INVESTIGATION OF THE OXIDATION MECHANISM OF SULPHUR DIOXIDE ON VANADIUM CATALYSTS

I. THE CHANGE IN ACTIVATION ENERGY WITH TEMPERATURE

By

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Introduction

The mechanism of the oxidation of sulphur dioxide over catalysts containing vanadium has been investigated by several authors. This is due partly to the great industrial importance of the reaction, and partly to the fact that the reaction appears to be one of the simplest catalytic processes. There are only two reactants and one end product, no side reactions occur, so that it seems to be a model permitting to study the characteristics of heterogeneous catalytic reactions in general, without disturbing side effects. However, a study of pertinent literature shows that notwithstanding many valuable results obtained so far, the mechanism of the reaction is not yet fully elucidated.

Description of the catalyst

The catalyst is a mixture of vanadium pentoxide and potassium sulphate or pyrosulphate, supported mostly on a silica carrier (Kieselguhr, silica gel, etc.). Vanadium pentoxide, present in 5 to 10 per cent by weight, is considered in general as the active component, it is a fact, however, that only a very poor catalyst can be prepared without substantial quantities of alkali metal pyrosulphate. In industrial catalysts the proportion of potassium sulphate exceeds that of vanadium pentoxide, potassium-vanadium molar ratio being about 2 or more.

At present, most of the investigators share the view that under normal operating conditions (above 450°C) the active component is in the liquid state [1—4]. It has been proved also by direct experiments [2] that the mixture $V_2O_5 - K_2SO_4$ melts above 430°C, at a temperature depending on the composition. In fact, even a publication has appeared [5], investigating the viscosity of the eutectic $2 K_2SO_4 - V_2O_5$ in the function of temperature.

The behaviour of the catalyst at lower temperatures is more problematic. It is generally assumed on a tacit understanding that the active component solidifies within a more or less wide temperature range and, in the opinion of several authors, the catalyst is active only in the liquid state.

Kinetics of the catalytic reaction

Several works deal with the formal kinetics of the reaction [1—3, 6—12], and various equations have been set up. A critical evaluation or comparison of these equations is very difficult, for different catalysts were investigated under different conditions.

Though kinetic equations published in the literature are often inconsistent with each other, opinions concerning the activation energy of the reaction more or less agree. It is a general view that activation energy is greater at lower than at higher temperatures, i.e., the $\lg k - 1/T$ diagram exhibits an inflection.

The transition point is at about 440°C, this temperature, however, depends on the nature of the catalyst, on the gas composition and on the fact whether the transition temperature is approached by increasing or by decreasing the temperature (hysteresis). This phenomenon is shown in Fig. 1, according to BORESKOV [7]. Starting from 400°C, the rate constant increases quite rapidly with temperature and, at a temperature not very well defined, this increase becomes abrupt. After that, the increase becomes slower than at low temperatures.
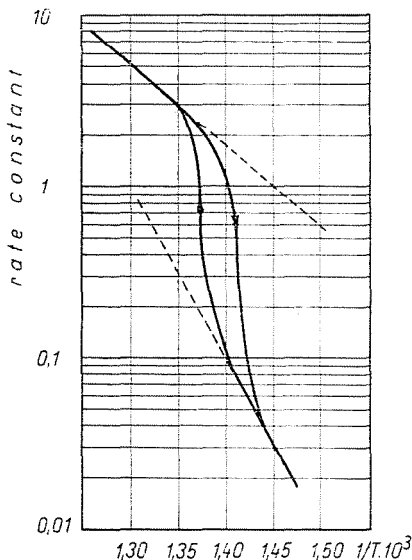

Fig. 1

When we begin to cool the system, the sudden decrease of the rate constant occurs only at a temperature lower than that of the sudden increase, whereas at still lower temperatures the rate constant does not depend any more on the direction of the temperature change.

The occurrence of hysteresis and the change in activation energy were explained by Soviet authors [15, 16] as a result of chemical transformation of the catalyst. At low temperatures, vanadium is tetravalent, and vanadyl sulphate is the active component, whereas at higher temperatures the catalyst is potassium pyrosulphovanadate, containing quinquevalent vanadium, having a substantially higher activity. The two forms can be transformed into each other at a temperature depending on the gas composition, and this is the cause of the sudden changes in activity.

MARS and MAESSEN [17] present a totally different explanation. They are of the opinion that the rate of the reaction can be described by the equation:

$$r = k p_{O_2} \left(\frac{\sqrt{K p_{SO_2}}}{\sqrt{p_{SO_3}} + \sqrt{K p_{SO_2}}} \right)^m \tag{1}$$

where p_{O_2}, p_{SO_2} and p_{SO_3} are the partial pressures of the reaction components, K is the equilibrium constant of the reaction

$$2 V^{5+} + SO_2 \rightleftharpoons 2 V^{4+} + SO_3, \tag{2}$$
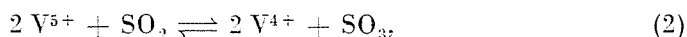
while $m \approx 2$ is an empirical constant. K decreases exponentially with increasing temperature, so that at low temperatures the first term, at high temperatures the second term of the nominator can be neglected. Thus, at low temperatures the apparent rate constant k' becomes equal to the true rate constant k, while at high temperatures

$$k' = k \cdot K^{m/2}. \tag{3}$$

Since both k and K depend exponentially on temperature, the apparent activation energy at high temperatures is

$$E' = E - \frac{1}{2} m Q$$

where E is the true activation energy, and Q is the heat of reaction (2).

Melting of the active component

Though both theories may explain the change in activation energy, they are not likely to be reassuring. In the case of the theory assuming two different catalysts it seems highly improbable that forms of two different oxidation grades of the same catalyst would catalyze the same reaction according to two different mechanisms, particularly if the basis of the catalytic activity is the very fact that these two forms are easily transformed into each other. Moreover, it is curious that the process of higher activation energy

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becomes predominant at low temperatures, whereas in the case of competitive reactions, usually just the opposite occurs. Though in the given case the ratio of the two forms changes with temperature, this change is not so rapid that it would explain this phenomenon, characteristic of consecutive reactions, or reactions hindered by diffusion.

MARS and MAESSEN [17] explain the change of apparent activation energy essentially by consecutive reactions. However, their theory does not explain the phenomenon of hysteresis. Though hysteresis may occur in exothermal reactions also on account of the heat of reaction, in the present case this is out of the question, due to the relatively low reaction rate [1].

Both hysteresis and change in apparent activation energy can be interpreted satisfactorily by assuming that the catalyst melts in the transitory region. According to this assumption, the reaction proceeds at low temperatures only at the surface of the solid catalyst, while at high temperatures the reactants penetrate also the interior of the liquid phase. (The fact that sulphur dioxide and sulphur trioxide are able to penetrate to the interior of the catalyst, has been proved earlier by our sorption experiments [18].) The extension of the reaction over the whole liquid phase means with other words that the number of active sites increases considerably, so that an increase in activity in the transitory temperature range is easily understood.

On cooling the catalyst, the sudden change in activity occurs at a lower temperature than does the sudden increase in activity on heating the catalyst. This could be explained most obviously by the undercooling of the liquid, however, we are of the opinion that also other factors interfere. Over a well functioning catalyst there is always a substantial quantity of sulphur trioxide formed in the reaction. This sulphur trioxide is able to dissolve in the liquid [18], decreasing thereby its melting point. Thus, the hysteresis is due not to undercooling, but to the actual depression of melting point. This statement is supported by test data of GERBURT-GEIBOVICH and BORESKOV [15], who introduced a partly converted mixture over the catalyst, and tested its activity. The temperature of the transition between low and high activation energies was found to be the lower, the higher was the degree of conversion of the mixture introduced over the catalyst. This phenomenon cannot be explained by undercooling, whereas it is readily explained by freezing point depression.

The role of diffusion

Not only hysteresis, but also the change in apparent activation energy can be explained by the melting of the catalyst. Indeed, if the rate of the reaction proceeding in the liquid phase is sufficiently high, the concentration of the reacting components will decrease towards the interior of the liquid, due to the limited rate of diffusion, and a part of the catalyst will not be utilized.

A similar phenomenon occurs also with porous catalysts, where the deeper parts of the pores are not utilized. For simple reactions, this problem has been treated by exact mathematical methods. On the basis of work done by THIELE, WHEELER [19] showed that in the case of a reaction of n-th order hindered by diffusion in the pores of the catalyst, the apparent activation energy would be only one half of the true activation energy, and the apparent kinetic order of reaction would be $(n + 1)/2$. It will be shown in the following that the case is similar if during a reaction proceeding in a liquid film, a part of this film is not utilized.

Let us consider a liquid film in which the gaseous substance A is soluble, and the dissolved substance is able to react with a component of the solution present in great excess. Let the concentration of the substance A be c_0 and $c = c(x)$ on the surface and in the interior of the film, resp., where x is the distance measured from the surface of the film. In the case of a reaction of n-th order, the reaction rate at a depth x will be

$$r = \frac{dc}{d\tau} = -k \cdot \gamma^n c^n \tag{5}$$

where γ is the activity coefficient of substance A in the solution. If a possible convection is neglected, only the chemical reaction and the diffusion can result in a change in concentration, so that it can be written under consideration of the second law of Fick:

$$\frac{\partial c}{\partial \tau} = D \frac{\partial^2 c}{\partial x^2} + r \tag{6}$$

In the steady state $\dfrac{\partial c}{\partial \tau}$ is zero, and thus

$$D \frac{\partial^2 c}{\partial x^2} - k\gamma^n c^n = 0 \tag{7}$$

When γ and D are considered to be constant, and $\gamma k/D$ is substituted by $(h/L)^2$, for a reaction of first order Eq. (7) leads to the expression

$$\frac{d^2 c}{dx^2} = \left(\frac{h}{L}\right)^2 c \tag{8}$$

where L is the thickness of the film, and $h = L\sqrt{\gamma k/D}$ a dimensionless parameter.

Except the constants, Eq. (7) is identical with the equation given by WHEELER [19] for the pore diffusion, and the solution of Eq. (8) gives the same concentration distribution as that obtained for pore diffusion:

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$$c = c_0 \, \frac{\text{ch} \left[h \left(1 - \dfrac{x}{L} \right) \right]}{\text{ch} \, (h)} \tag{9}$$

The only difference is that in the case of pore diffusion

$$h = L \sqrt{2k/rD}$$

where r is the pore radius, and k the rate constant per unit surface.

The apparent reaction rate is obtained by integrating the true reaction rate over the whole volume of the liquid film, and dividing by the volume:

$$r' = \frac{\int_0^v \gamma k c \, dV}{V} \tag{10}$$

Assuming uniform film thickness, which assumption has already been made implicitly earlier, when writing Eq. (6) for one dimension, Eq. (10) can be written in the following form:

$$r' = \frac{\int_0^L k \gamma \, c \, dx}{L} \tag{11}$$

Substituting the value of c from Eq. (9) and integrating, the expression

$$r' = k \gamma c_0 \, \frac{\text{th} \, (h)}{h} \tag{12}$$

is obtained.

If the diffusion rate is considerably higher in the gaseous phase than in the liquid phase, the activity of the substance A at the surface of the film can be taken as identical with its fugacity or rather with its partial pressure p, so that this parameter, characteristic of the gas phase and easy to determine, can be substituted for γc_0 in Eq. (12):

$$r' = k \cdot p \, \frac{\text{th} \, (h)}{h} = k' c_g \, \frac{\text{th} \, (h)}{h} \tag{13}$$

where c_g is the concentration of the substance A in the gaseous phase, and $k' = kRT$.

Substituting back the value of h in the nominator, the relationships

$$r' = \frac{\sqrt{kD/\gamma}}{L} \, p \, \text{th} \, (h) \tag{14}$$

and

$$r' = \frac{RT \sqrt{kD/\gamma}}{L} c_g \, \text{th}\,(h) \tag{14'}$$

are obtained.

Eqs (13) and (14) are completely analogous to those derived for pore diffusion [19], so it cannot be decided by kinetic measurements alone, which of the two cases is at issue.

It can be seen from the course of the th(h) function (Fig. 2) that for $h > 2$, i.e. when diffusion plays an important role, th(h) ≈ 1, and the apparent rate equation will have the form

$$r' = \frac{\sqrt{k\gamma D}}{L} c_0 \tag{15}$$

that is to say, the apparent reaction rate will be proportional to $\sqrt{k}$ instead of k. As has been shown already by WHEELER, this means that the apparent activation energy calculated from the temperature dependence of the reaction rate will be one half of the true activation energy. (If $h \ll 1$, i.e. diffusion is relatively fast as compared with the chemical reaction, th(h) $\approx h$, and in this case the original rate equation is obtained.)
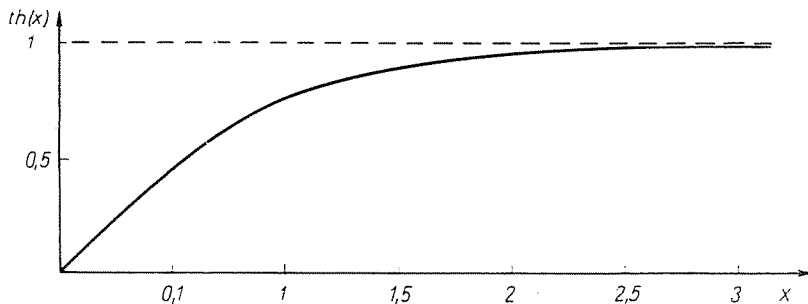

Fig. 2

Owing to the completely identical mathematical description, we can accept now, without further deduction, the conclusions of WHEELER even in the case where the reaction is of other than first order. It can be established, therefore, that in the case where the reaction is hindered by diffusion, independently of the order of the reaction, the apparent activation energy will be one half of the true activation energy, or strictly speaking, still more by 2—3 kcal, taking into consideration that the apparent reaction rate is proportional not simply to $\sqrt{k}$ but to $\sqrt{kD}$, and that in the liquid phase the activation energy of diffusion has usually a value of about 5 kcal. Experiments actually show that at high temperatures the apparent activation energy diminishes to about one half of its value at lower temperatures, which supports the correctness of the proposed theory.

It has still to be cleared why the catalyst operating at low temperatures contains vanadyl sulphate. It is known that the reducibility of the catalyst is dependent on the composition of the gaseous phase [2, 3, 4], provided that the process taking place is actually the reduction of the quinquevalent vanadium [18]. If the activity of a catalyst is low, the gaseous phase will contain a high proportion of sulphur dioxide, and consequently, the catalyst will bind much of it. The reasoning of BORESKOV and co-workers can be therefore inverted: according to our opinion, the low activity of a catalyst does not arise from its reduced state, but on the contrary, the reduced state of a catalyst results from the very fact that it has a low activity.

Summary

Hysteresis observed during the oxidation of sulphur dioxide over vanadium catalysts, and the temperature dependence of the apparent activation energy of the reaction can be simply explained by the fact that at lower temperatures the active component of the catalyst is in the solid state, whereas at higher temperatures in the liquid state. The melting temperature depends on the composition of the gaseous phase, and mainly on its sulphur trioxide content. At low temperatures, the reaction proceeds only on the surface of the catalyst, while at higher temperatures, also in the interior of the liquid phase. The decrease of the apparent activation energy at higher temperatures is due to the slowness of diffusion, the deeper layers of the liquid phase being not readily available for the reaction.

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