher than that of others at low temperature[1~7]. In 1988, TOPSΦE company of Denmark developed Cs-catalyst named VK38 as the first time, and then Monsanto Environment Chemistry Company of America and BASF Company of Germany developed Cs-110, Cs-120 and O4-111 type Cs-catalyst continually. Among them, the lowest operational temperature was 360~ 370 ℃ and the heat-resistant temperature reaches 640 ℃. All these catalysts can be used for oxidation of metallurgical fume whose concentration of SO_2 was 16% or higher to directly make sulphuric acid. In 1997, TOPSΦE company prepared another kind of Cs-catalyst named VK69, whose low temperature activity was twice as that of VK38, and as a result the emission concentration of SO_2 in off-gas was no more than 50~ 100 μL/L. Most researchers thought that Cs-salt could depress the melting point of active component (vanadium-alkalipyrosulfate complexes compound), reduce the precipitation of the quadrivalent vanadium, and therefore greatly increase the low temperature activity[7~11]. However, the adding of expensive Cs-salt into catalyst resulted in its price four times higher than common vanadium catalyst. Early in the 1960s, the domestic researchers developed low temperature catalyst named S105, S106 and S107, into which P_2O_5 had been added. Because P_2O_5 was easy to volatilize, the operating life span of catalyst was only three months. Thus, it is necessary to develop a new kind of low temperature catalyst with low price and high-activity.

There exist large amounts of alkali metal salts of Cs, Rb, K and Na in some carbonized mother liquors. Because nearly all the elements are useful and poisonous elements are very little, these carbonized mother liquors may be a good resource for producing low temperature sulphuric acid catalyst with high-activity and low-price.

2 EXPERIMENTAL

2.1 Preparation of Cs-Rb-V series catalyst

The refined diatomite was provided with a sulphuric acid catalyst plant. The main chemical reagents were vanadium pentoxide, sulphuric acid, and alkali metal sulfate or carbonate and sulphur powder, etc. Carbonized mother liquor mainly contained alkali metal carbonate and alkali metal hydroxide. Its composition is shown in Table 1.

The preparation process of Cs-Rb-V series sul-

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① **[Foundation item]** Project (59504005) supported by the National Natural Science Foundation of China
[Received date] 2000- 11- 07; **[Accepted date]** 2000- 12- 29

Table 1 Composition of carbonized mother liquor and its refined liquor g/L

Catalyst	K_2O	Na_2O	Cs_2O	Rb_2O	Li_2O
CML	292	24.2	5.4	21.6	3.7
A	242.4	25.8	4.2	25.6	2.9
B	75.3	10.2	1.6	8.7	–
C	8.0	4.6	3.2	9.6	–

phuric acid catalyst was almost the same as vanadium catalyst[12] (see Fig. 1). To begin with, vanadium pentoxide, sulphur powder, small amount of alkali metal sulfate was mixed proportionally with carbonized mother liquor in a tank. After they had been dissolved sufficiently, sulphuric acid was added into the tank in order to neutralize the liquor. Then, diatomite was added into the tank. After the stuff had been kneaded sufficiently, a ram extruder was adopted for shaping. Through drying, baking and sieving, catalyst sample was finally obtained.

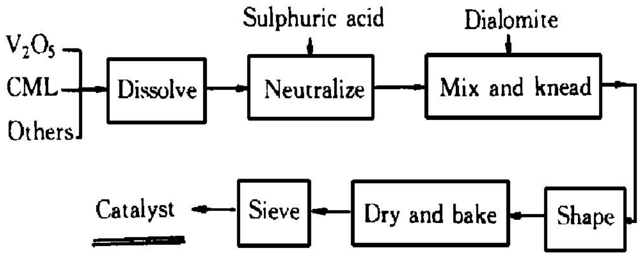

Fig. 1 Preparation of Cs-Rb-V series sulphuric acid catalyst used at low temperature

2.2 Analysis and testing methods

The experimental apparatus used to detect catalytic activity is shown in Fig. 2. The concentration of SO_2 in inlet gas was 10% (molar fraction) and the air speed was $3600\,h^{-1}$. The reactor is a stainless steel integral reactor whose nominal size is 20 mm × 2 mm. The temperature of catalyst bed was controlled by XT101 type silicon-controlled temperature-controller and the reaction temperature was detected through UJ36 type potentiometer. The concentration of SO_2 was analyzed through iodimetry. The partial pressure of oxygen was measured through CM type oxygen indicator which measurement accuracy of 1%. The total contents of alkali carbonate and alkali hydroxide were measured through double indicator titration. The contents of Cs and Rb were tested by PW1401 type maleinoid form X-ray diffraction fluorescent spectrometer. The contents of Li, Na and K were measured by PS-6 type inductively coupled plasma atomic emission spectrometer. DuPont 9900 type thermal analyzer was used to test the differential thermal analysis curve. X-650 type scanning electronic microscope was used to observe the form and structure of diatomite and catalyst.

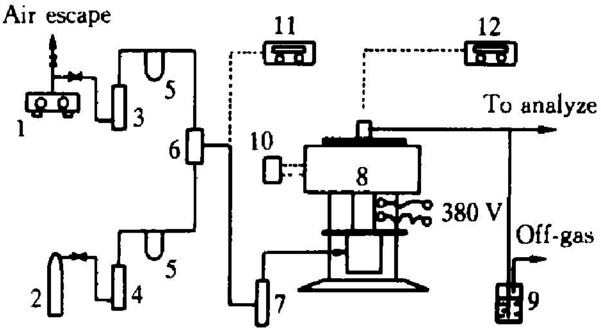

Fig. 2 Experimental installations used for determination of catalytic activity

1 —Air compressor; 2 —SO_2 steel cylinder;
3 —Silica gel drying bottle;
4 —Concentrated sulfuric acid drying bottle;
5 —Flowmeter; 6 —Gas mixer; 7 —Molecular sieve drying bottle;
8 —Integral reactor; 9 —Lye absorption bottle;
10 —Temperature controller; 11 —CM type oxygen indicator;
12 —UJ36 type potentiometer

3 RESULTS AND DISCUSSION

3.1 Preparation of Cs-Rb-V series catalyst with carbonized mother liquor

The preparation process of catalyst could be simplified and the production cost would be reduced if the carbonized mother liquor was added directly into kneading mixture so as to replace K and Na compounds. Therefore the first step was to study the accelerating effect of carbonized mother liquor on catalytic activity. At 410 ℃ and 485 ℃, keep the mass percent of V_2O_5 in the catalyst at 6.5%, the influence of the dosage of mother liquor to catalytic activity is shown in Fig. 3. With increasing $n(K)/n(V)$, the conversion of SO_2 was also increased. As $n(K)/n(V)$ equaled 3.0, the conversions of SO_2 reached a maximum which was 24.8% at 410 ℃ and 78.7% at 485 ℃. With further increase of $n(K)/n(V)$, the conversion of SO_2 began to decrease. Considering that the $n(Na)/n(V)$ in carbonized mother liquor was lower than common vanadium catalysts (shown in Table 2), the content of sodium salt in Cs-Rb-V series catalyst was adjusted through changing the dosage of carbonized mother liquor in order to keep $n(K)/n(V) = 3.0$. Then the relationship between $n(Na)/n(V)$ and conversion of SO_2 was obtained as Fig. 4. With increasing $n(Na)/n(V)$, the catalytic activity increased at first and then decreased. When $n(Na)/n(V)$ equaled 1.5, the catalytic activity reached the maximum. For example, the conversion was 35.6% at 410 ℃ and 85.7% at 485 ℃. All of the conversions were beyond the national standards of low temperature sulphuric acid catalyst S107 and medium temperature catalyst S101.

3.2 Preparation of Cs-Rb-V series catalyst with refined liquor

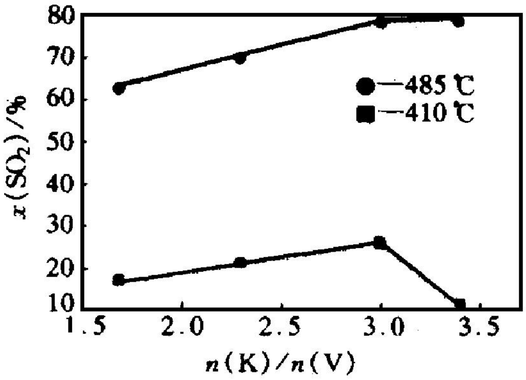

Fig. 3 Effect of dosage of mother liquor on catalytic activity
($w(V_2O_5) = 6.5\%$)

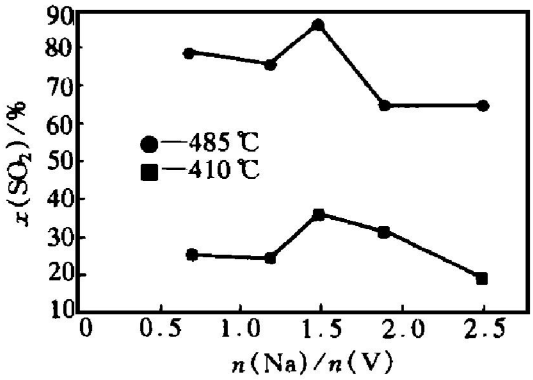

Fig. 4 Effect of $n(Na)/n(V)$ on catalytic activity
($w(V_2O_5) = 6.5\%$, $n(K)/n(V) = 3.0$)

Table 2 $n(Na)/n(V)$ in carbonized mother liquor and common vanadium catalysts

Catalyst	S107	S108	VK38	Lp120	Lp110	CML
$n(Na)/n(V)$	0.67	1.00	0.27	0.26	0.20	0.13

The promoter action of alkali metal elements could be increased with the increase of atomic ordinal number[13]. For example, the promoter action of Cs and Rb was higher than that of K, Na and Li. Thus, if the carbonized mother liquor was properly treated in order to increase the concentration of Cs and Rb and reduce the concentration of K and Li, it could be expected to improve the low temperature catalytic activity. In accordance with the difference of solubility of alkali metal salts in water and organic solvents, different methods were adopted to treat the carbonized mother liquor and then refined liquor A, B and C were obtained. Mixing the refined liquor with sodium compounds to make a mixture, then the mixture was used to prepare catalyst according to $n(K)/n(V) = 3.0$ and $n(Na)/n(V) = 1.5$. The change of catalytic activity is expressed in Fig. 5. The result shows that the catalytic activity made with refined liquor A was superior to B and C both at medium temperature and low temperature. In addition, the refining process of liquor A was very simple and its utilization ratio was relatively high. So refined liquor A was chosen to prepare high activity low temperature catalyst. Compared with the catalysts, in which only $n(Na)/n(V)$ was changed, the conversion of SO_2 on catalyst A at 410 ℃ increased from 35.6% to 36.6%, but at 485 ℃ the conversion decreased from 85.7% to 80.2%. So it was clear that Cs and Rb compound can improve the low temperature catalytic activity and the catalysts containing Cs and Rb compound were suitable for use in the low temperature segment of reactors.

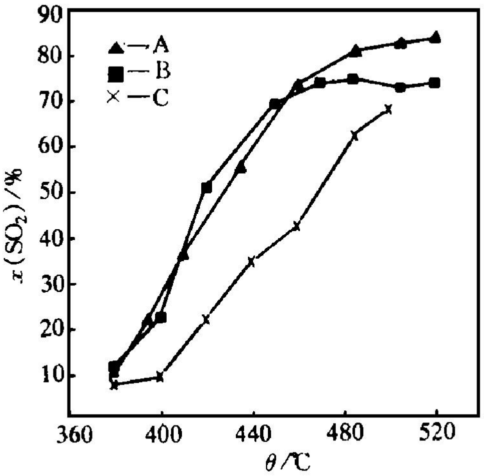

Fig. 5 Effect of refined liquor on catalytic activity
($w(V_2O_5) = 6.5\%$, $n(K)/n(V) = 3.0$, $n(Na)/n(V) = 1.5$)

3.3 Comparison of catalytic activity and differential thermal analysis

The comparison of activity between catalyst A made by refined liquor A and the other low temperature catalysts is shown in Fig. 6. It could be found that the activity of catalyst A was obviously higher than that of domestic catalyst S107, for example, about 8% higher at 380 ℃, 10% higher at 410 ℃. Comparing A with catalyst-LP110, their activities were approximately equal at 410 ℃, but when the temperature was beyond 410 ℃, the activity of cata-

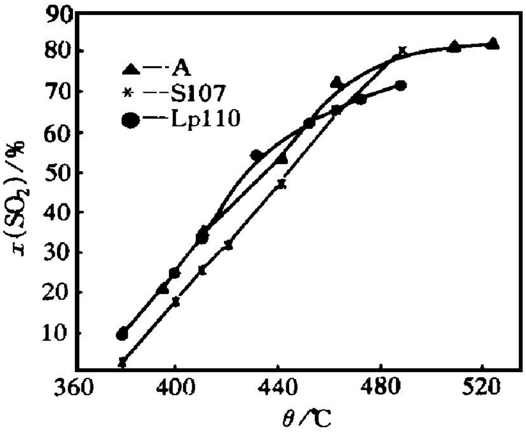

Fig. 6 Activity of several catalysts

lyst A was obviously higher than that of Lp110.

The differential thermal analysis of catalyst A is shown in Fig. 7. It is found that both endothermic peaks and exothermic peaks shift forward obviously. There exist endothermic peaks at 283.38 ℃ and 385.85 ℃, which means that the vanadate has begun to melt and produce fused salt, and there also exist obviously exothermic peaks at 321.9 ℃, 368.44 ℃ and 399.06 ℃, which means that chemical reaction had taken place. The main reason that the number of endothermic peaks and exothermic peaks was far more than one was that there existed multiple promoters in the refined liquor. In accordance with the result of differential thermal analysis, it could be concluded that large amount of Cs and Rb compounds existed in the carbonized mother liquor could reduce the melting point of vanadate, obviously depress the ignition temperature of catalyst and improve the low temperature catalytic activity.

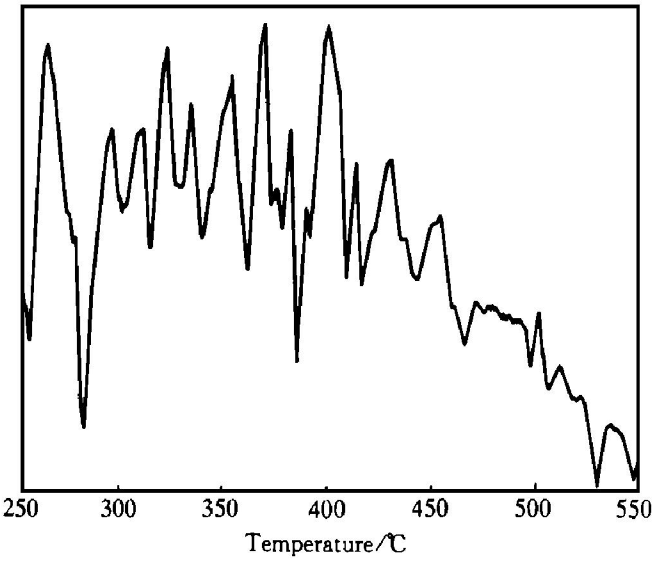

Fig. 7 Differential thermal analyses of catalyst A

4 CONCLUSIONS

1) Carbonized mother liquor was used as catalyst promoter to prepare Cs-Rb-V series catalyst. The low temperature activity of Cs-Rb-V series catalyst is the same as common low temperature catalysts and the conversion of SO_2 at 410 ℃ can reach 24.8%.

2) Through adjusting $n(\mathrm{Na})/n(\mathrm{V})$ of catalyst, the catalytic activity can be improved obviously at low temperature. As $n(\mathrm{Na})/n(\mathrm{V})$ equals 1.5, the conversion of SO_2 at 410 ℃ increases to 35.6%.

3) Refined liquor could improve the catalytic activity at low temperature. For example, the conversion of SO_2 at 410 ℃ increases to 36.6, but the activity at 485 ℃decreases a little.

4) Because of the existence of several kinds of promoters (Cs, Rb, Li, Na, K, etc) in the refined liquor, there exist several endothermic peaks and exothermic peaks in differential thermal analyses chart. The promoters would reduce the molten point of vanadate, depress the ignition temperature of catalyst and improve the catalytic activity at low temperature.

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(Edited by LONG Huai-zhong)