第二卷，第四號　　民國二十五年七月
Vol. II, No. 4.　　July, 1936

國立北平研究院

化學研究所叢刊

CONTRIBUTIONS

from the

INSTITUTE OF CHEMISTRY

NATIONAL ACADEMY OF PEIPING

[illegible]

張漢良
王耀球
——用製硫酐之觸媒研究

Study on the Catalyzers Used in the Manufacture of Sulphuric Anhydride

H. L. Tchang—C. Y. Wang

◆

國立北平研究院總辦事處出版課
Publication Office of the National Academy of Peiping
Peiping, China.

STUDY ON THE CATALYZERS USED IN THE MANUFACTURE OF SULPHURIC ANHYDRIDE

H. L. TCHANG—C. Y. WANG

~~(張漢良)—(王耀球)~~

15-7-1936

This paper is concerned with the use of various metallic oxides and inorganic salts as catalysts in the manufacture of sulphuric anhydride to substitute the most expensive platinum or vanadium oxides and salts. We have already numerous literatures published on this line of work, but our chief object is to find out some catalysts which (1) are expected to be of low cost, (2) will be sufficiently good as substitutes for platinum and vanadium, (3) may be found in China in such quantities that will be available for industrial purpose.

The catalysts are generally applied in conjunction with accelerators and carriers. The catalysts formerly used were platinum sponge(1), iron oxide(2), nickel sulphate(3), etc. Numerous patents have been lately registered on the use of various metallic oxides or salts either by themselves alone or mixed in place of the exceedingly expensive platinum(4). Unfortunately few of them, i.e., oxide of vanadium and vanadium salts, have been proved to be successful(5). Though the latter are also quite expensive things, they are now preferred for their equality in efficiency and lower cost comparing with platinum.

The accelerators are generally metallic oxides or salts, which are employed in conjunction with the catalysts to assist the reaction but in much smaller quantities. Oxides of iron, molybdenum, and tungsten etc. may be used together with oxide of vanadium(6), salts of bismuth, tin, manganese etc. with sulphate of vanadium(7), and the sulphates of iron, thorium, cerium, barium, copper etc. with platinum(8) to increase the efficiency of platinum and vanadium oxides or salts, even they are not good catalysts by themselves.

~~The carriers employed are generally asbestos, sulphate of~~ magnesia, pumice, kieselghur etc.(9), the principle use of which is to increase the surface of contact for the reacting gases. Recently the use of silica, kaolin, and oxides of tin, aluminium, chromium etc.(10) have been patented, but have not yet been proved to be successful.

As far as we know presently, in the manufacture of sulphuric anhydride by contact process, only platinum and vanadium have been proved to be satisfactory among the numerous catalysts found. They are, however, expensive materials and such deposits have not yet been traced out in Chinese territories. We, therefore carried on a series of investigations with the following oxides and salts of which we know that we have rich deposits in China:

1. salts of tungstic acid;
2. salts of chromic acid;
3. salts of phosphoric acid;
4. oxides of various metals.

From J. Pintsch's patent we know that tungsten(11) may be used as a catalyst for the manufacture of sulphuric anhydride. It appears to be very favorable to us as we have rich deposits of tungsten minerals. Neumann, however, pointed out its use being unsatisfactory: the conversion of SO_2 into SO_3 can hardly exceed 60%(12). Chromium oxides will give a yield over 80%, but this catalyst soon loses its activity. C. Ellis and G. Bortmann showed that if certain accelerators are added in small quantities, its activity may last much longer: oxides of tin, lead, antimony, cadmium, etc.(15) will serve well as such accelerators. Phosphorus compounds have been generally regarded as catalyst poison, but it will be interesting to know their catalytic effects when they are used by themselves. For ~~this reason we took phosphates of aluminium, silver, copper etc. as~~ catalysts under investigation.

The carriers choosen for our experiments were (1) asbestos; (2) pumice; (3) silica gel. The last named substance had been found very difficult to dry properly to fit our purpose. After 2 hours drying in an air oven at 200°-300°C. to constant weight, at higher temperature it still gave off some water which retarded the reaction. Both asbestos and pumice could be dried properly and were adopted throughout our experiments, the latter was the one preferred, for it is less voluminous than the former.

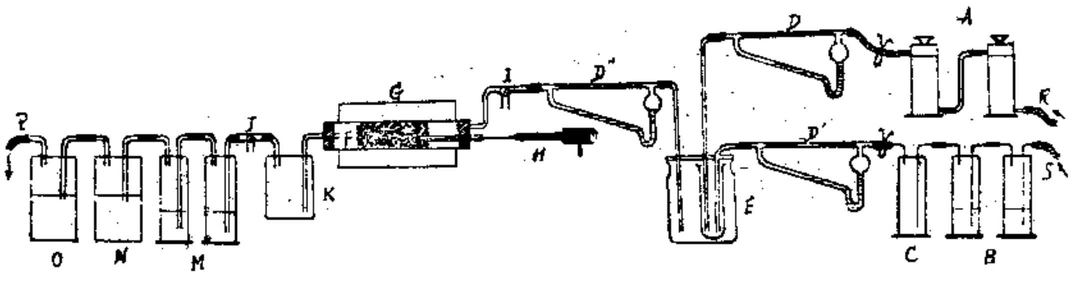
I. PREPARATION OF CATALYSTS FOR USE

(a) Catalyst with asbestos as carrier: The asbestos was boiled with sufficient HCl (1 : 1) to remove all the impurities which are soluble in this reagent. It was filtered, washed thoroughly with water, dried and ignited to constant weight, a definite quantity was then weighed and soaked in water with the addition of suitable quantity of sodium tungstate solution and well stirred. The tungstate was precipitated on asbestos by the addition of sufficient inorganic salt solution. After filtration, drying, heating to 300°-400°C. and igniting as before, it was then ready for use.

(b) Catalyst with pumice as carrier: We experienced certain difficulty in the preparation of catalyst when asbestos was used as carrier. As our oxidation chamber was not big enough to hold sufficient quantity of the catalyst for the bulk of asbestos, we used pumice carrier in order to hold larger quantity of the catalyst. The pumice was first powdered, and grains of about 3-4m/m size were taken and a certain quantity was weighed out, soaked in a calculated quantity of sodium tungstate solution or that of potassium chromate or sodium phosphate. The whole apparatus was put into an evacuating chamber to expel the air enveloped in the pores of the pumice, so that the pumice might be saturated with the solutions. Sufficient inorganic salt was then added to precipitate the catalyst on the pumice, and the whole well stirred. Filtration, washing, drying, and igniting were conduced just as in (a). When oxides were used, the oxides were simply mixed with the pumice with the addition of suitable quantity of water and well stirred. After drying, it was ready for use.

II. EXPERIMENTS ON CATALYSIS WITH THE CATALYSTS PREPARED

The mixed gases we used consisted of about 8% of SO_2 and about 92% of dried air by volume, and the rate of gas flow was 150 c.c. per sq.cm. of surface per minute. The whole apparatus was fitted in the following manner:



R	the inlet for dry air	G	electric furnace
S	the inlet for SO_2	F	combustion tube
A	calcium chloride bottles	F′	catalyst
B	sulphuric acid bottles	H	thermoscouple
C,K	empty bottles	M	sulphuric acid bottle (to absorb SO_3)
D,D′,D″	gas speed indicator	N,O	lime water and KOH bottles for removing SO_2.
E	bottle for gas mixing	P.	outlet for waste gases.
I,J	tubes for taking gas samples for analysis		

The air was regulated by the help of D, SO_2 by D', and the mixed gases by D''. The SO_2 content in the mixed gases might be determined by taking a certain volume of the mixed gases from I, and the SO_2 estimated by means of Reich's method. This consisted of diluting 5 c.c. N/10 iodine solution diluted with 300 c.c. of distilled water, 1 c.c. of starch solution being added as indicator. The mixed gases were passed through the solution until the blue colour just completly decolourised, and the volume of the escaped gases measured. If we let V c.c. stands for this volume, then the percentage of SO_2 in the mixed gases may be calculated by the following formula:

$$SO_2\% = \frac{5.585}{5.585 + v} \times 100.$$

A certain weight of catalyst was taken to fill the combustion tube, which was then heated gently to a definite temperature, when the mixture of sulphur dioxide and air was passed through at a definite rate for half an hour. Samples of gases mixtures were taken both from the inlet and outlet of the combustive tube F at I and J to determine their SO_2 contents. This was repeated three times after each quarter of an hour, and the average values were taken. The effet of variation of temperature on the catalytic reaction had also been investigated. Our experiments may be grouped under the following seven headings.

(A) Here we used 10 gms tungstate-asbestos containing 10% tungstate.

Catalyst	Length of Filling \ Temperature	450°C	500°C	550°C	600°C	650°C	700°C
Ag_2WO_4	20 cm	9.74	10.84	11.3	16.68	24 55	26.57
$CuWO_4$	24 cm	4.02	14.79	31.31	25.19	21.86	

Besides the tungstate of silver and copper, we have also tried those of barium, nickel and zinc, which were not satisfactory at all, especially under 500°C., at which temperature the amount of SO_3 formed being negligible.

(B) The catalyst was made by precipitating 20% tungstate on pumice, 30 gr. being taken for each experiment.

Catalyst	Length of Filling \ Temperature	500°C	550°C	600°C	650°C	700°C
Ag_2WO_4	20 cm	5.25	8.22	12.97	24.3	31.21
$CuWO_4$	18 cm	14.54	21.52	27.93	30	32.7
$Al_2(WO_4)_3$	20 cm	1.7	5.17	10.92	20.69	26.14
$MnWO_4$	19 cm	8.74	10.53	22.54	23.48	25.19
$SrWO_4$	18 cm	8.1	10.17	22.28	27.19	27.95
$Bi_2(WO_4)_3$	18 cm	12.24	21.89	32.64	23.22	22.4
$CaWO_4$	16 cm	3.83	11.11	21.52	30.69	28.5
UO_2WO_4	18 cm		5.26	5.38	19.79	24.45
$FeWO_4$	17 cm	25.14	28.35	43.64	32.62	
$Fe_2(WO_4)_3$	18 cm		17.15	30.27	42.32	38.62
$CoWO_4$	18 cm		13.3	27.73	29.35	32.62
$CdWO_4$	20 cm			19.95	25.43	27.31
$Sn(WO_4)_2$	18 cm		6.16	6.79	10.8	16.68
$PbWO_4$	16 cm				3.37	8.1
$Cr_2(WO_4)_3$	20 cm				5.47	22.15

From the above data we can see that the catalytic property of tungstates is much inferior to that of platinum and vanadium. Ferrious tungstate seems to be the best among this series, while those of chromium and lead show little activity below 600° C.

(C) Here we used a mixture of two tungstates in the proportion of 1:1. 30 gr. of the tungstate-pumice were used for each experiment:

Catalyst	Length of Filling Temperature	500°C	550°C	600°C	650°C	700°C	750°C
$CuWO_4$ + Ag_2WO_4	18 cm	15.71	29.14	43.8	45.45	36.66	
$Cr_2(WO_4)_3$ + $Al_2(WO_4)_3$	16 cm	18.35	26.55	28.72	30.6	24.61	
$CuWO_4$ + $CaWO_4$	18 cm	24.21	25.59	26.65	40.8	43.07	36.92
$FeWO_4$ + $MnWO_4$	18 cm		16.8	26.37	31.86	30.26	23.42

The first and the second contained 20% tungstate, whilst the third and the fourth 40%. They are also not good catalysts although some pairs are evidently more efficient than either of the salts acts individually. In the fourth pair, manganese salt appears to play the part of a negative catalyst towards iron tungstate.

(D) In these experiments 25 gr. of 25% chromate on pumice have been used as catalysts.

Temperature Length of Filling Catalyst		600°C	650°C	700°C	750°C
$Ag_2Cr_2O_7$	16 cm	11.58	19.43	21.69	23.95
$CuCrO_4$	17 cm	15.81	40.61	36.4	29.94
$Fe_2(CrO_4)_3$	16 cm	14.16	27.44	36.67	34.06
$BaCrO_4$	16 cm	10.73	29.42	30.83	24.41
$SrCrO_4$	16 cm		28.47	29.05	28.99
$ZnCrO_4$	16 cm	11.47		27.05	
$Sn(Cr_2O_7)_2$	16 cm	31.29	38.32	32.98	

All chromates, with the exception of that of tin which converted about 19% of SO_2 into SO_3 at 550°C. show little activity below 600°C.—

(E) 25 gr. of 25% phosphates on pumice were used for the following experiments:

Temperature Length of Filling Catalyst		550°C	600°C	650°C	700°C	750°C
Ag_3PO_4	18 cm	12.64	18.97	27.7	30.38	27.44
$Cu_3(PO_4)_2$	17 cm	27.06	34.31	36.75	38.06	32.85
$Ba_3(PO_4)_2$	17 cm		4.68	17.33	21.28	25.55
$FePO_4$	17 cm	11.0	24.4	44.68	38.88	36.76
$Ca_3(PO_4)_2$	18 cm			5.25	11.36	13.33
$AlPO_4$	17 cm		15.11	19.1	23.86	27.8

It is interesting to see that phosphates, a catalyst poison are equally active catalysts themselves as tungstates.

(F) 30 gr. of oxides on pumice were used here:

		Temperature					
Catalyst	Length of Filling	500°C	550°C	600°C	650°C	700°C	750°C
MnO_2	18 cm			12.34	24 83	28 27	29.16
TiO_2 + Fe_2O_3	18 cm	23.47	37.33	36.41	34.3		
TiO_2	18 cm		10 53	15 84	25.3	32.12	
Sb_2O_3	19 cm		14.75	16.93	18.8	23.56	
Sb_2O_3 + Sb_2O_5	18 cm		15.18	18.81	22.98	30.68	26.97

The first, second and the third contain 20% of the oxide or mixture of oxides for each; for the fourth and the fifth, the concentrations of the catalyst were 40%. From the above data, we find that mixture of oxides generally works better than simple oxides, but none of them may be regarded as efficient catalyst. The proportion of the oxides in the mixture were 1:1 by weight in all our experiments.

(G) From the results obtained in experiments (B) and (C), ferrous tungstate and the mixture of silver and copper tungstates appear to be the more efficient catalysts among all those we have tried. Here we increased the concentration of the catalysts on pumice from 20% to 50%, and the weight used from 30 gr. to 100 gr.

Catalyst	Length of Filling	Temperature				
		500°C	550°C	600°C	650°C	700°C
$FeWO_4$	50 cm	24.07	30.32	45.06	38.61	
$CuWO_4$ + Ag_2WO_4	50 cm		29.21	43.35	46.23	37.11

They seem to work a little better, but their catalytic activities are still far below what we expected.

CONCLUSION

From the above experimental data the activity of the various catalysts employed may be easily seen. Amongst all the catalysts, ferrous tungstate, ferric phosphate and the mixture of silver and copper tungstates have been found to be the most active (the conversion of SO_2 into SO_3 being 45-46%), ferric tungstate and copper chromate are not so active (41-42%), while the catalytic oxidation of SO_2 to SO_3 by the use of titanium oxide mixed with ferric oxide or ferric chromate by itself has been found to be only 37%. All these are not satisfactory as catalysts in the manufacture of sulphuric anhydride (> 90%), but the results of our experiments told us the following interesting points:

1. When equal weights of simple substance and mixture are used as catalysts, the mixture is generally the more active. This may be the reason why very complicated mixtures are frequently met in patents concerning to the catalytic oxidation process.

2. The nature of the carriers has a great influence on the catalytic reaction. In experiments (A) and (B), different weights of silver tungstate and copper tungstate were used, but the resulting percentage of SO_3 formed did not show much difference, and so

was the case with G. It is obvious that the porosity is one of the essential factors leading to success, for this will facilitate the reacting gases to be in close contact with the catalysts; otherwise the increase in weight of catalysts will not give a better yield.

3. The catalytic oxidation of SO_2 into SO_3 is a reversable reaction above 450°C. For a definite quantity of gas mixture, and definite physical conditons consequently the length of filling, the time of contact between the reacting gases and the catalysts, should be determined by the reaction velocity, seeing the increase in length of the catalyst in G to double that of B giving no better yield.

4. Kieselghur and its like may be a good carrier to be used with either ferrous tungstate or ferric phosphate, to which may be added some suitable accelerators. Better results may be expected from such a composition in future investigations.

REFERENCE

1. Knietsch, Ber., 34, 4093, 1910.
   Cf. Mon., Scient, [4]-16-289, ~~1902~~.
2. P. Pascal, Traité De Chemie Minérale, P. 546, 1932.
3. Ibid. P. 558, 1932.
4. L. Bradley Brit. 112153, Dec., 21, 1916.
   C. Ellis Can. 177145, May 22, 1917.
   186962, Oct. 15, 1918.
   G. Vortmann Ger. 316858, Nov. 28, 1919.
   H. F. Oxley, W. H. Groombridge & E. B. Thomas Brit. 354356, May 2. 1930.
   B. Neumann & E. Garbel Z. Electrochem. 34, 734-40, 1928.
5. De Haen, D.R.P. 128616.
   B.A.S.F. D.R.P. 291792.

J. M. Selden & Selden Co. Brit. 170022. Apr. 7, 1920.
A. P. Jaeger, Brit. 286708, Mar. 10, 1927.
E. B. Maxtead & N. J. Hassid, J. H. Von. Keler & A. Weindel U. S. 1183414 May 16, 1916.
J. Soc. Chem. Ind. 50, 399-500T, 1931.
~~6. Et. Kuhlmann B. F. 538139 et 572169, 1924.~~
I. Adadourov. G. Boreskov et Z. Lissianskaia J. Khim, Promychl. 8-606, à 612, 1931.
C. H. Mac. Dowell & H. H. Meyers U. S. 1420202 June 20, 1922.
7. ~~C. B.~~ Clark U. S. 1789460 Jan. 20, S. Robson. & P. S. Lewis Brit. 334862, June 8, 1929.
8. J. H. Perry U. S. 1914458 June 20, 1933.
E. I. Du. Pout. De Nemorers & Co. & Imperial Chem. Ind. Ltd. Brit. 354500 June 27, 1930, Brit. 348000, Sep. 13, 1929.
9. J. J. Etridge & Imperial Chem. Ind. Ltd. Brit. 333670 June 5, 1929.
A. O. Jaeger Brit. 348669, Jan. 22, 1929.
J. H. Perry U. S. 1914458, June 20, 1933.
10. B. Lambert & National Process Ltd. Brit. 301853, Sep. 6, 1927. Fr. 641619, Sep. 28, 1927.
J. A. Well Brit. 334268, June 1, 1929.
Holmes Ramsay & Elder Ind. Eng. Chem. 21, 850, 1929.
Holmes & Elder Ibid. 22, 471, 1930.
W. W. Scott & E. B. Layfield Ibid 23, 617, 1931.
11. Pintsch E. P. 5626, 1912.
12. P. Pascal Traité De Chemie Minérale, P. 550, 1932.
13. Ibid. P. 548, 1932. G. Bortmann D. R. P. 316858, 1918.

1223

1364 1