JOURNAL OF CATALYSIS 18, 83-89 (1970)

The Addition Effect of Sodium Oxide and Manganese Dioxide on the Activity of a Vanadium Catalyst for Sulfur Dioxide Oxidation

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Received September 12, 1969

On the basis of kinetic measurements, carried out in a wide temperature region, it is shown that an addition of Na_2O results in an increase of catalyst activity at temperatures below 430°C, while at higher temperatures it causes a decrease. The apparent activation energy by the addition of 7% by wt Na_2O decreases from 61 to 33 kcal/mole. This decrease in activation energy is attributed to the influence of Na_2O on the rate of the rate-determining step.

By addition more than 1% of manganese dioxide the activity of the catalyst decreases.

The conclusions from this study show the background of the high activity of several industrial vanadium catalysts at low temperatures.

I. INTRODUCTION

The active component of the vanadium catalysts used for sulfur dioxide oxidation is formed by vanadium pentoxide promoted by alkali metals. The promotive action of these metals has been the subject of study of many workers (*1–21*). However, most of them deal with the study of catalysts promoted only by a single alkali metal. Thus it was found that K, Rb, Cs are better catalyst promoters than Na and Li (*4*, *8–14*) and that the active component of the catalyst forms a liquid phase under the reaction conditions (*1–4, 8, 11, 20, 22*).

Only Topsoe and Nielsen (*4*) tried to combine two promotors. They replaced 10% of the potassium content of a catalyst with sodium. On the basis of comparison of conversions the authors arrived at the conclusion that the substitution of part of potassium with sodium decreases the activity of potassium–vanadium catalyst. However this comparison was made only at one temperature and by means of an integral reactor.

The kinetic measurements on a sodium–potassium–vanadium catalyst has been carried out as well by Mars and Maessen (*23*) and Šimeček *et al.* (*24*). The purpose of these studies was not to provide the information about the addition effect of sodium on catalyst activity, but, to ascertain if the oxidation on this type of catalyst proceeds according to the same mechanism as on catalysts promoted only by potassium (*22*, *25*).

From the point of view that the oxidation of sulfur dioxide occurs by the reduction–oxidation mechanism in which the reoxidation of tetravalent vanadium is rate determining, it appears convenient to add a compound capable of increasing the rate of the latter reaction. Such an influence should be expected in the case of manganese dioxide addition. Some observations of MnO_2 effect were made by Topsoe and Nielsen (*4*). Unfortunately, from these experiments it is

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not conclusively evident if the changes in activity can be attributed to the variations of MnO_2 or K_2O content.

It was the aim of this investigation to study the influence of the addition of sodium oxide and manganese dioxide on the activity of potassium–vanadium catalyst; and the observed results are discussed below. The model catalysts containing various amount of Na_2O and MnO_2 were prepared and then their reaction rates were measured.

II. Experimental Methods

The oxidation rate was measured by means of a differential reactor with gas recirculation. A description of the method of the measurements was given in an earlier publication (*26*).

The influence of addition effect of sodium and manganese on activity of potassium–vanadium catalyst was studied on eight model catalysts. The compositions of the prepared catalysts with different contents of sodium oxide and manganese dioxide are given in Table 1. We chose the molar ratio K_2O/V_2O_5 of about 3, because according to our separate unpublished experiments the catalyst with this molar ratio shows the maximum of activity. The method used for preparation of catalysts was analogous to that described previously (*24*); the catalysts were calcinated for 1 hr in air at 500°C. The support of all catalysts was kieselguhr. Diameters of catalyst particles used in the measurements were approximately 0.8 mm. This choice of particle size eliminated the diffusion influence on the oxidation rate on this type catalyst and in the investigated temperature region (*27*). Before starting the measurements proper, each catalyst was adapted for 10–12 hr to conditions of oxidation.

TABLE 1
Composition of the Model Catalysts with Different Amount of Na_2O

Catalyst	Vanadium oxide V_2O_5 (% by wt)	Mole ratio K_2O/V_2O_5	Na_2O (% by wt)	MnO_2 (% by wt)
1	6.1	—	6.5[a]	—
2	6.1	3.1	—	—
3	6.2	3.1	2.8	—
4	6.3	2.9	3.5	—
5	6.3	3.0	4.2	—
6	6.2	3.0	7.0	—
7	6.3	3.0	—	1
8	6.2	3.0	—	3

[a] The mole ratio of Na_2O/V_2O_5 is 3.1.

III. Results and Discussion

The reaction rate for catalysts with different amounts of sodium oxide were measured at 380–500°C and for catalysts containing MnO_2 at 440–500°C. The composition of the inlet gas was in both cases the same: 10% SO_2; 11% O_2; 79% N_2. In total, about 150 experimental points were measured. Typical data for Catalysts 1–6 are plotted in Figs. 1 and 2, and for Catalysts 7 and 8 in Fig. 3, respectively.

All the measured oxidation rate values were related with the rate equation (*24*):

$$r = C_2 \frac{{}^{I}\ {}_{M}p_{SO}\ /r_{SO_3}}{1 + (K_M p_{SO_2}/p_{SO_3})^{1/2}} \times \left(p_{O_2} - \frac{p_{SO_3}{}^2}{K_p{}^2 p_{SO_2}{}^2}\right), \quad (1)$$

which was derived on the basis of reduction–oxidation mechanism. The validity of this mechanism in cases of potassium–vanadium and sodium–potassium–vanadium catalysts was tested recently (*22–25*).

To the calculations of C_2 for catalysts

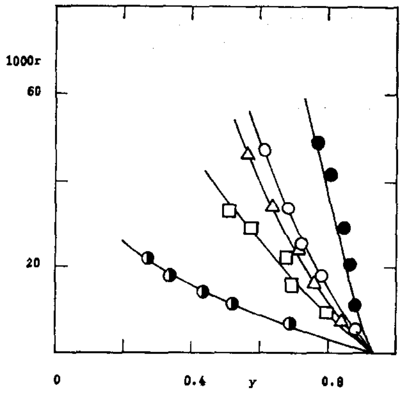

Fig. 1. Dependence of reaction rate r on conversion y at 500°C; concentration of Na_2O: ●, 0; ○, 2.8; △, 3.5; □, 4.2; ◑, 7.0% by wt Na_2O.

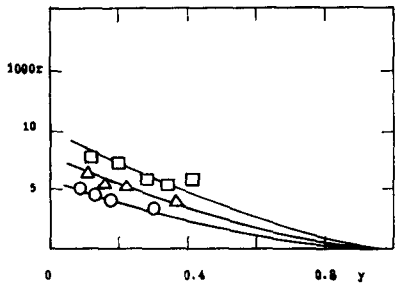

FIG. 2. Dependence of reaction rate r on conversion y at 400°C; concentration of Na_2O: ○, 2.8; △, 3.5; □, 4.2% by wt Na_2O.

promoted only by potassium we used the K_M values (*22*) given by the equation:

$$K_M{}^K = 2.3 \times 10^{-8} \exp (27\,200/RT). \quad (2)$$

which describes the position of the rapidly established equilibrium:

$$SO_2 + 2V^{5+} + O^{2-} \rightleftharpoons SO_3 + 2V^{4+}. \quad (3)$$

In a previous publication (*25*) we calculated the values of $K_M{}^K$ and C_2 by the least-squares method and found that the calculated $K_M{}^K$ values are in good agreement with those measured by Mars and Maessen (*22*). In the case of sodium–potassium–vanadium catalysts we calculated the C_2 values using the K_M values from the expression derived on the basis of Mars and Maessen (*23*) measurements:

$$K_M^{Na,K} = 7.06 \times 10^{-7} \exp (21\,200/RT). \quad (4)$$

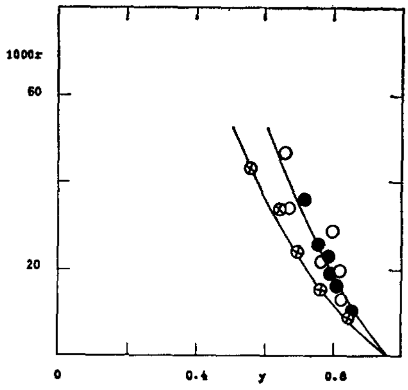

FIG. 3. Dependence of oxidation rate r on conversion y at 480°C: ●, Catalyst 2; ○, Catalyst 7; ⊕, Catalyst 8.

Regardless of these results, we determined the overall rate constants C_2 and equilibrium constant $K_M{}^{Na,K}$ simultaneously by graphical method. The values of $K_M{}^{Na,K}$ found from our kinetic measurements were practically the same as those given by Mars and Maessen (*23*).

Equation (1) describes the experimental data for all measured catalysts and in the whole temperature region with sufficient accuracy. The mean relative deviations of overall constants from their average values are under 20%. The value of the overall rate constant C_2 is used further as a standard of catalyst activity.

1. *The Influence of Sodium Oxide Addition on the Activity of Potassium–Vanadium Catalyst*

The influence of sodium oxide addition to the potassium–vanadium catalyst on its activity is shown in Figs. 1 and 2. Figures 1 and 2 show that at temperature 500°C the oxidation rate is the greatest on the catalyst promoted only by potassium and decreases with increasing content of Na_2O. While at 400°C the catalyst promoted only by potassium is active no longer, and also, the relation between activities of catalysts containing Na_2O changes. Results of the Na_2O addition effect in the whole temperature region studied, are shown in Fig. 4, in which the calculated average values of the overall rate constant C_2 for single catalysts are plotted against temperature. As shown, by addition of 0–7% by wt Na_2O the apparent activation energy of reaction decreases from 61 to 33 kcal/mole. This decrease in activation energy and Fig. 4 indicate that a compensation effect is involved and the decrease in activation energy caused by the addition of sodium oxide is accompanied by decrease in frequency factor. The linear relation between the logarithm of frequency factor and activation energy is shown in Fig. 5. We did not find any sudden change in the course of the straight lines in the Arrhenius plot for these catalysts.

Thus at lower temperatures the activity of sodium–potassium-promoted catalysts is higher than of potassium–vanadium cat-

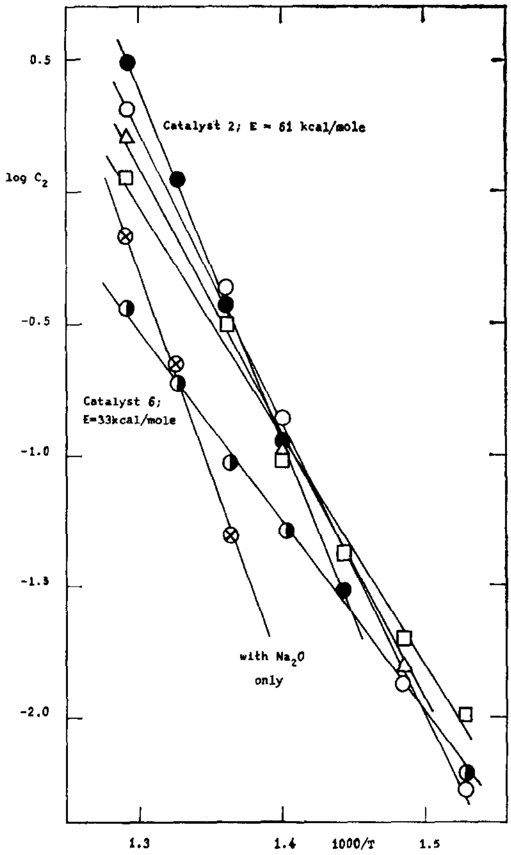

FIG. 4. Temperature dependence of overall rate constant C_2 for catalysts containing various amount of Na_2O; concentration of Na_2O: ●, 0; ○, 2.8; △, 3.5; □, 4.2; ◑, 7.0% by wt Na_2O; ⊗, Catalyst 1.

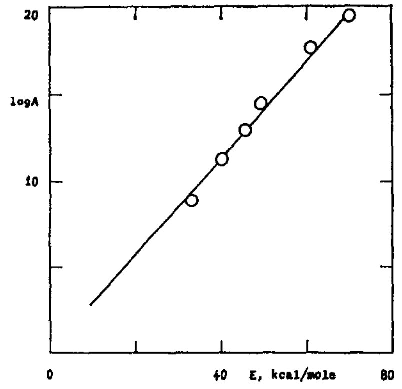

FIG. 5. The relation between the activation energy and logarithm of frequency factor—the compensation effect.

alyst and these catalysts work even at 380–410°C at which it is no longer possible to measure reproducible data on the latter. In the case of our model catalysts, the straight lines in the Arrhenius plot cross at temperature about 430°C.

In order to demonstrate that this finding is independent of the form of kinetic equation used, the kinetic data were correlated with the equation recommended by Mars and Maessen (*23*), but, the backward reaction was taken into account as well (*24*). Then the equation takes the form:

$$r = C \frac{K_M p_{SO_2}/p_{SO_3}}{[1 + (K_M p_{SO_2}/p_{SO_3})^{1/2}]^2} \times \left(p_{O_2} - \frac{p_{SO_3}^2}{K_p^2 p_{SO_2}^2}\right). \quad (5)$$

Results of correlation are displayed in Fig. 6 in the form of temperature dependence of overall rate constant C. Indeed, the same conclusion follows from Fig. 4 and as well as from Fig. 6.

The dependence of catalyst activity on

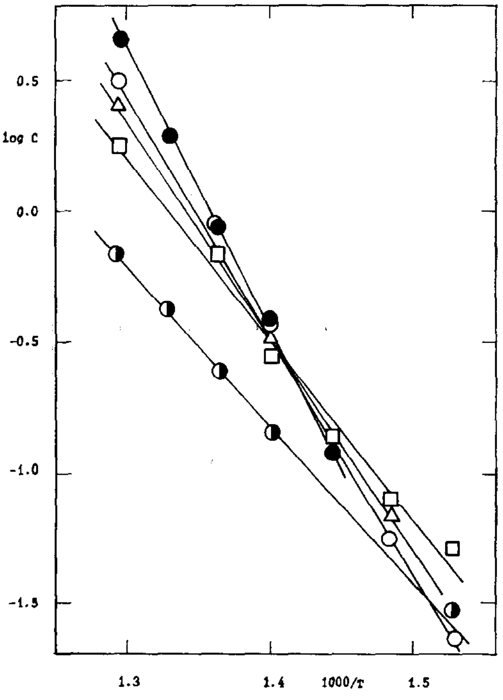

FIG. 6. Temperature dependence of overall rate constant of Eq. (4) C: ●, 0; ○, 2.8; △, 3.5; □, 4.2; ◑, 7.0% by wt Na_2O.

the amount of added Na_2O at single temperatures is shown in Fig. 7. On the basis of these experiments and the finding that sodium has a positive influence on the activity of potassium–vanadium catalyst at lower temperatures we could explain the extraordinary activity of several industrial catalysts (which active component contains sodium) at these temperatures.

Based on the mechanism of sulfur dioxide oxidation on vanadium catalysts (*22–25*), it is possible to suggest two probable causes of the Na_2O effect. The first one consists in the influence of Na_2O on the value of the equilibrium constant K_M of the reaction (3).

This supposition may be tested by using the same values K_M to the calculation of C_2 values for Catalyst 2 as well as in case of sodium–potassium–vanadium catalysts. We did such a calculation and found that the difference in values of $K_M{}^{K}$ (*22*) and $K_M{}^{Na,K}$ (*23*) has only small influence on the values of the apparent activation energy and hence cannot be considered as a main cause of the phenomenon under discussion. The conclusion is, therefore, that the sodium oxide addition effect on the reaction rate and on the activation energy is due to the influence of Na_2O on value of C_2.

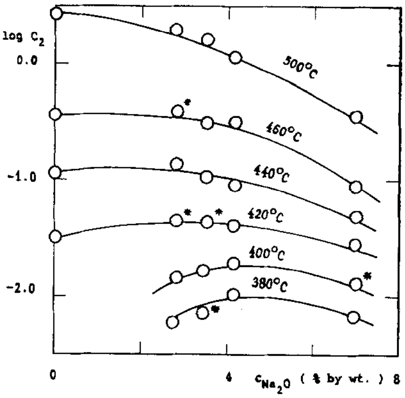

FIG. 7. Variation of overall rate constant C_2 with Na_2O content of catalyst at different temperatures.

The promoting effect of sodium addition is still more remarkable when we take in account the fact that a sodium–vanadium catalyst has a far much lower activity than a potassium–vanadium catalyst (Fig. 8). The activation energy of the reoxidation of V^{4+} (estimated from the temperature dependence of C_2—Fig. 4) amounts to 70 kcal/mol.

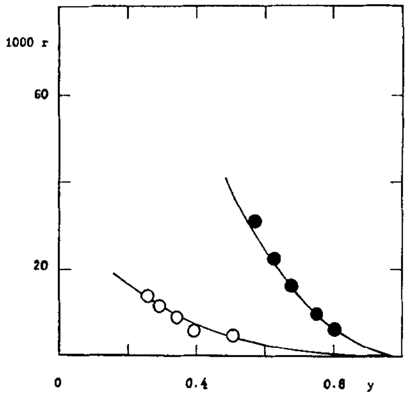

FIG. 8. Dependence of reaction rate r on conversion y at 460°C: ○, Catalyst 1; ●, Catalyst 2.

About the background of this influence of sodium on the values of C_2 and of the activation energy we may mention two speculations: The solubility of oxygen in the melt may have changed as well as the temperature dependence of this property. The second cause can be sought in the change of the environment of the tetravalent vanadium probably presented as complexes with O^{2-} and with (pyro)sulfate ions by addition of sodium ions (*28*). The presence of the latter, even in a small amount, lowers the symmetry around anions and can yield a polarization which facilitates the oxidation of vanadium ion to the pentavalent state. It may therefore be of interest to include combinations of more amounts of alkali metals in investigation in the future. Furthermore, it is possible to consider that the Na_2O addition has influence on: (a) the melting point of active component; (b) the viscosity of the melt of active component; (c) the strength of V=O bond. But, unfortunately, with respect to the shortage of data on the system $Na_2S_2O_7$–$K_2S_2O_7$–V_2O_5 we are not able to discuss these possibilities in detail. It is thus evident that this point cannot be considered as definitely solved; and that it is necessary to gather further information.

2. *The Influence of Manganese Dioxide Addition on Activity of Potassium–Vanadium Catalyst*

To study the effect of MnO_2 addition, the reaction rates were measured for Catalysts 7 and 8 in which the MnO_2 content had been changed from 1 to 3% by wt. Results of one series of experiments are shown in Fig. 3 in which reaction rates are plotted against conversion at 480°C. The Arrhenius plot of the C_2 values is shown in Fig. 9. From Figs. 3 and 9 it follows that the addition of more than 1% MnO_2 is accompanied by decrease of catalyst activity. This finding is in accordance with the theory of Topsoe and Nielsen (*4*). These authors found it useful to add a small amount of MnO_2, while an excess of this compound increased viscosity which results in a deterioration of the catalyst activity. It can be thus assumed that in the case of addition of more than 1% by wt MnO_2 the negative influence of MnO_2 is dominant.

CONCLUSIONS

The measurements carried out indicate that addition of sodium to the potassium–vanadium catalyst increases its activity at temperatures below 430°C and at higher temperatures it decreases. With addition of 0–7% by wt Na_2O, the apparent activation energy of reaction decreases from 61 to 33 kcal/mole. This decrease in activation energy must be attributed to the influence of Na_2O on the rate of the rate-determining reaction. On the basis of this finding it is possible, by addition of a suitable amount of Na_2O, to expand the useful range of vanadium catalyst for sulfur dioxide oxidation to lower temperatures. The addition of more than 1% by wt MnO_2 has negative influence on catalyst activity.

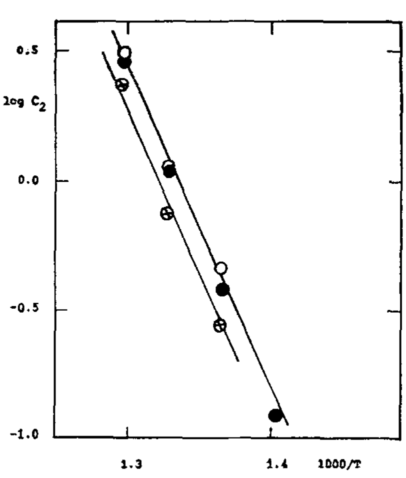

FIG. 9. Dependence of overall rate constant C_2 on temperature: ●, Catalyst 2; ○, Catalyst 7; ⊕, Catalyst 8.

ACKNOWLEDGMENT

The author is indebted to Professor P. Mars, Head of the Department of Physical Chemistry, Technical University Twente, Netherlands, for valuable suggestions and helpful discussions in the preparation of this paper.

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