

α -Cr₂O₃-Al₂O₃ Solid Solutions

I. The Formation and Stability of Adsorbed Oxygen

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The direct adsorption of oxygen gas and the formation of adsorbed oxygen by the controlled decomposition of nitrous oxide have been studied on α -Al₂O₃ and on α -Cr_xAl_{2-x}O₃ solid solutions ($x = 0.02 \rightarrow 2.00$). The activity of α -Al₂O₃ in both direct oxygen adsorption and N₂O decomposition is low, but is considerably enhanced by the addition of Cr³⁺. Solid solutions dilute in chromium display a high activity per chromium ion. There is, however, a minimum in the variation of activity with chromium content at $x = 0.2$; although activity rises beyond $x = 0.2$ the activity per chromium ion never quite reaches the value obtained in the dilute samples. The results are interpreted in terms of a variation in the capacity of the surface planes to adsorb oxygen as the chromium content is varied.

INTRODUCTION

Oxide solid solutions enable the properties of transition metal ions in adsorption and catalysis to be studied with a much higher degree of control over electronic and structural parameters than is possible with pure or supported oxides. Suitable diamagnetic matrices for use as solvent are magnesium oxide, α -alumina and spinel. Chromium ion activity has been studied for N₂O decomposition in MgO (1) and in MgAl₂O₄ (2) as a matrix, and for H₂-D₂ exchange (3, 4) isobutane dehydrogenation (5) and isopropanol decomposition (6) in α -Al₂O₃ as a matrix. In all of these cases the chromium ion activity is not a linear function of its concentration in the solvent.

The present work is part of an intensive study of the solid state and surface prop-

erties of α -Cr₂O₃-Al₂O₃ (7, 8). Magnetic and optical measurements have established the nature of the electronic interactions between chromium ions as a function of concentration, and this is a necessary first stage in understanding the behavior of α -Cr_xAl_{2-x}O₃ ($0 < x < 2$) in adsorption and catalysis. In this paper we report on the adsorption of oxygen from oxygen gas and on the formation of adsorbed oxygen by the controlled decomposition of nitrous oxide.

It is well known that the activity of both metal and oxide catalysts in N₂O decomposition may be strongly influenced by the ease or difficulty with which oxygen is desorbed. By studying N₂O decomposition at sufficiently low pressure a situation can be created in which the number of molecules reacting is always less than the capacity of the oxide surface for adsorbed oxygen. This device enables us in Part I to examine in isolation the activity of α -Cr_xAl_{2-x}O₃ for fission of the N-O bond and to compare it with the activity pattern for oxygen adsorption as a function of chromium content in the solid solution. The activity pattern for the *sustained* catalysis of N₂O decom-

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TABLE 1
 OXYGEN ADSORPTION COVERAGES AND ARRHENIUS PARAMETERS IN THE CATALYSIS
 OF N₂O DECOMPOSITION ON α -Al₂O₃, α -Cr₂O₃ AND α -Cr_xAl_{2-x}O₃ SOLID SOLUTIONS

Oxide cata- lyst	x in Cr _x Al _{2-x} O ₃		Surface area (m ² g ⁻¹)	Oxygen adsorp- tion ^a (% cover- age at 1 N m ⁻²)		N ₂ O decomposition Arrhenius parameters	
	From chemical analysis	From XPS (ESCA) analysis		683 K	883 K	E (kJ mol ⁻¹)	log[A(cm min ⁻¹)]
α -Al ₂ O ₃	—	—	2.0	0.21	0.15	41.0	-1.15
AC 0.1	0.002	—	2.1	0.17	0.11	33.5	-2.07
AC 1	0.020	0.02	2.2	0.79	0.32	23.9	-1.68
AC 3	0.054	0.05	2.1	—	—	24.7	-1.44
AC 5	0.068	0.07	2.0	—	—	15.5	-1.93
AC 7	0.098	0.10	2.0	—	—	30.1	-1.03
AC 10	0.182	0.15	1.9	0.28	0.63	18.4	-2.28
AC 25	0.400	0.42	0.4	—	—	10.5	-2.08
AC 66	0.794	—	0.3	3.72	4.28	—	—
AC 150	1.200	1.12	0.5	3.55	6.31	17.6	-0.95
α -Cr ₂ O ₃	2.000	—	0.9	27.6	16.8	8.2	-1.36

^a Oxygen 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 surface cations of a corundum structure is then 0.20 cm³ m⁻² at STP. AC 3, AC 5, AC 7 and AC 25 were not studied in direct oxygen adsorption. AC 66 was not studied in N₂O decomposition or in XPS analysis.

position is reported and discussed in Part II (14).

EXPERIMENTAL METHODS

Materials. The preparation and characterization of the corundum-phase solid solutions have been described elsewhere (7). The catalysts used are listed in Table 1 using a nomenclature adopted previously (3, 7) in which AC N denotes an α -Cr_xAl_{2-x}O₃ solid solution with N Cr atoms per 100 Al atoms. The Cr/Al ratio obtained by X-ray photoelectron spectroscopy (4), which preferentially samples the surface crust, is compared with the overall bulk Cr/Al ratio obtained by conventional chemical analysis in Table 1. The agreement is good. BET surface areas, obtained with krypton at 77 K, are also listed in Table 1.

Gases. Cylinder N₂O was purified by double distillation from a 77 K trap into a 195 K trap, only the middle fraction being collected. Oxygen-free nitrogen was dried by passing the gas through several 77 K traps. Specpure Kr was used for the BET measurements.

Apparatus and Procedures

O₂ Adsorption

A low volume system (~20 cm³) was used to measure the uptake of O₂ on the solid solutions. A thermistor (Stantel M20) enclosed in a glass envelope and calibrated with oxygen gas was used as the pressure sensor. It was thermostated at 273 K and employed a constant current circuit, the potential necessary to maintain 10 mA through the thermistor as the gas pressure was varied being measured on a recorder. Before each adsorption measurement the catalyst was pretreated for 18 hr at 1120 K and 10⁻³ N m⁻² (1 Torr = 133 N m⁻²). The amount of oxygen adsorbed at 683 K and 883 K was measured at a pressure of 1 N m⁻².

N₂O Decomposition

N₂O decomposition was followed in a system (~100 cm³) using a Pirani gauge as a pressure measuring device. N₂O was admitted to the catalyst at 2 N m⁻² pressure; after a set time the catalyst was isolated and the N₂O in the remainder of the system

was frozen out in a trap cooled at 77 K. The pressure of the uncondensed gas due to the decomposition of N₂O was measured. Mass spectrometric analysis showed that the uncondensed gas was pure N₂. Thus all the oxygen produced remained adsorbed. After the pressure measurement, the condensed N₂O was rapidly evaporated and reconnected with the catalyst section via a stop-cock. The N₂ pressure was measured in this way at suitable intervals, and since there was no evidence of significant N₂ adsorption, the progress of the reaction could be followed. Before each reaction the catalyst was outgassed at 1120 K at 10⁻³ N m⁻² for either 18 or 1 hr. In most cases it was found that 1 hr was sufficient to attain reproducibility in reactivity. The reaction was studied at different temperatures in the range 298–770 K. The mass of each catalyst used was chosen such that there was ample surface available to accommodate in the adsorbed layer all the oxygen produced in the reaction. Absolute velocity constants k_{obs} were calculated as previously (2).

In addition to the usual calibrations necessary when using a Pirani gauge, a check showed that there was no detectable reaction on the wire of the Pirani gauge.

RESULTS AND DISCUSSION

Oxygen Adsorption from Molecular Oxygen

The effect of outgassing at 1120 K was to produce surfaces on which oxygen was readily adsorbed. The adsorption was irreversible at 683 K, as could be established by outgassing for 30 min at 10⁻³ N m⁻² after adsorption was complete, and then re-exposing to oxygen. Adsorption at 883 K was partly reversible. Percentage coverages at $p = 1$ N m⁻² are shown in Table 1. It is seen that the general effect of incorporating chromium is to enhance oxygen adsorption, although for AC 0.1 the adsorption is slightly less than on α -Al₂O₃. Even so, the addition of Cr has very variable effect. A trend of particular interest is the way the adsorption per chromium ion (θ_{Cr}) changes with increasing Cr content. The general be-

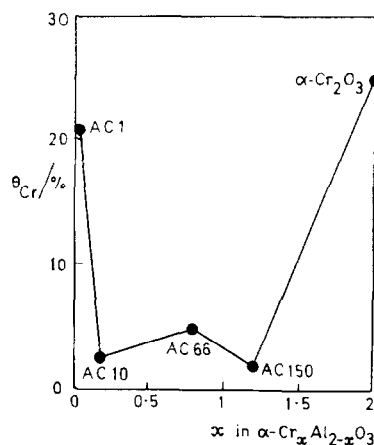


FIG. 1. The variation of the oxygen coverage per surface chromium ion with the chromium content of the oxide at 683 K and an oxygen pressure of 1 N m⁻².

havior is illustrated in Fig. 1.* We note a sharp drop in θ_{Cr} from AC 1 to AC 10, then between AC 10 and AC 150 θ_{Cr} changes rather little, and finally there is a sharp increase to α -Cr₂O₃.

N₂O Decomposition

The results for N₂O decomposition are summarized in Fig. 2 and Table 1. α -Cr₂O₃ is seen to be much more effective than α -Al₂O₃. However, Fig. 2 also shows that activity does not rise uniformly with Cr content. The effect of the Cr addition is highlighted in Figs. 3 and 4 where the results for 555 and 773 K are presented as a function of Cr content. Figure 4 expresses the data as activity on a per chromium ion basis and the form is similar to that for oxygen adsorption in Fig. 1. Activity per chromium ion decreases from AC 0.1 to AC 10 and rises in the region AC 10 to α -Cr₂O₃. α -Cr₂O₃ generally features among the less

* To present the data in this way, some arbitrary assumption must be made about the effect of the small adsorption on the Al-O component of the surface. In preparing Fig. 1 we have assumed a nil contribution; however, the general characteristics of Fig. 1 would not be changed if the other arbitrary assumption were made of deducting the observed coverage on α -Al₂O₃ (or some fraction of it) from all the other coverages.

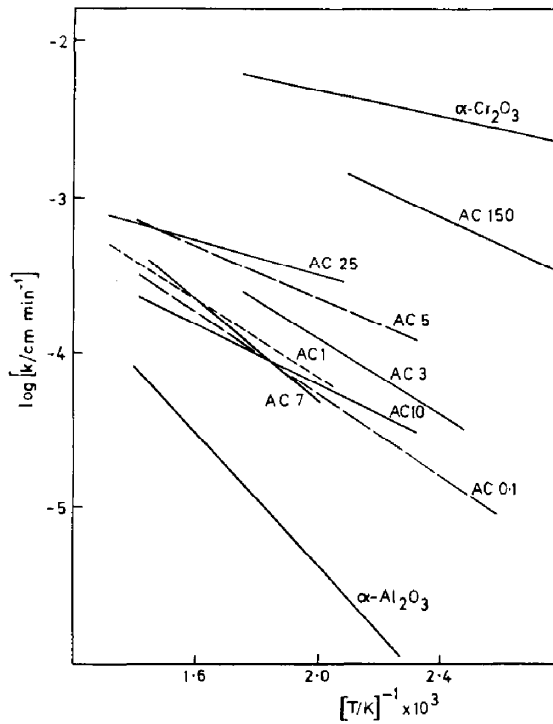


FIG. 2. Arrhenius plots for N_2O decomposition on $\alpha\text{-Al}_2\text{O}_3$, $\alpha\text{-Cr}_2\text{O}_3$ and $\alpha\text{-Cr}_x\text{Al}_{2-x}\text{O}_3$ (AC) solid solutions.

active oxides for N_2O decomposition (9), and its susceptibility to inhibition by oxygen is well established (10). Figure 2 shows that in our studies of the primary steps,

namely N_2O adsorption and decomposition with retention of the released oxygen, $\alpha\text{-Cr}_2\text{O}_3$ is extremely active. N_2O will decompose to yield adsorbed oxygen even

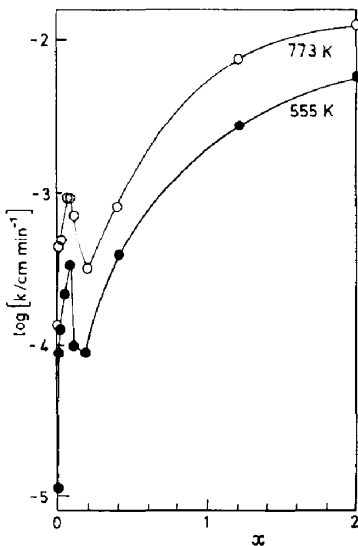


FIG. 3. The variation of $\log k_{\text{obs}}$ for N_2O decomposition with the chromium content of $\alpha\text{-Cr}_x\text{Al}_{2-x}\text{O}_3$ at 555 and 773 K.

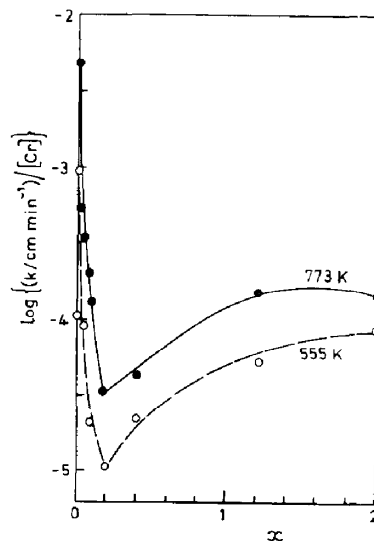
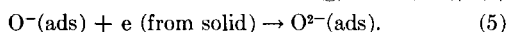
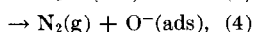
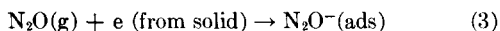
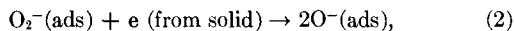
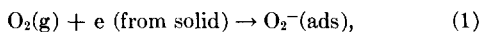


FIG. 4. The variation of the activity per chromium ion in N_2O decomposition with the chromium content of $\alpha\text{-Cr}_x\text{Al}_{2-x}\text{O}_3$ at 555 and 773 K.

at room temperature. Recent infrared spectroscopic studies of N₂O adsorption on α -Cr₂O₃ confirm this observation (11).

The conventional description of oxygen adsorption and N₂O decomposition on oxides includes the following charge transfer steps:



There is good evidence from EPR studies (12) that O₂⁻(ads), O⁻(ads) and N₂O⁻(ads) are stable adsorbed species on some oxides, although O₂⁻(ads) and N₂O⁻(ads) are likely to decompose to give O⁻(ads) or O²⁻(ads) at the temperatures used in this work. In any event, it is evident that the reactions will only occur if the adsorbent can supply electrons for the adsorption bond. The charge transfer may only be partial; a molecular orbital description with the formal charge on the adsorbate species signifying the principal characteristics of the electron distribution is equally valid.

Figure 3 shows that for the production of adsorbed oxygen from N₂O there are three distinct regions of activity as a function of chromium content in the oxide, namely:

- I. α -Al₂O₃ → AC 5 (rising activity),
- II. AC 5 → AC 10 (falling activity),
- III. AC 10 → α -Cr₂O₃ (rising activity).

The oxygen adsorption results at 683 K also distinguish these three regions.

In Region I, only small quantities of Cr ions have been dispersed in the insulating matrix of α -Al₂O₃. An increased facility for electron transfer from the bulk (or effects linked with semiconductivity) cannot easily be invoked to explain the increase in reactivity shown by these very dilute solutions. It is true that a "hopping" process for conductivity could occur and as such could cause activity to rise with Cr addition, but the steep fall in activity per chromium ion (Fig. 4) speaks against this interpretation. We prefer to attribute the increased activity to some specific effect of

isolated Cr ions. The presence of electrons in unfilled *d*-orbitals may assist the formation of σ -bonds with adsorbed oxygen. Crystal field considerations also suggest that incompletely coordinated surface Cr³⁺ (*d*³) ions will have a much stronger tendency than Al³⁺ ions to complete sixfold coordination by the adsorption of oxygen or N₂O. Figure 1 shows that θ_{Cr} is below 100%. Furthermore, the oxygen coverage of the chromium ions computed from the extent of N₂O decomposition is in the region of 20-30% (assuming for this calculation that only Cr ions adsorb oxygen), so it is quite tenable to suggest that the Cr ions may be the major active sites. Nevertheless α -Al₂O₃ is itself active; thus it would seem to be unreasonable to suggest that very small quantities of Cr dopant would kill the activity of the α -Al₂O₃ host. However, the activation energy of N₂O decomposition over AC 0.1 is some 8 kJ mol⁻¹ less than over α -Al₂O₃, and the activity is approximately an order of magnitude higher. Clearly the small addition of Cr to α -Al₂O₃ has a profound effect on its capacity to adsorb and decompose N₂O.

Elsewhere the (111), (100) and (001) surface planes of corundum have been analyzed (4, 7, 8). Table 2 provides a summary of the cation configurations and charge distributions on the various surface planes. Although each plane is electrically neutral overall, some sites (where a site is defined for the present context as a cation and associated anions) are charged positive and some are charged negative. Cations having a coordination number of 5 can form sites having a slight positive or a slight negative charge, while cations having a coordination number less than 5 form positively charged sites. Both electrostatic and (in the case of Cr ions) crystal field stabilization considerations would suggest that these latter sites would possess a high tendency to adsorb oxygen. The (111)_a surface would seem to be especially favorable in this respect. If adsorption is accompanied by the formal transfer of an electron from the cation valence orbitals to the adsorbed molecule, as could occur with a chromium ion, the overall electric charge at the site (now cation + anions + ad-

TABLE 2
COORDINATION, CONFIGURATION AND ELECTRONIC CHARGE DISTRIBUTION AROUND CATIONS
ON THE PRINCIPAL SURFACE PLANES OF CORUNDUM

Plane	Surface charge	Cation coordination with oxygen ions, and relationship with cation neighbors	Local charge at surface cation sites* (relative to neutral)
(100)	Neutral	Each cation in the (100) surface is 5-coordinate with oxygen and has: <i>either</i> (Case A) one basal pair cation neighbor <i>or</i> (Case B) one <i>c</i> -axis cation neighbor	Case A: one cation of the pair is a $\delta+$ site, and the other a $\delta-$ site, where $ \delta+ = \delta- $ Case B: half the pairs constitute $\delta+$ regions, and the other half $\delta-$ regions, where $ \delta+ = \delta- $
(001)	Neutral	Half the surface cations are 4-coordinate with oxygen (Case C) and half are 5-coordinate (Case D) Cations form a hexagonal array	Case C cations are $\delta+$ sites Case D cations are $\delta-$ sites where $ \delta+ = \delta- $
(111) _a	Outermost surface is positive (subsurface is negative)	Two types of surface cation feature: Case E: isolate cations, 5-coordinate with oxygen Case F: cations in cation pairs, one of which (F ₁) is highly exposed and 3-coordinate with oxygen, the other (F ₂) being recessed and 5-coordinate with oxygen	Case E cations are $\delta+$ sites Case F: F ₁ cations are strongly positive sites; F ₂ cations are mildly positive sites
(111) _b	Outermost surface is positive (subsurface is negative)	Half the surface cations are 4-coordinate with oxygen (Case G) and half are 5-coordinate (Case H) Cations are in <i>c</i> -axis (G and H) pairs	Case G cations constitute $\delta+$ sites, and Case H cations constitute $\delta-$ sites, where $ \delta+ > \delta- $

* For the present purpose, a site is defined as being made up of the cation *and* its surrounding anions.

sorbed molecule) will remain unchanged. By virtue of this the site may continue to be favorable as an adsorption center, even though the charge distribution within it will have changed. This discussion suggests that Cr³⁺ ions with their availability of *d*-electrons will form more active adsorption centers than the essentially inert Al³⁺ ions. It is thus not surprising that the inclusion of Cr³⁺ ions in α -Al₂O₃, even at low concentration, results in a substantial rise in N₂O decomposition.

In Region II activity decreases markedly. Table 2 shows that the dominant characteristic of each of the surface planes is that most of the cations appear in pairs of the *c*-axis or basal plane type. It is in this region that many of the chromium ions in the solid solutions are paired almost covalently with other chromium ions in the *c*-axis and probably in the basal plane (7).

In every case, except the *c*-axis pairs on the (100) plane, there is a difference in the magnitude and in some cases the sign of the charge associated with the two partners (cation plus associated anions) in the pair. Thus on the (100) and (001) surfaces there is a charge imbalance within the exposed basal-plane pairs, while on the (111) surfaces there is imbalance within the exposed *c*-axis pairs. If the two partners in a pair are Cr ions, charge imbalance may be smoothed out by the electron sharing mentioned above. Thus the tendency of the Cr ions to adsorb N₂O or oxygen may be reduced due to the loss of the "positively" charged sites and to the decreased availability of valence electrons. The conclusion is that the isolated *Cr pairs* found in AC 7 and AC 10 have little activity in N₂O decomposition and oxygen adsorption, while the isolated Cr ions active in Region I

will continue to be active although their numbers are on the decrease. The formation of these isolated Cr pairs as the Cr content is increased accounts for the falling activity per chromium ion (Fig. 4).

In Region III activity rises considerably in N₂O decomposition and in direct oxygen adsorption (Figs. 3, 4 and Fig. 1). The fact that there is also a rise in activity *per chromium ion* implies that a cooperative phenomenon is present. As Cr content increases, the movement of electrons within the bulk and the surface becomes increasingly efficient. The Cr ions lose their isolated nature both as single ions and as pairs. Under the pretreatment conditions there may be a tendency for chromium in the surfaces of the catalysts in this concentration range to be reduced, possibly at positively charged sites. A concentration of electrons available at the surface due to such reduction would encourage interaction with N₂O and oxygen by reactions (1)–(5).

On α -Cr₂O₃, N₂O yielded adsorbed oxygen at room temperature. The relatively low catalytic activity of α -Cr₂O₃ to sustained N₂O decomposition is due to the reluctance with which the oxide releases adsorbed oxygen. The active sites become blocked. Zecchina *et al.* (11, 13) have shown by ir studies that oxygen adsorption on α -Cr₂O₃ leads to strongly bonded forms of oxygen and this is confirmed in our work by the observed high coverage of oxygen, even at 883 K (Table 1).

Table 1 also shows that the coverage of oxygen on α -Cr₂O₃ is larger than on AC 66 and AC 150, and the rise in the adsorbed amount between 683 and 883 K for these latter solids illustrates the activated nature of the chemisorption. The introduction of Al³⁺ ions into the α -Cr₂O₃ structure reduces the availability of electrons at the surface, and thermal activation is required on AC 66 and AC 150.

There is a further point from the adsorption data in Table 1 which deserves comment. Although the coverages for AC 150, AC 66 and AC 10 rise between 683 and 883 K, those for α -Al₂O₃, AC 0.1 and AC 1 fall. Adsorbed oxygen on α -Al₂O₃, AC 0.1

and AC 1 will be more weakly held than on the high Cr content samples because the adsorption centers are isolated and electron supply to them is difficult. The temperature above which the oxygen adsorption-desorption equilibrium behaves conventionally (coverage decreasing with increasing temperature) will accordingly be lower. This temperature is evidently not reached on the chromium-rich solids below 883 K; the activation energy for desorption is too great.

CONCLUSION

It has been demonstrated that there are two types of site in α -Cr_xAl_{2-x}O₃ capable of decomposing N₂O efficiently. First there is the isolated Cr³⁺ ion site, which because of the insulating nature of the host structure utilizes only its "own" valence electrons in adsorbing oxygen. It seems that *single* Cr³⁺ ions are necessary, because as soon as isolated Cr *pairs* appear, the activity drops. The second type of site is the surface Cr ion which is part of a linked electron exchange system of many Cr ions. Electron movement to the surface from the bulk is then facile, and as this facility develops further the Cr sites become increasingly active.

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