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The Decomposition of Nitrous Oxide on Doped Oxides of Nickel and Zinc

The Decomposition of Nitrous Oxide on Doped Oxides of Nickel and Zinc

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The kinetics of the decomposition of nitrous oxide on nickel oxide and zinc oxide containing small amounts of foreign ions, such as Li^+, Al^{3+} and Cr^{3+}, have been investigated by a flow method in the temperature range 350–550°C. The rate expression, $-dP_{N_2O}/dt = kP_{N_2O}/(1 + k'P_{O_2}^{1/2})$ is applicable to all the systems studied. The addition of foreign ions gives little effect on the velocity constant for the rate-determining step, but gives a remarkable effect both on the number of the sites available for the reaction and the adsorption coefficient of oxygen k'. Such variation in k' affects the apparent activation energy of the reaction, thus leading to a plausible explanation of the results concerning the effect of such doping reported by Hauffe, Schwab and others.

1. Introduction

The decomposition of nitrous oxide by oxide catalysts have been investigated by various workers, particularly in recent years as a test reaction to study the electronic factor in oxide catalysis.[1] Since the principle of controlled valency was established, Hauffe,[2] Schwab[3] and other workers[4, 5] have investigated the decomposition of nitrous oxide with doped oxides of nickel and zinc and discussed the relation between the catalytic activity of oxides and their properties as semiconductors. However, as has been suggested by Winter,[6] most of these workers have not made a detailed study of kinetics, and in addition, have not taken in consideration the effect of adsorbed oxygen, which seriously affects the features of this reaction. We have recently made an extensive study of the chemisorption of oxygen on doped oxides of nickel and zinc.[7] On the basis of these studies of chemisorption, it was undertaken in the present work to carry out a detailed kinetic study of the decomposition of nitrous oxide on these doped catalysts and to obtain a definite conclusion for or against the significance of the electronic factor in these systems.

2. Experimental

Materials:— Preparation of pure nickel oxide, zinc oxide and also of doped catalysts was already described in the previous paper.[7] Nitrous oxide from a cylinder was purified by passing through an aqueous solution of ferrous sulfate followed by repeated fractional distillation with liquid nitrogen. Other gases used were prepared as described previously.

Apparatus and Procedure:— The reaction was studied in a flow system. The

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apparatus is shown diagrammatically in Fig. 1; the section I was used in the flow experiment at a low pressure ($10^{-3}-5\times10^{-1}$ mm Hg) and the section II in the usual flow experiments where the total pressure of flowing gas was always kept at almost 1 atm. The amount of decomposed nitrous oxide was determined by freezing the gas leaving the reaction vessel in liquid nitrogen and by evaporating the frozen gas into the vessel of a known volume. In case of the flow experiment at 1 atm, the relation between the amount of decomposed nitrous oxide and the contact time was obtained from the experiments of varying flow rates as usual, while with the flow experiments at low pressures, this relation was determined from the experiments of a constant flow rate but with varying amounts of the catalyst. From the relation thus obtained the initial rate of decomposition can be easily determined.
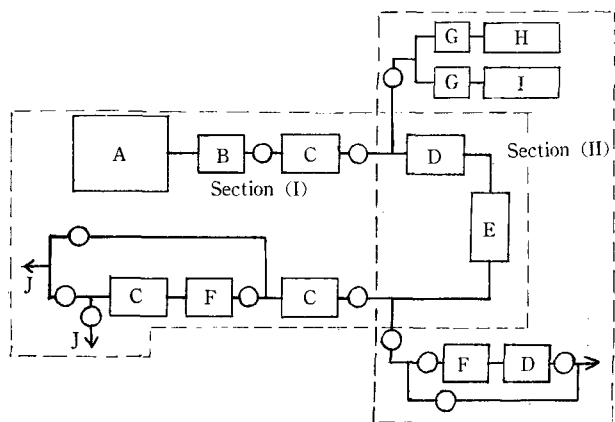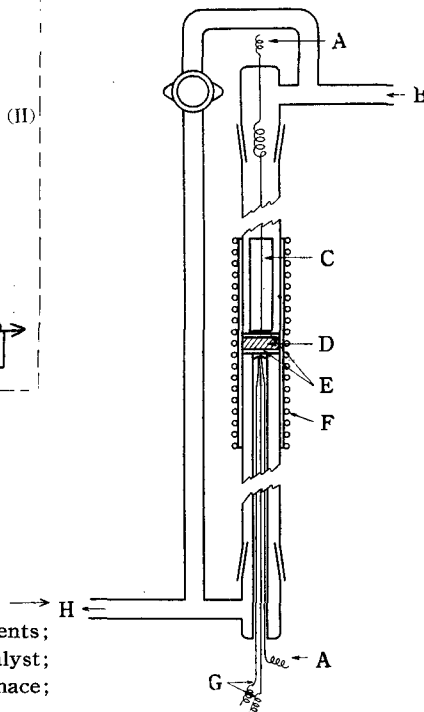

Fig. 1. Schematic diagram of the apparatus.
A, Reservor (N_2O+O_2); B, Gas leak; C, McLeod gauge; D, Mercury manometer; E, Reaction vessel; F, Trap; G, Flow meter; H, N_2O cylinder; 1, N_2 cylinder; J, Pump.

Fig. 2. Reaction vessel.
A, Lead wires for conductivity measurements; B, Gas inlet; C, Weight (500g); D, Catalyst; E, Platinum electrode; F. Electric furnace; G, Thermocouple; H, Gas outlet.

The measurements of the electrical conductivity during the reaction were made by means of the conductivity cell shown in Fig. 2; A weight applied a constant pressure to the catalyst held between two platinum electrodes. Conductivity was determined by a Wheatstone bridge. It was confirmed that the presence of the electrodes and lead wires beared no effect on the rate of reaction.

3. Results

The rate of decomposition of nitrous oxide at a constant oxygen pressure was found to be proportional to P_{N_2O}, that is

$$-dP_{N_2O}/dt = kP_{N_2O}$$

A constant k decreases with increasing oxygen pressure, an example being given in Fig. 3. Fig. 4 shows the electrical conductivity of zinc oxide during the reaction (in the mixture of N_2, O_2 and N_2O) together with that of the same catalyst in pure oxygen; there is little difference between the two conductivity values. Similar results were obtained with nickel oxide and also with doped catalysts.
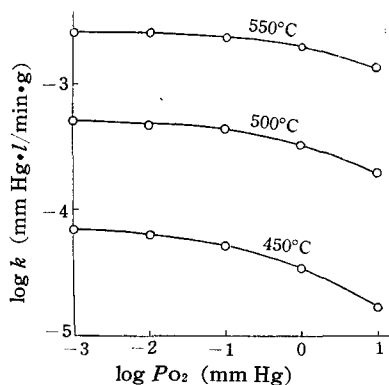
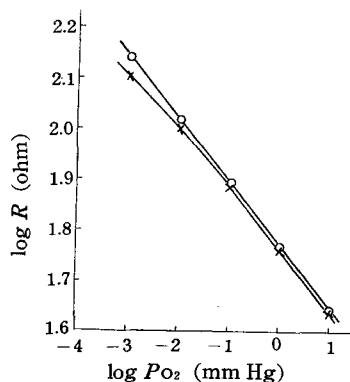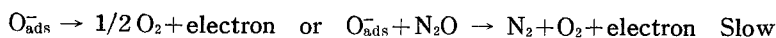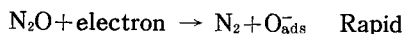Fig. 3.   Decrease in k on pure zinc oxide with increasing P_{O_2}.

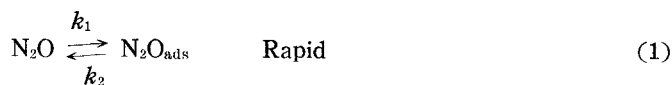Fig. 4.   Electrical resistance of pure zinc oxide as a fuuction of P_{O_2}. ○ in O_2; × during the reaction
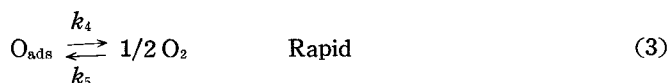
4. Discussion

Hauffe et al.[2] showed that the doping with lithium which leads to an increase in the concentration of positive holes in nickel oxide also increased its activity for the nitrous oxide decomposition. From this result together with the fact that p-type oxide is the best catalyst for this reaction, they concluded that the rate-determining step of this reaction on oxides is the desorption of chemisorbed oxygen, O^-_{ads}, that is

$$N_2O + electron \rightarrow N_2 + O^-_{ads}   \text{Rapid}$$

$$O^-_{ads} \rightarrow 1/2\, O_2 + electron   \text{or}   O^-_{ads} + N_2O \rightarrow N_2 + O_2 + electron   \text{Slow}$$

On the other hand, from a detailed study of the kinetics, Parravano and Rheaume[3] have concluded that the rate-determining step of the decomposition of nitrous oxide on α-MnO is the decomposition of adsorbed N_2O molecules.

As described above, the electrical conductivity of the catalysts during the reaction is almost the same as that obtained in pure oxygen of the same pressure, indicating that the adsorption equilibrium of oxygen is established during the reaction. In addition, the rate of reaction is proportional to P_{N_2O}. It may therefore be concluded that the same reaction mechanism as that proposed by Parravano is applied to the present system:

$$N_2O \underset{k_2}{\overset{k_1}{\rightleftarrows}} N_2O_{ads}   \text{Rapid} \tag{1}$$

$$N_2O_{ads} \xrightarrow{k_3} N_2 + O_{ads} \quad \text{Slow} \qquad (2)$$

$$O_{ads} \underset{k_5}{\overset{k_4}{\rightleftarrows}} 1/2\,O_2 \quad \text{Rapid} \qquad (3)$$

Winter has recently shown from an isotopic exchange experiment that the decomposition of N_2O on nickel oxide takes place on a small fraction of the total sites.[6]   This suggests that the sites catalyzing step (2) will probably be associated with a narrow range of activation energy, that is, they are energetically almost uniform, although the surface is undoubtedly heterogeneous. Under such conditions the rate of decomposition will be

$$-\frac{dP_{N_2O}}{dt} = \frac{k_3(k_1/k_2)P_{N_2O}[s_0]}{1+(k_1/k_2)P_{N_2O}+(k_5/k_4)P_{O_2}^{1/2}} \qquad (4)$$

$[s_0]$ is the number of active sites.   Since the rate is proportional to P_{N_2O}, $(k_1/k_2)P_{N_2O}$ $\ll 1+(k_5/k_4)P_{O_2}^{1/2}$.   Hence, Eq. 4 becomes

$$-\frac{dP_{N_2O}}{dt} = \frac{k_3(k_1/k_2)P_{N_2O}[s_0]}{1+(k_5/k_4)P_{O_2}^{1/2}} \qquad (5)$$

The constant k defined by Eq. 1 is given by

$$k = \frac{k_3(k_1/k_2)[s_0]}{1+(k_5/k_4)P_{O_2}^{1/2}} \qquad (6)$$

Rearranging Eq. 6

$$\frac{1}{k} = \frac{1}{k_3(k_1/k_2)[s_0]} + \frac{(k_5/k_4)P_{O_2}^{1/2}}{k_3(k_1/k_2)[s_0]} \qquad (7)$$

According to Eq. 7, if $1/k$ is plotted against $P_{O_2}^{1/2}$, the result should be a straight line. It was found that such a linear relationship actually holds with all the catalysts; a typical example is shown in Fig. 5. From the intercept and slope, values of $k_3(k_1/k_2)[s_0]$ and k_5/k_4 were calculated with the results shown in Table 1. Since k_5/k_4 represents the adsorption eqilibrium constant of oxygen, its temperature dependence should give the heat of adsorption of oxygen referred to the active site s_0 mentioned above; the heats of adsorption thus obtained are 34 kcal/mol for ZnO systems and 50 kcal/mol for NiO systems, in approximate agreement with the heats of adsorption at $\theta \simeq 0.5$ directly obtained from the adsorption experiments.
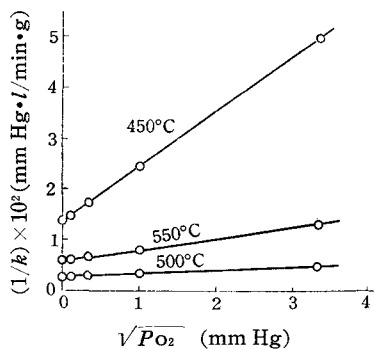

Fig. 5.   Relation between $1/k$ and $\sqrt{P_{O_2}}$ on pure nickel oxide.

Effect of Doping:— As seen in Table 1, the values of $k_3(k_1/k_2)[s_0]/S_A$ are almost independent of doping for both nickel oxide and zinc oxide systems, indicating that $k_3(k_1/k_2)$ as well as $[s_0]/S_A$ is almost constant on each system.   Such constant value

Table 1*

Catalyst	$k_3(k_1/k_2)[s_0]$ (mm Hg·l/min·g)	$k_3(k_1/k_2)[s_0]/S_A$	k_5/k_4
ZnO	3.0×10^{11} e$^{-42,000/RT}$	1.30×10^{12} e$^{-42,000/RT}$	7.8×10^{-6} e$^{17,000/RT}$
ZnO + 0.5 % Li$_2$O	3.9×10^{11} e$^{-42,000/RT}$	1.30×10^{12} e$^{-42,000/RT}$	5.0×10^{-6} e$^{17,000/RT}$
ZnO + 1 % Li$_2$O	9.4×10^{11} e$^{-42,000/RT}$	1.34×10^{12} e$^{-42,000/RT}$	1.0×10^{-6} e$^{17,000/RT}$
ZnO + 1 % Al$_2$O$_3$	2.4×10^{11} e$^{-42,000/RT}$	1.33×10^{12} e$^{-42,000/RT}$	4.0×10^{-5} e$^{17,000/RT}$
NiO	6.8×10^{5} e$^{-16,500/RT}$	6.80×10^{5} e$^{-16,500/RT}$	2.7×10^{-8} e$^{25,000/RT}$
NiO + 0.1 % Li$_2$O	4.8×10^{5} e$^{-16,500/RT}$	6.86×10^{5} e$^{-16,500/RT}$	8.0×10^{-9} e$^{25,000/RT}$
NiO + 1 % Li$_2$O	2.7×10^{5} e$^{-16,500/RT}$	6.85×10^{5} e$^{-16,500/RT}$	8.3×10^{-9} e$^{25,000/RT}$
NiO + 1 % Cr$_2$O$_3$	1.1×10^{5} e$^{-16,500/RT}$	6.87×10^{5} e$^{-16,500/RT}$	5.0×10^{-8} e$^{25,000/RT}$

* For both systems it was found that values of $E_4 - E_5$ obtained from the temperature dependence of k_5/k_4 were almost the same on all the catalysts with or without doping within the experimental error, $\pm 5\%$. Values of $E_4 - E_5$ represented in Table 1 are the mean of the experimental values obtained with each catalysts. The Boltzmann factors in $k_3 \cdot k_1/k_2 \cdot [s_0]$ in Table 1 are also such mean values.

of $k_3(k_1/k_2)$, in turn, suggests that doping gives little effect on both k_3 (the rate constant of the decomposition of N$_2$O$_{ads}$) and k_1/k_2 (the adsorption equilibrium constant of N$_2$O). On the other hand, the constant value of $[s_0]/S_A$ indicates that the number of active sites $[s_0]$ is affected by doping, varying in proportion to the amount of oxygen adsorbed at saturation, S_A. Since the value of S_A is increased with the concentration of lattice defects[7], it follows that the number of active sites is larger on the catalyst with a higher concentration of lattice defects.

Although, as seen in Table 1, the adsorption equilibrium constant of oxygen k_5/k_4 is varied by doping, its temperature dependence is unaffected. Such behavior of k_5/k_4 would be expected from the results of oxygen chemisorption described in the previous paper.

The frequently reported change in the activation energy of the decomposition of N$_2$O appears to be explicable in terms of the following concept: The variation in k_5/k_4 caused by doping described above will affect the equilibrium coverage of oxygen at a given pressure, which is probably reflected in the apparent activation energy of the reaction. For both nickel oxide and zinc oxide the doping with lithium which

Table 2

Catalyst	Activation energy (kcal/mol)
ZnO	48.7
ZnO + 0.5 % Li$_2$O	46.5
ZnO + 1 % Li$_2$O	41.6
ZnO + 1 % Al$_2$O$_3$	53.5
NiO	25.5
NiO + 0.1 % Li$_2$O	20.0
NiO + 1 % Li$_2$O	20.5
NiO + 1 % Cr$_2$O$_3$	34.5

decreases k_5/k_4, will also decrease the activation energy of the reaction, while the doping with aluminum will have a reverse effect. In fact, as seen in Table 2, the apparent activation energy calculated from the values of k at 1 mmHg varies in an expected manner. Similar variation in the activation energy is observed with the results of Hauffe and other workers as seen in Table 3. It seems therefore unjustified to conclude, as done by Hauffe and other workers, that such a change in the activation energy as shown in Table 3 provides conclusive evidence that the slowest step is the desorption of chemisorbed oxygen ion O^-_{ads}, since similar change in the activation energy can be expected on the ground of a different mechanism of the reaction.

Table 3

Catalyst	Activation energy (kcal/mol)		
	Schwab	Hauffe	Dewing
ZnO	47		
ZnO+0.5% Li₂O	29		
ZnO+1% Li₂O	45		
ZnO+1% Al₂O₃	64		
NiO		31.7	8
NiO+0.1% Li₂O		15.9	5
NiO+1% Li₂O		24.6	5
NiO+1% In₂O₃		27.3	
NiO+1% Cr₂O₃			16

As for the work of Dewing and Cvetanovic, somewhat different mechanism seems to be necessary to explain their experimental results, considering an extremly low pressure of oxygen used in their work. The effect caused by doping, however, is again probably attributed to a change in the equilibrium coverage of oxygen during the reaction as suggested by themselves. Furthermore, an extensive study of this reaction catalyzed by doped nickel oxide has been recently made by Winter,[9] who considers that the reaction proceeds by the same mechanism as that advanced by Parravano and the present authors, although his results are somewhat different from ours.

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