

THE SORPTION PROPERTIES OF SUPPORTED POTASSIUM-VANADATE CATALYSTS

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Catalysts in the industrial production of sulphuric acid are normally made from diatomite impregnated with potassium vanadate solutions of different compositions. During the reaction the potassium will be transformed into sulphates or pyrosulphate salts. There is no definite view at present about the reactions involving the vanadium content and nothing is known about the role of the carrier substance in the catalytic oxidation. According to some opinions the silica forms part of the catalytically active ingredient, while others think that it only provides stabilizing effect for the active component. It has been experimentally proved that vanadium catalysts containing alkaline sulphates have much higher activity than that of pure vanadium pentoxide, moreover, the catalytic activity increases with the atomic weight of the alkaline metal. Several explanations were suggested for these experimental findings. Some of these are given in the followings:

1. An increase of the SO_3 pressure of the alkaline sulphate-vanadyl sulphate system is brought about by the alkaline sulphates resulting in increased catalytic activity.

2. The catalytically active component is the pentavalent vanadium whose oxidation state is stabilized against the reductive effect of SO_2 to a different extent by alkaline metals.

3. The catalysts form a glassy liquid or semiliquid layer on the surface of the supporting substance and the viscosity of this layer depends on the choice of alkaline metal salts.

4. The alkaline metal oxide, SO_3 and vanadyl oxides form catalytically active complexes to some composition ratio.

TANDY [1] has examined reactions of alkaline sulphate (pyrosulphate) — vanadate catalysts of different compositions at different temperatures by equilibrium mixtures of air— SO_2 — SO_3 and tried to establish the degree of reduction of vanadium after equilibration with these mixtures along with the change in the weight of the catalysts. He did not use supporting substances in these studies and tried to measure the reduction percentage of vanadium by cooling and immersing the system into aqueous solutions. According to

his results the increase in weight cannot generally be correlated with the amount of vanadium reduced which is present in the form of VOSO_4 according to the author's opinion.

Since TANDY's experiments there have not been further studies neither into the problem of oxidation state of vanadium nor pertaining to the quantity and quality of gaseous components sorbed during the reaction. For this reason we have decided to continue the research along these lines.

In our experiments the sorption capacity of the functioning catalysts-support system for SO_3 , SO_2 and O_2 gases and the reversibility of this sorption

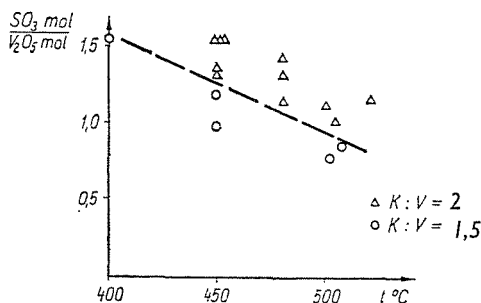


Fig. 1

process have been studied. As experimental technique the method of frontal gas chromatography as developed by us was applied with detection systems appropriately modified for the gas components in question. By the application of the BET method for the determination of the specific surface area it became evident that the quantities of SO_3 sorbed have greatly surpassed that which is necessary to cover the surface by a unimolecular layer. The surface area of the catalyst samples were about $5 \text{ m}^2/\text{g}$ while the quantity of sorbed SO_3 was approximately $0.4 \text{ mmol}/\text{gr}$ catalyst.

Assuming that the molecule SO_3 covers an area of about 30 \AA^2 , the quantities sorbed would cover roughly 80 m^2 in case of a unimolecular, tight-fitting layer. This quantity sorbs reversibly on (or in) the catalyst and can be desorbed completely by flushing the catalyst with an inert gas.

Since multimolecular physical adsorption cannot be realized at temperatures $450\text{--}500$ centigrade, it is evident that the SO_3 sorbed will be found inside the catalyst, not on its surface. This phenomenon is in accordance with the view mentioned above: i.e. the catalyst phase is a viscous liquid. It cannot be considered, however, as a proof for that view, since the whole inner phase of e.g. magnetite catalysts is also accessible, at higher temperatures: 500 centigrade the total quantity of the iron oxides can quickly be reduced or oxidized by H_2 , air or water vapour via the chemical route of ferrite-magnetite

phases. Similar experiences are available for nickel catalysts on supports at temperatures: 900 centigrade.

Our studies have been extended to the pressure and temperature dependence of the SO_3 sorption, however, we have examined its dependence on the composition of the catalyst phase. The measurements gave much scatter, the cause of which we shall give later. Fig. 1 illustrates the temperature dependence of the sorption of SO_3 . As it can be seen, there is a definite temperature dependence in each case in spite of the scatter of experimental points. The temperature dependence is roughly the same for the two samples of different composition

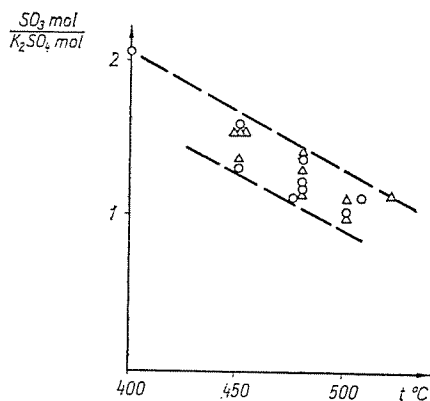


Fig. 2

and it is definitely higher than that described in TANDY's papers previously detailed. (TANDY's results refer to measurements without supporting materials.) Catalysts of the same V_2O_5 content give results depending on the K : V ratio, those with K : V = 2 : 1 sorb more SO_3 in the whole temperature interval than those with K : V = 1.5 : 1. If the ratio SO_3 sorbed : K_2SO_4 is calculated, we find the two series of measurements practically coincident (See Fig. 2) i.e., the quantity of SO_3 sorbed is proportional to the K content. The molar ratio of SO_3 sorbed : K_2SO_4 is half of that of SO_3 : V_2O_5 .

There are no literature references to the sorption of SO_2 . According to our measurements the catalyst sorbs significant quantities of SO_2 and the sorption takes place in the whole catalyst-phase similarly to the sorption of SO_3 . The results of these measurements are shown in Fig. 3.

The sorption of SO_2 is evidently more reproducible than that of SO_3 and it is constant in a broad temperature range. The same can be said about the pressure sensitivity of the SO_2 sorption; there is no significant influence of pressure on the sorbed quantities between 1 atm and 0.032 atm. As our experiments showed the supporting material — containing about 0.5% Al

and Fe — itself also sorbs SO_3 evidently in the form of sulphates and it is probably the incomplete desorption of SO_3 bound in such way that causes the experimental scatter in the SO_3 sorption measurements. In contrast neither the supporter nor the K_2SO_4 do sorb SO_2 . When pure V_2O_5 is deposited on the supporting material neither SO_3 nor SO_2 sorption can be observed.

We have examined the simultaneous sorption of SO_2 and SO_3 by two methods. First the catalyst column was saturated by SO_3 , then it was flushed with pure SO_2 gas. The column saturated with SO_3 sorbed the same quantity of SO_2 as what was sorbed on the totally desorbed catalyst. The same result

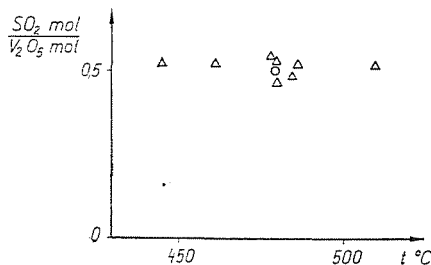


Fig. 3

was obtained when the column was flushed with SO_2 — air mixtures containing excess SO_2 ; in these cases the equilibrium gas mixture contained significant quantities of unconverted SO_2 . Having the column saturated by such gas mixtures the gas desorbed was composed of SO_2 and SO_3 quantities corresponding to the sorption processes involving only one component.

On the basis of the sorption studies it became necessary to revise the view about the reducibility of the vanadium content in the catalyst by the effect of SO_2 . When the functioning catalyst is brought into contact with pure SO_2 and subsequently it is cooled, an analysis of the aqueous solution of the vanadium content for oxidation state reveals that there has been an apparent reduction by SO_2 . The method of TANDY was similar when studying the reducibility of catalysts coming into contact with equilibrium gas mixtures.

When, however, the SO_2 on the catalyst is desorbed by some inert gases, the whole quantity of SO_2 is desorbed in chemically unchanged form i.e. as SO_2 , which goes to prove that it does not remove oxygen from the surface, in other words, it does not have a reducing effect. Therefore it seems that we are right in assuming that related data in the literature show the reducing effect of SO_2 bound to the catalyst and that the "quantity of reduced vanadium" means, in fact, the quantity of bound SO_2 .

On the basis of these results and considerations it seems necessary to reevaluate current assumptions about the oxidation mechanism of SO_2 on supported potassium vanadate catalysts.

Summary

The sorption of the components of the oxidation reaction $\text{SO}_2 - \text{SO}_3$ on kieselguhr-supported potassium vanadate catalyst has been investigated in flow system during the reaction. SO_2 and SO_3 are both sorbed in a measure exceeding the full monolayer capacity of the catalyst surface by a factor of 10 resp. 20 approximately, indicating the presence of a liquid or semiliquid catalyst phase, accessible in the bulk. Pressure- and temperature-dependence of the sorption processes have been measured. The amounts sorbed of SO_2 and SO_3 are independent of each other, the SO_2 sorbed can be desorbed unchanged: it does not itself have a reducing effect on the catalyst.

Literature

1. TANDY, G. H.: J. appl. Chem. **6**, Febr. (1956).

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