

## Nitrous Oxide decomposition over Metal Oxide Catalysts

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### 〈Abstract〉

Activities of vanadium-containing metal oxide solid solution catalyst in nitrous oxide decomposition was studied.

A pure vanadium oxide is quite active for  $N_2O$  decomposition. But it was shown that introduction of chromium had some effects on the absolute rate constant. An increasing of the introduced amounts of  $Cr^{3+}$  enhanced the activity for  $N_2O$  decompositions, which rised to a maximum at  $V_{1.93}Cr_{0.07}O_3$  inspite of the highest activation energy.

The introduction of a small amount of aluminium does not decrease the activity for  $N_2O$  decomposition. But thereafter the activity steadily falls in keeping high activation energy.

The mechanism of the decomposition of  $N_2O$  on the metal oxide has been suggested.

### 금속산화물 촉매에 의한 $N_2O$ 의 분해에 관한 연구

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### 〈요 약〉

금속산화물 촉매( $Cr_2O_3$ - $V_2O_5$  계열과  $Al_2O_3$ - $V_2O_5$  계열 고용체)에 의한 산화질소( $N_2O$ )의 분해반응에 대하여 연구하였다.

두계열 공히  $V_2O_5$  만으로도 상당히 큰 활성을 갖고 있으나  $Cr^{3+}$  이온을 첨가하면  $N_2O$  분해반응에 대한 활성을 확실히 증가시키고 있음을 알수 있었다. 활성도는  $V_{1.93}Cr_{0.07}O_3$ 의 경우 큰 활성화에너지를 갖고 있음에도 불구하고 제일 높은 것으로 나타났다. 반면  $Al^{3+}$  이온을 첨가함에 따라  $N_2O$  분해반응에 대한 활성을 감소시켜 줄을 알수 있었다.

금속산화물 촉매에 의한 산화질소 분해반응에 대한 메카니즘도 조사하였다.

### I. Introduction

Heterogeneous catalysis is of enormous importance for the large scale production of chemicals.

Most solid catalysts are prepared in supported form with the active component dispersed over

a refractory carrier. Both bulk and surface information are required for a thorough understanding of the active component. Important bulk properties include composition, structure, crystal shape, crystal size and size distribution and interaction with support. Surface properties include exposed planes, atomic configuration, and modes, amounts and energetics for the

chemisorption of specific adsorbates.

Most successful industrial catalysts are not well defined solids in terms of their structure, solid state and surface properties. The precise way in which they affect the activity and selectivity of a catalysed reaction is not well understood.

So, although the catalytic researcher cannot yet design a solid-state catalyst so that precise selectivities may be predicted, a continuous research effort is devoted to improving the effectiveness of these catalysts.

A number of theories have been put forward by scientists over the years in order to provide an insight into the governing factors of catalysis. The most notable are the crystalfield theory, the 'multiplet' theory and the electronic theory of catalysis. No one theory takes into consideration all the important parameters which might determine catalyst reactivity. Perhaps the greatest disadvantage of these "universal" theories lies in their attempts to correlate too many reactions and too many catalysts. As Roginskii<sup>(1)</sup> rightly observed, the diversity of catalysis and the mechanisms involved preclude the possibility of finding a comprehensive solution. It would, therefore, be fair to see these theories as essentially non-competing since in the main, they concern different aspects of catalysis. It is on this basis that we would discuss briefly, some of their assumptions, successes and limitations. Later in this work, we will attempt to employ them, where appropriate, in the interpretation of some of our experimental results.

The crystal field theory is useful in understanding some physical properties of transition metals like optical and electronic absorption<sup>(2)</sup>. It also gives us an insight into the adsorption behaviour on oxide catalysts<sup>(3)</sup>. As has been shown in the text, the catalytic activity of the transition metal oxides is a function of the number of d-electrons in the t. m. i.

Balandin's theory<sup>(4)</sup> does help us to understand how reacting molecules adsorb on the catalyst surface and particularly emphasises the importance of geometric and energetic factors in the understanding of activity and selectivity patterns over solid catalysts.

Formulation and application of the electronic theory<sup>(5,6)</sup> of catalysis on metal oxides is faced with a lot of formidable problems when it comes to matching theory with experiment. Its applicability is limited since the presence of a large variety of trapping levels and the inter-relation of semiconducting and defect properties complicate the interpretation of rate measurements as have been demonstrated by Harkins et. al.<sup>(7)</sup>, Gray and Lowrey<sup>(8)</sup>. As Stone<sup>(9)</sup> has rightly pointed out, we also have to take account of the following factors:

(1) The localised energy states of a solid oxide are numerous and widely distributed.

(2) The appropriate electron affinities and ionisation energies of reactant molecules are not unique quantities and may not even be those of the ground state.

(3) Kinetic control of catalysis may reside entirely in a configurational activation of mobile species already chemisorbed and it is certainly clear that many chemisorbed forms are co-existing. Thus, it is hardly surprising that in many cases, activity patterns in catalysis do not match the expectations of the theory.

However, Volkenshtein's effort has provided some solution to some of the limitations of this theory. His treatment of the adsorption process in terms of conduction behaviour of the catalyst is a description in terms of the collective electronic properties of the solid. The change in work function and electrical conductivity under the influence of chemisorption is an important consequence of the theory. The theory thus provides us with a means of investigating the parameters which determine the activity and selectivity of some catalysts.

This project is designed to study the solid-state and catalytic properties of some chromium and aluminium containing in a vanadium-oxide matrix.

An attempt will be made to identify the catalyst parameters which are important in determining the reactivity and selectivity of these oxidation catalysts.

## II. Experimental

### 1. Catalyst Preparation

Catalyst designers generally adjust metal ion concentration, method of preparation, type of support and additives to maximise the exposed metal surface and provide resistance to loss of surface area. The crystallite size is important because the smaller the radius of the particles, the higher will be the exposed surface per volume. Some reactions occur on specific types of surface sites e.g. atoms on crystal corners, edges, preferred faces, etc. Since the fraction of surface atoms of a given surface varies with the crystallite size, the activity per unit surface area is a function of radius.

Operating catalysts seldom exhibit unisize crystallites. Thus catalysts may have the same measured surface area but because of distribution inequalities, exhibit differing activities. So, size dependent factors must be integrated over the distribution.

Most catalysts are prepared in supported form with the active component dispersed on a refractory carrier.

In certain cases, it is necessary to control the oxidation or reduction of the resulting catalyst. The  $V_{2-x}Cr_xO_3$  solid-solution catalysts were prepared having compositions corresponding  $x=0, 0.005, 0.01, 0.02, 0.03, 0.04, 0.07$  and  $0.10$ . Stoichiometric amounts of vanadium trioxide and chromium trioxid (Analar, BDH) were mixed in platinum crucible and fired in a furnace at  $1,200^\circ\text{C}$  for 24hours in He/Ar

atmosphrere. During this heating period, the catalysts were removed three or more times from the furnace, cooled and throughly ground. Vanadium trioxide was prepared from ammonium metavanadate (Analar, BDH). The  $V_{2-x}Al_xO_3$  solid solution cutalysts were prepared by same method.

### 2. Surface Area Measurement

The surface areas of the metal oxide catalysts can be measured by a continuous flow method first proposed by Nelson and Eggersten<sup>(10)</sup>. It involves the measurement of the amount of gas adsorbed from a flowing mixture of  $N_2$  (adsorbate) and Helium (diluent) at liquid nitrogen temperature. A known nitrogen-helium mixture at atmospheric pressure is continuously passed over the catalyst and the adsorbed  $N_2$  is then desorbed by warming the catalyst.

The amount of gas desorbed is measured by a well-isolated thermistor block of thermal conductivity detectors placed in a water bath and maintained at a constant temperature of about  $30^\circ\text{C}$ . The response of the thermal conductivity detectors is shown on the chart of a recording potentiometer which also has an integrator.

The sample cell is immersed in liquid nitrogen and the cooled catalyst adsorbs nitrogen at liquid nitrogen temperature and therefore temporarily reduces the nitrogen concentration in the  $N_2$ -He mixture. The adsorbed  $N_2$  is liberated when the sample tube is warmed and thus the  $N_2$  in the effluent is temporarily increased.

The adsorption and desorption processes are represented as peaks on the recorder chart and the areas of these peaks are direct functions of the amount of nitrogen adsorbed and desorbed by the catalysts.

Linearity of detector response over the entire  $N_2$ -He composition range is assumed. Since the limits are narrow, this assumption will not produce errors greater than  $\pm 10\%$  in most cases<sup>(11)</sup>

In cases of samples with small surface areas as in our work, the change in gas flow-rate as a result of the desorption process is not great.

Determinations were made at relative nitrogen pressures ( $p/p_0$ ) between 0.05 and 0.30. The isotherm was calculated using the Brunauer-Emmett-Teller (B. E. T.) equations<sup>(12)</sup>

$$\frac{P}{V_s(P-P_0)} = \frac{1}{V_m C} + \frac{(C-1)}{V_m C} \cdot \frac{P}{P_0} \quad (1)$$

$P$  = partial pressure of nitrogen

$P_0$  = saturation pressure of nitrogen

$V_m$  = monolayer capacity

$V_s$  = volume of nitrogen adsorbed

$C$  = is a constant.

If  $X = \frac{P}{P_0}$ , (relative pressure of  $N_2$ )

$$\text{then } \frac{X}{V_s(1-X)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} \cdot X \quad (2)$$

From a BET plot of  $\frac{X}{V_s(1-X)}$  against  $X$ , the specific surface areas are calculated. The results obtained are shown on Tables 1 and 2

**Table 1. The Surface Area of  $V_{2-x}Cr_xO_3$  Series Catalysts**

| Catalyst                       | Surface Area ( $m^2g^{-1}$ ) |
|--------------------------------|------------------------------|
| $V_{2-x}Cr_xO_3$ ( $x=0$ )     | 1.52                         |
| $V_{2-x}Cr_xO_3$ ( $x=0.005$ ) | 1.04                         |
| $V_{2-x}Cr_xO_3$ ( $x=0.01$ )  | 1.33                         |
| $V_{2-x}Cr_xO_3$ ( $x=0.02$ )  | 1.43                         |
| $V_{2-x}Cr_xO_3$ ( $x=0.03$ )  | 1.45                         |
| $V_{2-x}Cr_xO_3$ ( $x=0.04$ )  | 1.26                         |
| $V_{2-x}Cr_xO_3$ ( $x=0.07$ )  | 1.09                         |
| $V_{2-x}Cr_xO_3$ ( $x=0.10$ )  | 1.31                         |

**Table 2. The Surface Area of  $V_{2-x}Al_xO_3$  Series Catalysts**

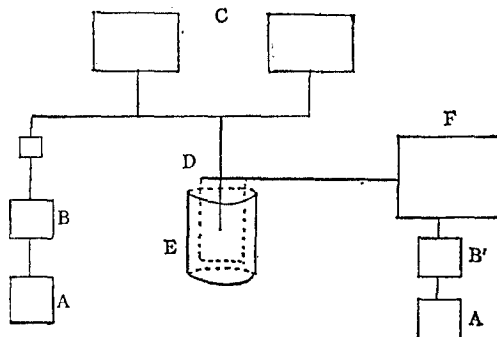
| Catalyst                       | Surface Area ( $m^2g^{-1}$ ) |
|--------------------------------|------------------------------|
| $V_{2-x}Al_xO_3$ ( $x=0$ )     | 1.52                         |
| $V_{2-x}Al_xO_3$ ( $x=0.005$ ) | 1.17                         |
| $V_{2-x}Al_xO_3$ ( $x=0.01$ )  | 3.00                         |
| $V_{2-x}Al_xO_3$ ( $x=0.02$ )  | 2.44                         |
| $V_{2-x}Al_xO_3$ ( $x=0.03$ )  | 2.77                         |
| $V_{2-x}Al_xO_3$ ( $x=0.04$ )  | 2.57                         |
| $V_{2-x}Al_xO_3$ ( $x=0.07$ )  | 2.19                         |
| $V_{2-x}Al_xO_3$ ( $x=0.10$ )  | 2.16                         |

### 3. X-Ray Powder Diffraction

Crystal structure was monitored by X-ray diffraction measurements using a Debye-Scherrer camera and Ni-filtered  $Cu K\alpha$  radiation.

### 4. The Decomposition of $N_2O$

$N_2O$  decomposition was carried out in a silica reactor of volume  $65cm^3$ , at a pressure of about  $21 \pm 2$  Torr. (1 Torr =  $133.3Nm^{-2}$ ) in the temperature range  $300 \sim 500^\circ C$  using the system shown in Fig. 1.



**Fig. 1. The system used for the decomposition of  $N_2O$**

- (A) Rotary pump
- (B) Mercury diffusion pump
- (B') Oil diffusion pump
- (C) Stored gases
- (D) Reactor
- (E) Furnace
- (F) Mass spectrometer (MS 10)

Approximately 0.5gm of catalyst was used for each experiment. Catalyst pretreatment consisted in outgassing the samples initially for 16 hrs at  $800^\circ C$  and  $10^{-5}$  Torr. Outgassing at  $800^\circ C$  for 30 mins. between each reaction gave reproducible results. The catalysts were protected from mercury contamination by liquid- $N_2$  traps. The  $N_2O$  used was purified by freezing in liquid nitrogen and pumping off incondensable impurities and was then stored in a gas reservoir over mercury. The extent of reaction was followed by continuous sampling

of the products through a capillary leak to the head of an A.E.I. MS10 mass spectrometer which had been calibrated for sensitivity to  $N_2$ ,  $O_2$  and  $N_2O$ .

### III. Results

The absolute velocity constants were calculated from the equation<sup>(13)</sup>

$$K_{obs} = P_{N_2} V (P_{N_2O} A t)^{-1} \text{ cm min}^{-1}$$

where  $P_{N_2}$  is the pressure of  $N_2$  gas produced (Torr),  $V$  is the volume of the reaction vessel ( $\text{cm}^3$ ),  $P_{N_2O}$  is the initial  $N_2O$  pressure (Torr),  $A$  is the surface area of the catalyst ( $\text{cm}^2$ ) and  $t$  is the reaction time (min). Values of  $K_{obs}$  were calculated using the equation above and the kinetic parameters. The results for both

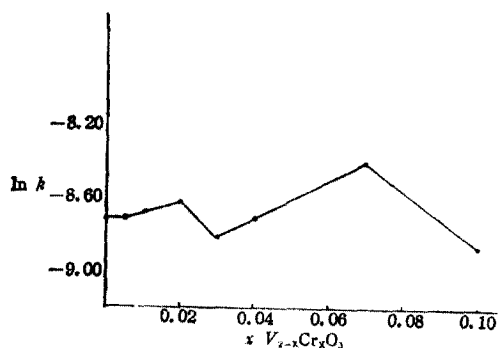
series of solid solutions are presented in Tables 3-5.

**Table 4. Kinetic Parameters for  $N_2O$  Decomposition on  $V_{2-x}Al_xO_3$  Solid Solutions.**

| Catalyst  | ln k   |        |        | ln     |
|-----------|--------|--------|--------|--------|
|           | 500°C  | 470°C  | 440°C  | (k/Al) |
| $x=0.000$ | -8.72  | -9.27  | -9.66  |        |
| $x=0.005$ | -8.71  | -9.35  | -9.84  | -3.41  |
| $x=0.01$  | -9.56  | -10.19 | -10.72 | -4.95  |
| $x=0.02$  | -9.38  | -9.72  | -10.22 | -5.47  |
| $x=0.03$  | -9.59  | -10.00 | -10.41 | -6.08  |
| $x=0.04$  | -9.72  | -10.49 | -11.04 | -6.50  |
| $x=0.07$  | -9.95  | -10.47 | -10.97 | -7.29  |
| $x=0.10$  | -10.47 | -11.28 | -11.98 | -8.17  |

**Table 3. Kinetic Parameters for  $N_2O$  Decomposition on  $V_{2-x}Cr_xO_3$  Solutions**

| Catalyst  | ln k  |       |       | ln     |
|-----------|-------|-------|-------|--------|
|           | 500°C | 470°C | 440°C | (k/Cr) |
| $x=0.000$ | -8.72 | -9.27 | -9.66 | —      |
| $x=0.005$ | -8.72 | -9.35 | -9.86 | -3.42  |
| $x=0.01$  | -8.69 | -9.36 | -9.87 | -4.08  |
| $x=0.02$  | -8.63 | -9.24 | -9.80 | -4.72  |
| $x=0.03$  | -8.82 | -9.33 | -9.84 | -5.31  |
| $x=0.04$  | -8.72 | -9.13 | -9.84 | -5.50  |
| $x=0.07$  | -8.41 | -9.03 | -9.70 | -5.75  |
| $x=0.10$  | -8.87 | -9.29 | -9.71 | -6.56  |



**Fig. 2. The variation of ln k with chromium content for  $V_{2-x}Cr_xO_3$  solid solution at 500°C.**

**Table 5. Activation Energy for  $N_2O$  Decomposition on  $V_{2-x}Cr_xO_3$  and  $V_{2-x}Al_xO_3$  Solid Solutions**

| Catalyst         |           | Activation Energy (Kcal/mole) | Catalyst         |           | Activation Energy (Kcal/mole) |
|------------------|-----------|-------------------------------|------------------|-----------|-------------------------------|
| $V_{2-x}Cr_xO_3$ | $x=0$     | 15.0                          | $V_{2-x}Al_xO_3$ | $x=0$     | 15.0                          |
|                  | $x=0.005$ | 21.3                          |                  | $x=0.005$ | 19.8                          |
|                  | $x=0.01$  | 21.5                          |                  | $x=0.01$  | 20.8                          |
|                  | $x=0.02$  | 21.1                          |                  | $x=0.02$  | 15.3                          |
|                  | $x=0.03$  | 18.8                          |                  | $x=0.03$  | 15.2                          |
|                  | $x=0.04$  | 20.3                          |                  | $x=0.04$  | 23.4                          |
|                  | $x=0.07$  | 24.4                          |                  | $x=0.07$  | 19.5                          |
|                  | $x=0.10$  | 15.7                          |                  | $x=0.10$  | 27.7                          |

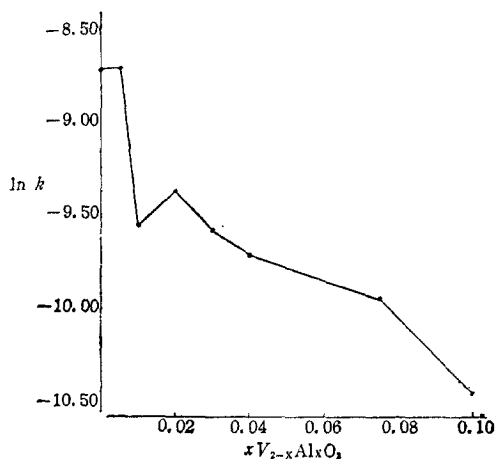


Fig. 3. The variation of  $\ln k$  with aluminium content for  $V_{2-x}Al_xO_3$  solid solution at  $500^\circ C$

#### IV. Discussion

From Table 5, a small decrease in activation energy is observed from  $V_{1.995}Cr_{0.005}O_3$  to  $V_{1.97}Cr_{0.03}O_3$ .  $E_a$  rises again to a maximum value at  $V_{1.93}Cr_{0.07}O_3$ .

Fig. 2 shows the variation of the absolute rate constant content with chromium content at  $500^\circ C$  for this series of solid solutions.  $V_2O_3$  is quite active but the introduction of chromium has a some effect on the absolute rate constant. Clearly, this introduction of  $Cr^{3+}$  ions enhances the activity for  $N_2O$  decomposition. Thus, activity rises to a maximum at  $V_{1.93}Cr_{0.07}O_3$  inspite of the highest activation energy. Activity finally falls sharply at  $V_{1.90}Cr_{0.1}O_3$ . As seen Table 5, apparent activation energy is highest for  $V_{1.90}Al_{0.1}O_3$ .

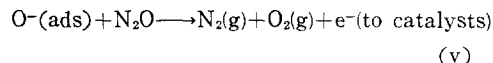
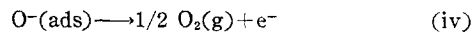
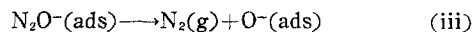
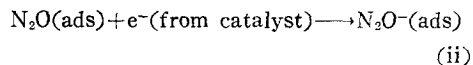
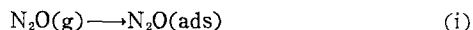
Fig. 3 shows that  $V_{1.90}Al_{0.1}O_3$  is the least active for  $N_2O$  decomposition at  $500^\circ C$ .  $V_2O_3$  is quite active but introduction of a small amount of aluminium at  $V_{1.995}Al_{0.005}O_3$  has a some effect on the absolute rate constant. Clearly, this introduction of  $Al^{3+}$  ion decreases the activity for  $N_2O$  decomposition with increasing

the apparent activation energy some what. But, activity rises to a maximum at  $V_{1.995}Al_{0.005}O_3$ . Thereafter, activity steadily falls at  $V_{1.9}Al_{0.1}O_3$  in keeping with its comparatively high activation energy.

The catalytic activities of several transition metal oxide solid solutions for  $N_2O$  decomposition, have been extensively investigated.<sup>(14-15)</sup> There is general agreement that for such catalysts; (a) the "d-correlation" with maxima of activity at  $d^{3-4}$  and  $d^{7-8}$  and minima at  $d^0$ ,  $d^5$  and  $d^{10}$  is observed; (b) the dilute solid solutions appear to be more active per cation; (c) the activity is not a monotonic function of the transition metal ion concentration in the solvent; and (d) the octahedrel sites are more active than the tetrahedral sites.

Nitrous oxide decomposition over transition metal oxide catalysts is frequently utilized as a test reaction in order to examine the electronic properties of these catalysts.

The mechanism of this reaction is thought to follow the scheme below<sup>(15)</sup>;



It is, therefore, clear that electron transfer to and from the catalyst is important in terms of initial adsorption step (ii) and desorption step (iv). Measurement of the overall reaction kinetics and the extent to which oxygen is retained on the catalyst surface, enables one to correlate the ease of electron transfer during the reaction with the electronic features of the various catalysts.

The decomposition of  $N_2O$  over transition metal oxide catalysts (e.g. Chromia Alumina catalysts), has been classified as a "donor" type reaction<sup>(15)</sup>. It therefore follows that the

introduction of positive holes into the catalyst (e.g.  $\text{Li}_2\text{O}$  into  $\text{NiO}$ ), will increase the reaction rate while the introduction of electrons (e.g.  $\text{In}_2\text{O}_3$  into  $\text{NiO}$ ), will decrease the rate<sup>(16)</sup>. P-type semi-conductors thus appear to be better catalysts than n-type semi-conductors<sup>(17)</sup>. This high activity of p-type oxides for  $\text{N}_2\text{O}$  decomposition has been attributed to their low Fermi level since electrons furnished in the desorption reaction are in these cases readily absorbed by the positive holes in the valence band<sup>(18)</sup>. The relative activity pattern for various catalysts is given as p-type > n-type > insulators<sup>(17)</sup>, though other authors<sup>(16)</sup>, suggest that the sequence p-type > insulators > n-type is perhaps more appropriate.

The kinetic analysis of this reaction assumes that there is no change in the number of catalytic sites with temperature<sup>(19)</sup>, and earlier work<sup>(20)</sup> at low pressures, has indicated that generally, the overall activation energy is distinctly less than at high pressures. In most cases, the reaction has required relatively high temperatures (300–600°C), and it is thought unlikely that such temperatures, crystal field effects will be of much importance in determining the course and energetics of the reaction since appreciable surface mobility must be present under reaction conditions.

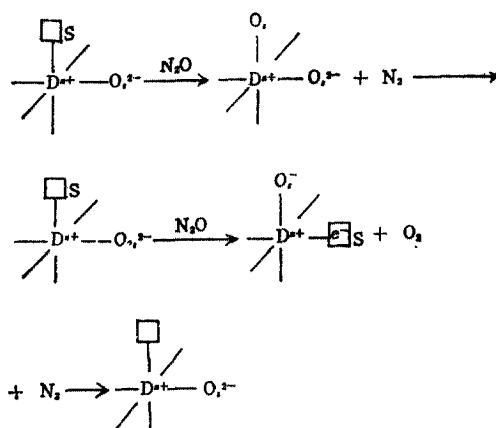
However, it is useful to note that at temperatures where the oxide ions of the lattice are readily removed and replaced, any agency which increases the number or stability of anionic vacancies in the surface appears to facilitate the decomposition process. This is because these anionic vacancies, (which have been identified<sup>(21)</sup> as the reaction sites in the chromia clusters on the surface of Chromia-Alumina catalysts), would be expected to facilitate the occurrence of reaction.

$\text{N}_2\text{O} + e_-(\text{from catalyst}) \rightarrow \text{N}_2 + \text{O}^-(\text{ads})$ ,  
leading to increased activity as such temperatures<sup>(17)</sup>.

Only one adsorption site is required in  $\text{N}_2\text{O}$  decomposition since the oxygen atom is directly produced from the nitrous oxide molecule. Thus the dissociation of  $\text{N}_2\text{O}$  leaves an oxygen atom chemisorbed on the centre responsible for this dissociation. Suppose this centre is D, then the dissociation step can be represented by



The next logical step must therefore be the breaking of the O–D bond. The released of oxygen can occur through the migration of the oxygen atom as follows:



Here,  $\square$  is an oxygen vacancy,  $e^-$  is an electron,  $n$  is the valence of the cation and  $s$  refers to surface position. (unspecified bonds lead to bulk or to other surface atoms). As can be seen, the release of  $\text{O}_2$  therefore facilitated by factors which favour the formation of the peroxide ion. This "peroxide mode" has been postulated by Bickley and Stone<sup>(22)</sup>. Since the strength of the O–D bond can be altered by various electron transfer processes (such as the donation of electrons from the bulk), a continuous change of catalyst-oxygen, bond strength can therefore be envisaged the two forms ( $\text{O}^-$  and  $\text{O}^{2-}$ ) being extreme cases. Irrespective of their nature, however, production of the weak form tends to be sustained during

catalysis. The catalytic process can, therefore, be correlated with the chemisorption of oxygen, and the nature and strength of the oxygen-surface complex will thus be responsible for catalytic activity.

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