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α-Cr_2O_3–Al_2O_3 Solid Solutions

II. The Catalytic Decomposition of Nitrous Oxide

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The sustained catalytic decomposition of nitrous oxide has been studied over α-Al_2O_3, α-Cr_2O_3 and a series of solid solutions α-$Cr_xAl_{2-x}O_3$. Activity *per chromium ion* is very high in the dilute solid solutions and declines with increasing Cr content, attaining an almost constant level between $x = 0.2$ and $x = 2.0$. The reduced activity in the chromium-rich solutions is shown to arise because of the retention of strongly adsorbed oxygen at the surface.

INTRODUCTION

In the preceding paper (Part I) (*1*), it was shown that α-Al_2O_3 has low activity for the adsorption of oxygen and the decomposition of N_2O at pressures where oxygen is not desorbed. When chromium ions are introduced in solid solution, the activity rises rapidly. In dilute solid solutions of α-$Cr_xAl_{2-x}O_3$ $(0 < x < 0.02)$, activity *per chromium ion* is very high, but this parameter then declines to pass through a minimum at $x \sim 0.2$ ($\sim$10% Cr). In chromium-rich solutions, the activity per chromium ion rises steadily, but does not achieve the values found in very dilute solutions. In this paper we extend the study of the decomposition of N_2O to conditions of sustained catalysis, i.e., conditions such that oxygen must be continually desorbed for reaction to progress. By comparing the results with those in Part I, it is possible to establish the influence of retained oxygen on the activity pattern as a function of chromium content.

The catalytic activity of Cr^{3+} and other transition metal ions for N_2O decomposition has been studied extensively in recent years by Cimino and co-workers (*2*), who have observed consistently higher turnover numbers when the ions are in dilute solutions in the relatively inert matrix of MgO than when they are concentrated. The activity of chromium ions dissolved in $MgAl_2O_4$ has also been studied (*3*), and we are now able to extend the comparison to the matrix α-Al_2O_3.

EXPERIMENTAL METHODS

The catalysts used were α-Al_2O_3, α-Cr_2O_3 and seven solid solutions α-$Cr_xAl_{2-x}O_3$ $(0.02 < x < 1.02)$. Their preparation and properties are summarized in Part I (*1*).

Oxygen adsorption was measured as in Part I. However, 40 N m^{-2} (1 Torr = 133 N m^{-2}) was chosen as the pressure at which adsorbed amounts were determined, since this was close to that prevailing in N_2O decomposition experiments after 50 min reaction, the normal duration of a catalytic run.

N_2O decomposition was studied in the apparatus described previously, N_2 and O_2 production being determined mass spectrometrically (*3*).

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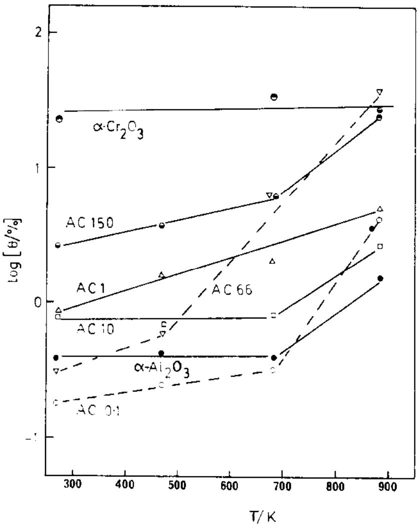

FIG. 1. Oxygen adsorption as a function of temperature at an equilibrium pressure of 40 N m^{-2}.

The reaction was studied at five or more temperatures from 673 to 893 K at a pressure (initially) of 4 kN m^{-2}, using ~0.5 g of catalyst. The pretreatment was an outgassing (~18 hr) at 1120 K and 10^{-3} N m^{-2}. Reproducible results were obtained by outgassing at 1120 K for 1 hr between runs.

RESULTS

Oxygen Adsorption

Oxygen adsorption was studied at 273, 473, 683 and 893 K. The data are presented in Fig. 1 as plots of log(θ/%) vs T for the steady state pressure of 40 N m^{-2} over the sample. Compared with the results at the steady state pressure of 1 N m^{-2} reported in Part I (*1*), the adsorption above 683 K rises more rapidly. The isobar for α-Cr$_2$O$_3$ is almost level, and the amount adsorbed on AC 0.1* at 683 K (and below) is less than on α-Al$_2$O$_3$ (cf. Part I). In the variation of oxygen coverage with chromium content at 683 K, which is at the beginning of the temperature range studied in N$_2$O decomposition, there is a maximum at AC 1, a minimum at AC 10 and then a rise to α-Cr$_2$O$_3$.

N$_2$O Decomposition

Absolute velocity constants were derived from the initial rates (*3*). The activation energies and pre-exponential factors obtained using the Arrhenius equation are shown in Table 1. It is noteworthy that activation energies for α-Al$_2$O$_3$ to AC 10 are some 12 to 40 kJ mol^{-1} below those for AC 25 to α-Cr$_2$O$_3$, whereas in the low pressure studies of Part I, it was the chromium-rich samples which had the low activation energies. Thus the fission of the N–O bond requires more energy of activation in the chromium-dilute samples than in the chromium-rich samples, whereas the reverse is true for the desorption of oxygen.

The variation of activity at 833 K is shown as a function of chromium content in Fig. 2. Data from the earlier study with spinel-phase solid solutions (*3*) are also shown in Fig. 2. It is interesting that the α-Cr$_x$Al$_{2-x}$O$_3$ catalysts are considerably more active than the MgCr$_x$Al$_{2-x}$O$_4$ catalysts. Clearly a matrix effect is important here. As in the case of MgAl$_2$O$_4$, the addition of a small quantity of Cr^{3+} to α-Al$_2$O$_3$ enhances the activity for N$_2$O decomposition at 833 K. The enhancement is, however, considerably less than on MgCr$_x$Al$_{2-x}$O$_4$. Increasing the chromium content beyond AC 1 results in a decreasing activity until at AC 10 activity is lower than on α-Al$_2$O$_3$ [cf. MgCr$_{0.67}$Al$_{1.33}$O$_4$ (SMAC 50) and MgAl$_2$O$_4$ (*3*)]. A further increase in [Cr]

TABLE 1

SURFACE AREAS OF α-Al$_2$O$_3$, α-Cr$_2$O$_3$ AND α-Cr$_x$Al$_{2-x}$O$_3$ SOLID SOLUTION CATALYSTS AND ARRHENIUS PARAMETERS FOR N$_2$O DECOMPOSITION

Catalyst	Surface area (m^2 g^{-1})	E (kJ mol^{-1})	log(A/cm s^{-1})
α-Al$_2$O$_3$	2.0	75.0	0.37
AC 1	2.2	77.5	0.47
AC 5	1.9	63.7	−0.30
AC 10	1.9	74.6	0.04
AC 25	0.4	97.8	1.46
AC 66	0.3	96.1	1.43
AC 150	0.5	85.5	1.41
α-Cr$_2$O$_3$	0.9	118.5	3.65

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* The nomenclature AC N denotes a solid solution α-Cr$_x$Al$_{2-x}$O$_3$ with N Cr atoms per 100 Al atoms.

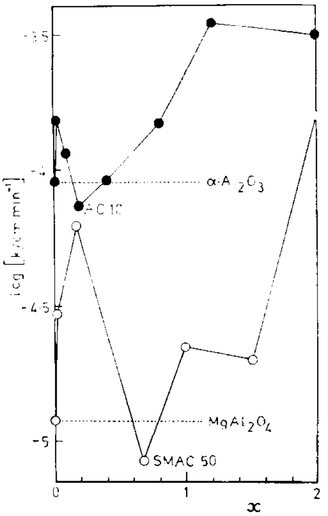


FIG. 2. Variation of activity at 833 K as a function of chromium content x in the corundum (α-$Cr_xAl_{2-x}O_3$) catalysts (●) and the spinel ($MgCr_xAl_{2-x}O_4$) catalysts (○) [Ref. (3)].

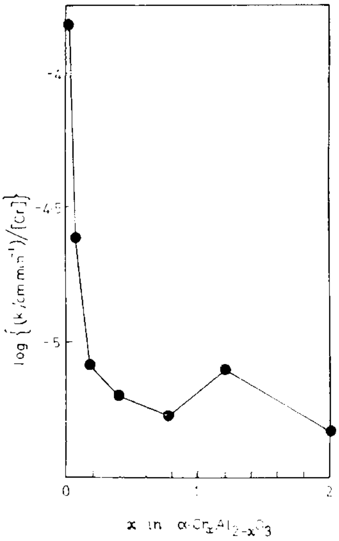


FIG. 3. Variation of activity per chromium ion as a function of the chromium content of the catalysts.

restores activity. Maximum activity is found on AC 150, followed by a decrease to α-Cr_2O_3. However, due to the higher activation energy, the activity of α-Cr_2O_3 will be greater than that of AC 150 at higher temperatures.

Additional light is shed on the activity pattern if we consider the variation of activity *per chromium ion.* Figure 3 demonstrates that increasing the Cr content, and thus increasing the electronic interactions between the Cr ions, has a marked effect on the activity per Cr ion. After the steep fall to AC 10 there is no pronounced rise in $k/[Cr]$. This contrasts markedly with the low pressure decomposition pattern and with the behavior on the spinels (3).

The N_2/O_2 Ratio

The N_2/O_2 ratio in the reaction vessel during decomposition of N_2O throughout the course of all the reactions was measured. The ratio deviated from the theoretical value of 2.0 in the direction of higher values as the temperature of reaction was decreased. This implies preferential adsorption of oxygen as the temperature is reduced. Figure 4 shows the ratio observed after 50 min reaction as a function of the reaction temperature. Although the ratio 2.0 is obtained on α-Al_2O_3 above 773 K, it rises rapidly below 723 K, indicating a considerable retention of oxygen. As [Cr] increases, the temperature at which a given ratio is observed increases to AC 5, then de-

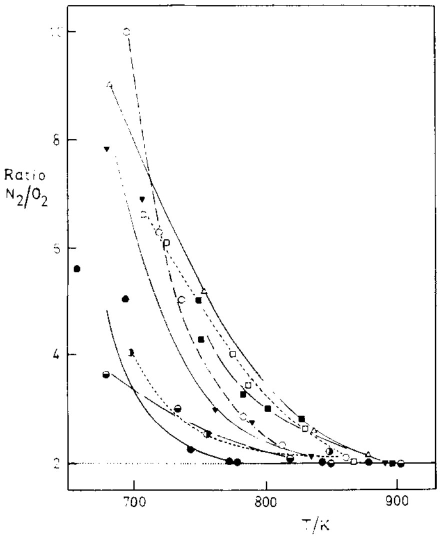


FIG. 4. Variation of N_2/O_2 ratio as a function of temperature for each catalyst after 50 min of reaction. (●) α-Al_2O_3; (○) AC 1; (□) AC 5; (▲) AC 10; (◑) AC 25; (■) AC 66; (◒) AC 150; (△) α-Cr_2O_3.

TABLE 2
OXYGEN RETENTION DURING THE CATALYTIC DECOMPOSITION OF N_2O

	T = 773 K				T = 833 K			
Catalyst	% reaction	N_2/O_2	θ%	θ_{Cr}%	% reaction	N_2/O_2	θ%	θ_{Cr}%
α-Al_2O_3	2.5	2.0	0	0	5.5	2.0	0	0
AC 1	2.5	2.8	15	1010	6.3	2.2	11	775
AC 5	2.7	3.5	38	540	4.4	2.3	13	190
AC 10	2.0	2.5	18	140	4.3	2.1	4	37
AC 25	0.8	2.6	12	45	3.4	2.2	17	54
AC 66	0.7	2.9	25	50	1.7	2.4	18	39
AC 150	2.8	2.4	32	46	8.8	2.1	20	29
α-Cr_2O_3	3.7	2.5	42	42	5.4	2.5	42	42

creases to AC 150 before increasing again to α-Cr_2O_3. This gives a further measure of the extent and strength of oxygen adsorption at the surface. However, it is more revealing, and more accurate, to calculate the oxygen coverage (Table 2). The coverages were calculated assuming dissociative adsorption of oxygen with equal areas of (100), (001) and (111) planes presented at the surface; the monolayer volume for oxygen adsorbed dissociatively on the cations of the corundum structure is then 0.20 cm^3 m^{-2} at STP. In Figure 5 the oxygen coverage is shown as a function of catalyst Cr content for reactions at 773 and 833 K. The oxygen partial pressure at this stage of the reaction is about 40 N m^{-2} (the same pressure at which oxygen adsorption was measured in the direct studies). There is a maximum of retained oxygen at AC 5 followed by a minimum at AC 10 (773 K) or AC 25 (833 K). Thereafter the coverage rises to about 50% on α-Cr_2O_3.

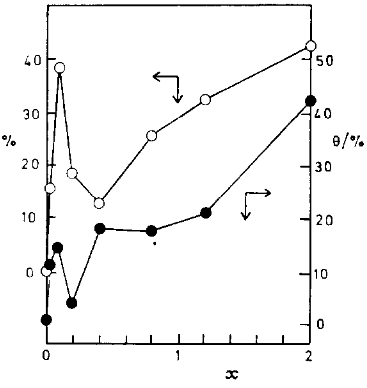


FIG. 5. Oxygen coverage during N_2O decomposition as a function of chromium content for reactions at 773 K (○) and 833 K (●).

It is clear that the Cr ions play a large part in the increased oxygen retention; significant information may therefore be obtained from a consideration of the oxygen coverage per chromium ion. In deriving this quantity it was not possible to correct for oxygen adsorption occurring during the decomposition reaction on the α-Al_2O_3 component of the solid solutions, since no oxygen retention was observed on pure α-Al_2O_3 from which extrapolation could be made. Nevertheless, the incorporation of Cr in α-Al_2O_3 results in oxygen retention on the α-Al_2O_3 component of the chromium-dilute solid solutions, since AC 1, AC 5 and AC 10 (at 773 K) all have θ_{Cr} values in excess of 100% (Table 2). The Cr ions do not seem to have a merely additive effect on the adsorptive properties of the α-Al_2O_3 host; their influence appears to be more fundamental. It would, therefore, be inappropriate to correct the *direct* oxygen adsorption data on the solid solutions for adsorption on α-Al_2O_3. In Fig. 6 $\log[\theta_{Cr}/\%]$ has been plotted as a function of chromium content for both the oxygen adsorption data obtained from the N_2/O_2 ratios at 833 K and the static adsorption data at 893 K. There is a broad correlation between the two sets of results. Two very significant results emerge from these data. First there is the result touched on above, that at 833 K the θ_{Cr} values are considerably over 100% for AC 1 → AC 5 (AC 10 at 773 K), though they decrease with chromium content. This

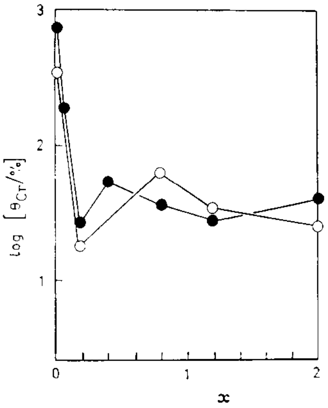


FIG. 6. Variation of oxygen coverage per chromium ion from both N_2O decomposition at 833 K (○) and static oxygen adsorption measurements at 893 K (●).

means that the addition of each chromium ion in going from α-Al_2O_3 to AC 1 leads to the adsorption of *more than one* oxygen atom. Secondly, the values of θ_{Cr} on AC 25 → α-Cr_2O_3 are approximately constant at 773 and 833 K at about 40–50%, which implies one oxygen atom per pair of Cr ions. Similar behavior involving a spill-over of oxygen has been found with CoO–MgO solid solutions (*4*).

Comparison of the Activation Energies for N_2O Decomposition in the Presence and Absence of Sustained Catalysis

If the reaction is assumed to be strongly inhibited by adsorbed oxygen, the rate equation will be of the form

$$-\frac{d(N_2O)}{dt} = \frac{kP_{N_2O}}{P_{O_2}{}^{0.5}}.$$

Since there is no desorption of oxygen in the low pressure reactions studied in Part I, the activation energy for the catalytic decomposition (E_c) will be related to that for the earlier low pressure reactions (E_L) by the expression

$$E_c = E_L + 0.5\, E_D,$$

where E_D is the activation energy for desorption of oxygen. From this expression we can obtain at least a rough estimate of the energy required to desorb oxygen from each of the catalysts. These data are collected in Table 3.

TABLE 3
ACTIVATION ENERGY OF DESORPTION OF OXYGEN

Catalyst	E_D (kJ mol^{-1})
α-Al_2O_3	32.4
AC 1	52.0
AC 5	46.0
AC 10	53.6
AC 25	84.0
AC 66	80.0[a]
AC 150	64.0
α-Cr_2O_3	105.2

[a] Estimated value.

DISCUSSION

In the previous paper (*1*) it was shown that isolated Cr ions and Cr ions which were part of an extensive electron exchange system were especially active in the initial step of N_2O decomposition. Isolated *pairs* of Cr ions had correspondingly smaller activity in this decomposition step.

Compared with the low pressure studies there are a number of contrasting features clearly evidenced in the present investigation. Nevertheless, the three distinctive regions of activity noted before (*1*) are still present. It is appropriate to discuss them in turn.

α-Al_2O_3 → AC 5

In Part I (*1*) it was suggested that the isolated Cr ions were the active sites in this Cr content region. In the low pressure system the number of chromium sites was always greater than the number of oxygen species retained. In the present pressure zone, however, the reverse is true; thus for reaction to continue, oxygen must be continually removed from the surface. Desorption of oxygen is more difficult on the Cr catalysts than on α-Al_2O_3. Thus although there is an activity increase on addition of Cr ions it is not so marked as in the low pressure zone. Maximum activity lies in the AC 1/AC 5 region, though as before, activity per Cr ion drops rapidly from AC 1. Clearly, isolated ions still form the basis of the favorable type of site. However, their mode of operation requires discussion.

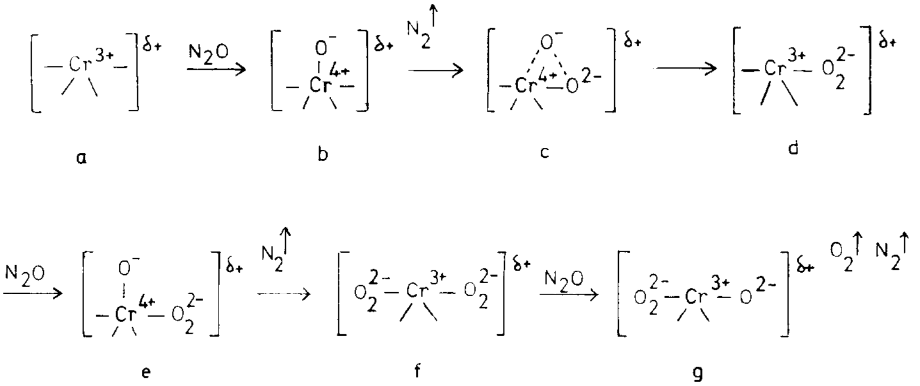
Before discussing the influence of Cr on the α-Al_2O_3 matrix, it is appropriate to consider the mechanism by which reaction may take place on α-Al_2O_3. Since α-Al_2O_3 is an insulator, the source of electrons on the surface is severely limited, so a formal electron transfer mechanism is not to be preferred. Evidence has been obtained, using ESR, to show that, as with MgO, peroxide ions can be formed on α-Al_2O_3 after adsorption of O_2 (*5*). Furthermore, the rate of oxygen exchange between gaseous oxygen and oxide oxygen on α-Al_2O_3 is somewhat higher than on MgO (*6*). It seems reasonable, therefore, to suggest that a scheme such as that proposed by Cimino and Indovina (*2*e) is followed in this case. The lower activation energy reflects the greater ease with which oxygen is lost from the surface. Thus it is suggested that the active site of initial reaction is coordinatively unsaturated Al^{3+}. Thereafter the adsorbed oxygen migrates to an oxide ion to form a peroxide ion and eventually oxygen gas is desorbed. The thermal stability of the adsorbed peroxide radical is not great and there is effectively no retained oxygen above 773 K (Fig. 4).

When a small number of chromium ions are incorporated in the α-Al_2O_3 structure (i.e., AC 1), an increase in activity occurs. Oxygen retention also rises substantially. The activity rise terminates in the region AC 1/AC 5, and activity per chromium ion decreases continuously from AC 1 to AC 10.

All the available evidence shows that the solid solutions are homogeneous in the surface and in the bulk (*1*, *7*). It seems, therefore, that the increased activity must be attributed to *isolated* Cr ions. As the Cr ions pair up, their activity drops. The question arises as to how isolated Cr ions cause increased activity in N_2O decomposition. Is the increased activity due to Cr ions per se or due to the activating influence of the Cr ions on the α-Al_2O_3? The fact that the coverages of retained oxygen are in excess of 100% when referred to the Cr concentration suggests that the Cr ions are influencing the surrounding anions and cations.

In a separate paper (*8*), the unique character of the exposed surface planes is described. Table 2 in Part I (*1*) lists the important details. The major feature is that all three planes expose cation pairs, within the majority of which there is an inhomogeneous distribution of charge. In the Cr concentration region presently under discussion, most of the cation pairs will consist of Al ions, a few will consist of Al and Cr ions, and, as the Cr content rises, an increasing number will consist only of Cr ions. It is clear that the increased activity must center around the Al–Cr pairs. After surface pretreatment, one or both of these surface ions will be coordinatively unsaturated (see Part I, Table 2). It has been suggested that the driving force favoring 6-coordination for $Cr^{3+}(d^3)$ due to C.F.S.E. will cause the surface to adapt during pretreatment to produce 6-coordinate Cr^{3+} and low-coordinate Al^{3+} (*9*). Such a coordinatively unsaturated Al^{3+} could act as a rather more active center of decomposition (compared to similar sites in α-Al_2O_3). The adsorbed oxygen species may then migrate to surrounding oxygen anions to form peroxide species. The surrounding oxide ions will be under the influence of the Cr^{3+} ion whose stronger attraction for the oxygen anions may increase the strength of bonding of the peroxide species, hence increasing the surface coverage of retained oxygen. In this type of explanation it is clear that surface coverages of oxygen greatly in excess of the number of Cr ions are possible.

It could be argued that the C.F.S.E. changes are not sufficiently large to cause the removal of oxygen from an Al^{3+} ion during pretreatment. If this is so, then the Cr^{3+} ion can be envisaged as the site of initial adsorption and decomposition. Nevertheless, due to the close proximity of the Al^{3+} ion, it is still considered that the surface oxygen anions surrounding the cation Al–Cr pair will be influenced such that oxygen migrating to them is more strongly held than on pure α-Al_2O_3. Precision as to the electronic state of the adsorbed species is obviously difficult. It is usually thought that N_2O is adsorbed as a negative species, so that in the case of α-Al_2O_3, a trapped electron (e.g., F-center) would have to be invoked close to the Al^{3+} pairs. Bearing in mind the close parallelism between the activity of these catalysts in isopropanol dehydration (*10*) and their activity in N_2O decomposition, it is possible to envisage a form of electron sharing between the oxygen of N_2O and the coordinatively unsaturated Al^{3+} Lewis acid site, thus causing bond rupture between the nitrogen and the oxygen. This parallelism may be due to the cation pair nature of the site, and thus two types of activity, having different mechanisms, may be possible on the same Al–Cr site. In Part I (*1*), it was suggested that adsorption of N_2O was likely to occur on Cr sites having a positive charge (i.e., where there is a deficit of negative anion charge). If this occurs on Cr^{3+} with a formal transfer of charge, then due to the isolation of the Cr^{3+} ion and the insulator nature of the host lattice, a change to Cr^{4+} will result. This, however, will have no effect on the overall positive charge at the site and, as a result, it will continue to be active as an adsorption center while still retaining a large proportion of the adsorbed oxygen. Thus the following scheme involving a coordinatively unsaturated (cus) Cr ion and adjacent (cus) oxygen ions might be envisaged for the activity of *isolated Cr ions* in the composition range up to AC 5:



The chromium ion could be initially 5-coordinate or 4-coordinate with oxygen. The slow step would probably be (f) → (g) and it is possible that quite a large number of surface oxide ions could be transformed to a species like O_2^{2-}, thus explaining the high surface coverages of retained oxygen and the lower increase of activity between α-Al_2O_3 and AC 1/AC 5 in the sustained decomposition studies compared to the low pressure studies.

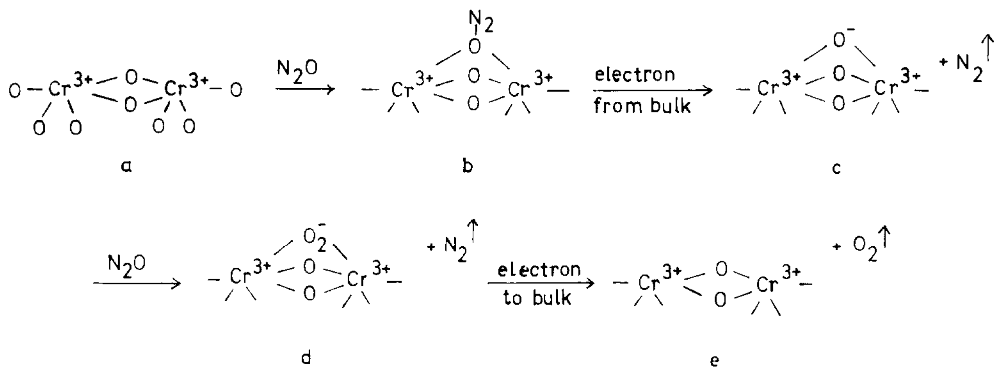
AC 5 → AC 10/25

As the catalyst Cr content increases to AC 10 and AC 25, activity drops markedly to a level below that on α-Al_2O_3. Although there are still a few isolated Cr ions, the vast majority are paired with other Cr ions (*7*). The strong *c*-axis pairing amounts to covalent metal ion–metal ion bonding. The electrons and orbitals are thus less available for bonding with N_2O. This pairing reduces the possibility of electron donation to the N_2O molecules. Thus the site which was especially active in low temperature H_2–D_2 exchange (*8*, *11*) inhibits reaction in N_2O decomposition [and, significantly, in isopropanol dehydration (*10*)].

AC 25 → α-Cr_2O_3

This region is characterized by rising activity per Cr ion in the low pressure studies and decreasing activity per Cr ion in the sustained catalysis studies. The solid state properties indicate that the localized, strongly paired Cr ions are being lost and that electron delocalization is increasingly important (*7*). This will have two consequences for surface Cr ions: (a) their orbitals and electrons are freer and are therefore more able to interact with adsorbate molecules and (b) they can increasingly obtain electrons from the bulk of the solid so that the charge variation from site to site across the surface may well be smeared out. These effects will have two opposing consequences. The activity of the catalysts in the decomposition step will rise, as observed previously in Part I. However, *overall* activity is unlikely to rise markedly because oxygen will be retained more firmly at the surface. Thus the activity per Cr ion decreases slowly and the energy required for desorption of oxygen increases dramatically.

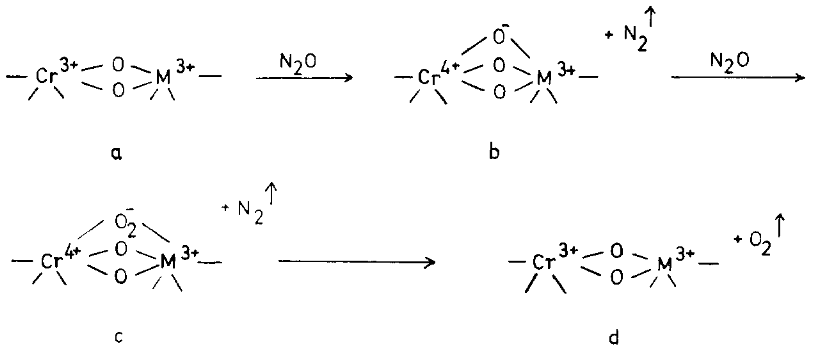
It is interesting that the surface coverage of oxygen (in terms of atomic O) per Cr ion is around 40–50% at 773 and 833 K; gen anions will have been restored in the form of strongly bonded oxygen. We therefore take as our starting point a surface chromium pair site in which one of the oxygen atoms of the triangle of three, which in the bulk would make up the common octahedral face, is missing. The following scheme may then be postulated for the surface Cr_2O_8 double octahedron when electron transfer is efficient:



that is, during reaction there is one O atom retained per pair of Cr ions. Remembering that the surface planes expose pairs of cations, this fact is rather suggestive. It can be inferred that due to the change in the electronic situation surrounding the Cr–Cr pairs, they are now active in N_2O decomposition. After vacuum pretreatment, it is likely that such pairs, which in the bulk exist as Cr_2O_9 double octahedra (*11*), will have at least two oxygen anions missing (*8*). However, after reaction has proceeded for some time, some of these missing oxy-

The steps (c) → (e) will be the difficult part of the path. Hence the oxygen retention will be high and reaction will be reduced.

The higher activity on AC 150 compared to Cr_2O_3 must be attributed to the disturbing influence of Al^{3+} ions on the pair sites and on electron exchange through the "Cr" lattice. Thus the above scheme might be modified in the following manner, yielding adsorbed species which are less strongly bound and hence more conducive to catalysis [cf. Cimino *et al.* (*2*)]:



M^{3+} may be either Al^{3+} or Cr^{3+}. When M^{3+} is Cr^{3+} the adsorbed radical will be more strongly held than when M^{3+} is Al^{3+}, since the latter has no *d*-electron density to donate nor can it provide crystal field stabilization.

Comparison Between $Cr_xAl_{2-x}O_3$ *and* $MgCr_xAl_{2-x}O_4$ *Catalysts*

The following are the main points of contrast:

1. Activity on corundum solid solutions is about one order of magnitude greater than on the spinel solid solutions reported earlier (*3*), though the activating influence of the Cr ions is rather greater on spinel solutions.
2. Oxygen retention during reaction is much greater on corundum than on spinel.
3. Activation energies on the Cr-dilute corundum samples are ~40 kJ mol^{-1} less than on the spinel samples, while at the Cr-rich end, they are about the same.

The origin of this contrasting behavior almost certainly lies in the different abilities of corundum and spinel to lose oxygen from the lattice. α-Al_2O_3 releases lattice oxygen relatively easily, compared with other insulator oxides (*6*), whereas $MgAl_2O_4$ is more reluctant to lose it (*12*). Thus the Cr-dilute spinel solid solutions are less active in a process involving the formation of peroxy species between adsorbed oxygen ions and oxide ions, followed by desorption.

The activity of α-Cr_2O_3 in oxygen exchange is somewhat lower than that of $MgCr_2O_4$ (*13*). Hence it is thought that oxygen mobility is probably somewhat greater in the case of $MgCr_2O_4$. However, electron exchange properties suggest that the efficiency of electron supply at the surface will be much less in $MgCr_2O_4$ than in α-Cr_2O_3. Thus there are two partially conflicting effects which result in rather similar catalytic activity but greater amounts of retained oxygen on α-Cr_2O_3 than on $MgCr_2O_4$.

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