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The Catalytic Activity of Chromium Ions in Magnesium Aluminate for the Decomposition of Nitrous Oxide

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The catalysis of N_2O decomposition has been studied over $MgAl_2O_4$ and a complete range of solid-solutions $MgCr_xAl_{2-x}O_4$ ($x = 0.02 \rightarrow 2$). The activity of $MgAl_2O_4$ is low but is considerably enhanced by the addition of Cr^{3+}. The samples dilute in chromium display a high activity per chromium ion. There is a minimum in the variation of activity with chromium content at $x = 0.7$; thereafter activity rises again, though the activity per chromium ion never reaches the value obtained in the dilute samples. The results are interpreted in terms of the variation of the type of adsorption site with chromium content.

INTRODUCTION

There has been considerable interest in recent years in the catalytic activity of transition metal ions in solid solution in oxides which are themselves catalytically rather inert (*1–3*). In such oxide systems it is possible to control the interaction of the transition metal ions in a fairly precise manner, and hence to study the electronic structure of the ion in some detail using X-ray and magnetic techniques. The information so provided can then be used to gain an insight into the surface properties and catalytic activity of the transition metal ions. To date, systems in which the transition metal ion concentration is rather low have received most attention (*2, 4–6*). However, industrially important catalysts are generally rather concentrated in the active atoms, and it is of great interest to study the variation of catalytic activity over a much wider range of transition metal ion concentration, from the very dilute to the very concentrated. In this way we can investigate not only the activity of isolated ions but also the changes in activity which occur with their increasing interaction.

Studies of N_2O decomposition over chromia–magnesia–lithia catalyst (*4*) and H_2–D_2 exchange over chromia–alumina solid solutions (*5, 6*) have already been reported. Both these studies involved chromium contents of less than 10%. In this paper we report a study of N_2O decomposition over a complete concentration range of spinel solid solutions $MgCr_xAl_{2-x}O_4$.

METHODS

Materials. A series of spinel solid solutions of $MgCr_2O_4$ in $MgAl_2O_4$ have been studied. They have been prepared at 1350°C according to procedures described elsewhere (*7*). The chromium content of the samples is designated by the nomenclature SMAC *N*, i.e., a magnesium spinel (SM) having a chromium (C) content of *N* atoms of chromium for 100 atoms of aluminium (A). The catalysts are listed in Table 1: the surface areas were measured by the BET method with Kr at −196°C. A detailed study of the solid state proper-

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ties of the solid solutions was carried out and is reported elsewhere (7).

Gases. Cylinder N_2O was purified by double distillation from a —196°C trap into a —78°C trap, only the middle fraction being collected. Oxygen-free nitrogen was dried by passing through several liquid nitrogen traps. Spec-pure krypton was used for the BET measurements.

Apparatus and Procedures

N_2O decomposition was studied in a circulation system of volume 650 ml, at a pressure of about 30 Torr (1 Torr = 133.3 Nm^{-2}) in the temperature range 450°C → 620°C. Approximately 0.5 g of catalyst was contained in a silica vessel, through which N_2O was circulated by means of a reciprocally acting Toepler pump. The catalyst was protected from mercury contamination by acetone–solid CO_2 traps. The extent of reaction was followed by continuous sampling of N_2 and O_2 via a capillary leak to the head of an A.E.I. MS10 mass spectrometer which had been calibrated for sensitivity to N_2 and O_2. Unreacted N_2O was trapped by means of a liquid nitrogen trap before the sampled gases reached the mass spectrometer head.

Catalyst pretreatment consisted in outgassing the oxide initially for ~18 hr at 850°C and 10^{-5} Torr. Outgassing at 850°C

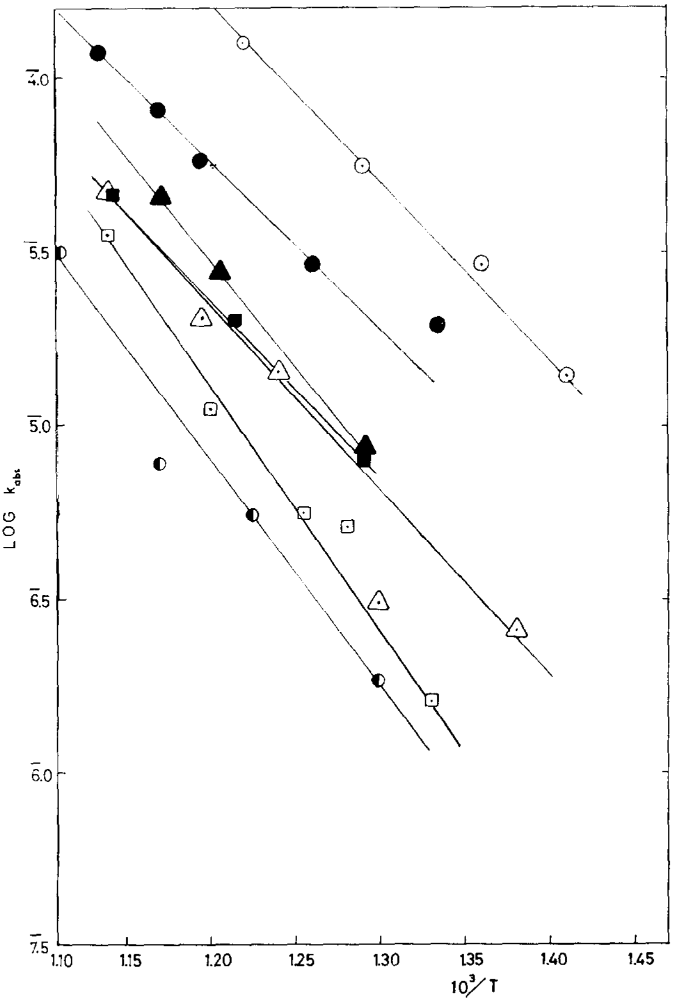

FIG. 1. Plot of absolute rate constant against $1000/T$°K: □, $MgAl_2O_4$ (SMA); ▲, SMAC1; ●, SMAC10; ◐, SMAC50; ■, SMAC100; △, SMAC300; ⊙, $MgCr_2O_4$ (SMC).

for 30 min between each reaction gave reproducible results.

RESULTS

From the initial rates, the "absolute velocity constants" were derived using the following equation (*3*):

$$k_{\mathrm{abs}} = P_{\mathrm{N}_2} V_e P_{\mathrm{N}} A t^{-1} \text{ cm min}^{-1},$$

where P_{N_2} = total pressure of nitrogen gas (Torr); V_e = volume of reaction vessel (cm^3); P_{N} = initial N_2O pressure (Torr); A = area (cm^2); and t = reaction time (min). The results are presented in Fig. 1 as an Arrhenius plot. The activation energies obtained from these plots are shown in Table 1. It can be seen that there is a minimum in the activation energy at SMAC10 followed by a large rise at SMAC50. From SMAC100 to SMC the activation energy of 21–25 kcal mole^{-1} is relatively constant. It is significant to compare the variation of activity with the chromium content of the catalysts at 560°C. Figure 2 shows this variation, which correlates well with the variation of activation energy.

TABLE 1
APPARENT ACTIVATION ENERGIES AS A FUNCTION OF CHROMIUM CONTENT

Catalyst	x^a	Surface area (m^2/g)	Apparent activation energy (kcal/mole)
SMA	0	0.64	32.6
SMAC1	0.019	0.68	27.6
SMAC10	0.182	0.73	22.8
SMAC50	0.667	15.0	29.6
SMAC100	1.000	10.1	21.4
SMAC300	1.500	1.40	24.2
SMC	2.000	1.60	23.3

[a] $MgCr_x Al_{2-x}O_4$.

The addition of Cr^{3+} ions to $MgAl_2O_4$ clearly enhances the activity for N_2O decomposition and decreases the apparent activation energy. There is, however, a limit

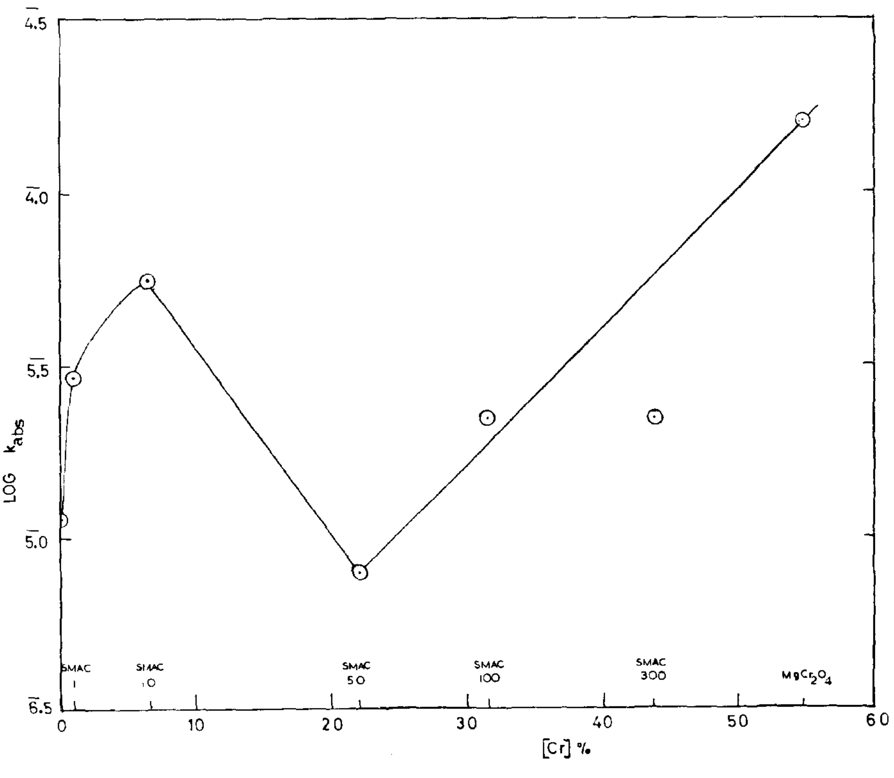

FIG. 2. The absolute rate constant at T = 560°C as a function of the chromium content of the catalysts.

to the effectiveness of increasing the Cr^{3+} concentration in the $MgAl_2O_4$. The rate of increase of activity with $[Cr^{3+}]$ falls off between SMAC1 and SMAC10. Further addition of Cr^{3+} ions results in a large decrease in activity at SMAC50. Activity thereafter rises again with further addition of Cr^{3+} ions, but only at SMC does the activity rise above that attained on SMAC10. This variation of activity with Cr^{3+} content is emphasized if we consider the variation of catalytic activity *per chromium ion*. In order to obtain k_{abs} $[Cr]^{-1}$ it is assumed that the surface molar fraction of chromium is the same as the bulk molar fraction. The regular variation of lattice constant with chromium content (7) indicates that deviations from this assumption are small. Figure 3 demonstrates clearly that the observed variation in activity can be related to the environment of the Cr^{3+} ions in the different catalysts. Isolation of Cr^{3+} ions in SMAC1 results in high $k_{abs}/[Cr]$; increasing the interaction of Cr^{3+} ions results in significant changes in $k_{abs}/[Cr]$.

The N_2/O_2 Ratio

The N_2/O_2 ratio was measured throughout the course of all reactions. The theoretical value of 2 was reached fairly rapidly in the case of SMA, SMAC1 and SMAC10 at high temperature. Samples SMAC50 to SMC maintained values in excess of 2 at all temperatures throughout the period of reaction. As the temperature of reaction was reduced the N_2/O_2 ratio rose. Figure 4 shows the variation of the N_2/O_2 ratio with time for all the catalysts at a reaction temperature of 560°C. It is interesting to note the SMAC100 and SMAC300 show the largest deviation from 2.

In view of the wide variation in the surface areas of the catalysts it is more significant to consider the surface coverages of oxygen which these N_2/O_2 ratios imply.

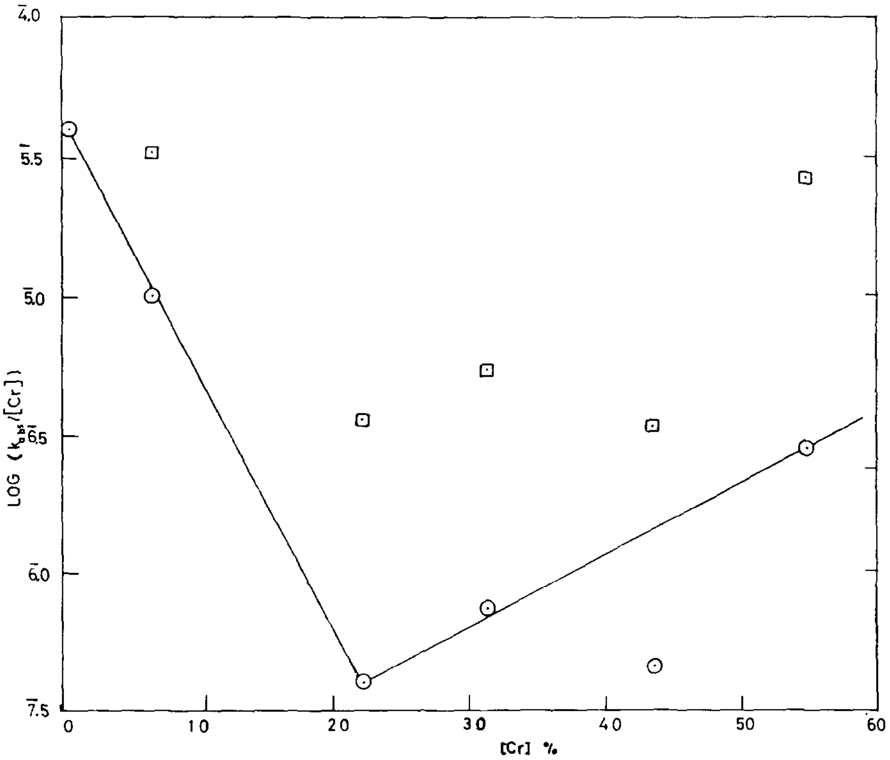

FIG. 3. The absolute rate constant per chromium ion at T = 560°C as a function of the chromium content of the catalysts: ⊙, absolute rate constants per chromium ion; ⊡, modified value using the estimated concentration of isolated chromium ions.

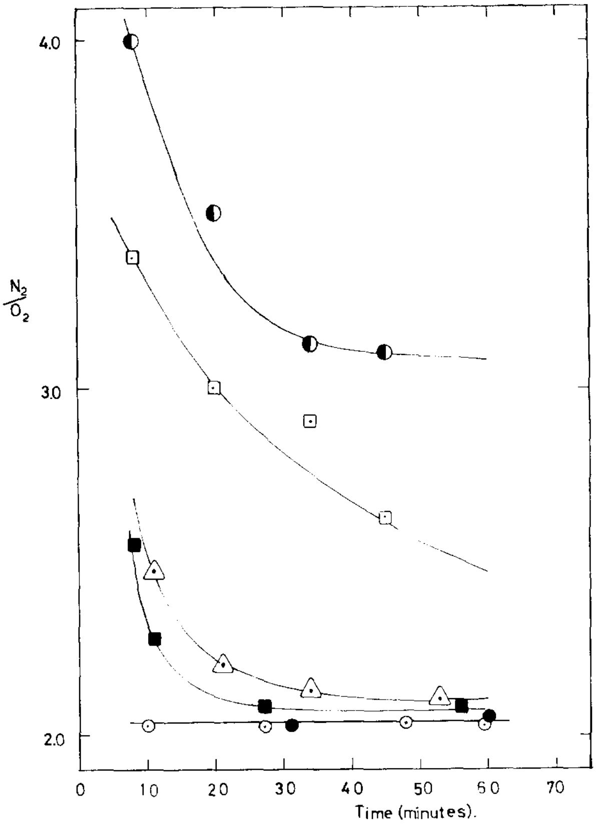

FIG. 4. Variation of N_2:O_2 ratio with time at 560°C: ●, SMAC1; ⊙, SMAC10; ■, SMAC50; ◐, SMAC 100; ⊡, SMAC300; △, SMC.

In this respect it should be noted that due to the low surface areas of the specimens SMA to SMAC10, computation of surface coverages will be subject to a relatively large error. Coverage values are computed on the basis of equal areas of the [100], [110], and [111] planes; the monolayer value of oxygen atoms on the cations of spinel is then 0.14 cm^3 at STP. Table 2 lists these coverages for a reaction time = 50 min at $T = 490$ and 560°C. The coverages given correspond to a rather wide variation of the extent of reaction over the different catalysts but two points are clear. Firstly

TABLE 2

NITROGEN:OXYGEN RATIOS OF PRODUCT AFTER 50-MIN REACTION

	T = 490°C			T = 560°C		
Catalyst	% Reaction	N_2/O_2	θ%	% Reaction	N_2/O_2	θ%
SMA	0.1	3.35	4.6	0.5	2.10	0.7
SMAC1	0.2	2.80	4.0	0.5	2.10	2.9
SMAC10	0.3	3.20	4.0	2.1	2.10	1.4
SMAC50	0.6	3.50	0.9	1.7	2.20	0.9
SMAC100	1.5	3.47	4.6	3.4	3.18	4.6
SMAC300	0.1	3.90	5.6	0.5	2.60	5.6
SMC	1.2	2.43	14.0	5.9	2.10	14.3

the coverages decrease from SMAC1 to SMAC50 and then increase again; secondly, and perhaps of more significance, the coverages for SMAC50 to SMC remain constant with temperature. The value of 14.3% found for oxygen coverage on SMC is in good agreement with 15.4% found by Cimino and co-workers (*4*).

DISCUSSION

An electron spin resonance study (*7*) of the solid state properties of these spinel solid solutions has given an insight into the increasing electronic interaction of the Cr^{3+} ions as a function of chromium content. The esr data clearly indicate that the Cr^{3+} ions in SMAC1 are isolated from one another by relatively large distances. In SMAC10 the appearance of an additional broad resonance ($\Delta H \sim 1400$ G) indicative of Cr–Cr interaction indicates that a fraction of the ions have at least one chromium ion as a nearest neighbor. At SMAC50 the broad resonance is the only signal. The line width is reduced ($\Delta H \sim 600$ G) indicating increasing interaction of the Cr ions. Statistically it is expected that each Cr^{3+} ion in SMAC50 will have between 2 and 3 other chromiums as nearest neighbors. For SMC all six nearest neighbors will be chromium ions. These changes in the extent of interaction of Cr ions in the bulk of the solid solutions will be mirrored in the surface in a qualitative if not quantitative manner.

It is clear from the catalytic data presented above that the variation of Cr ion interaction from catalyst to catalyst has an important effect on the activity of the Cr ion in the catalysis of N_2O decomposition. Activity on SMAC1 confirms yet again the well established observation that isolated transition metal ions are particularly active in catalysis (*2*, *4*). Although the activity increases from SMAC1 to SMAC10 the activity *per ion* decreases (Fig. 3). This reduction can be attributed to the appearance of Cr ion interactions. The esr data (*7*) and statistical considerations suggest that ~70% of the Cr ions in SMAC10 have one chromium nearest neighbor. The large decrease in activity and large rise in apparent activation energy over SMAC50 appears to support the idea that interacting ions are far less active for catalysis. In this connection it is interesting to calculate the $k/[Cr]$ for SMAC10 assuming that "paired ions" make a negligible contribution to the activity, that is, only 30% of the Cr ions at the surface are active. This results in a $k/[Cr]$ for SMAC10 which is 90% of the $k/[Cr]$ for SMAC1, whereas previously it was only 25%. Tentative support is thus provided for the contention that it is ("isolated") single ions that are of primary importance in SMAC10. The reduced activation energy for activity on SMAC10 can probably be attributed to an increased number of active sites.

Turning to a consideration of the activity over specimens SMAC50 to SMC, the most obvious feature is the reduction in $k/[Cr]$ compared with SMAC1 and SMAC10 of between 10 and 100-fold. In previous studies of the chromia–magnesia and nickel oxide–magnesia systems, it has been suggested that the high activity on dilute catalysts may be correlated with the ability to form weakly adsorbed oxygen species of the O^- type. The reduced activity on concentrated catalysts has been attributed to poisoning by a strongly adsorbed species of the O^{2-} type (*4*). The N_2/O_2 ratio and coverage data indicate the presence of a strongly adsorbed species on the catalysts SMAC50 to SMC since the coverage is unchanged with temperature. These adsorption sites are unlikely to be involved in the catalysis of N_2O decomposition. These sites, however, account for only 14% of the Cr sites on SMC and only 2% of the Cr sites on SMAC50. There are clearly additional reasons for the reduced activity over these catalysts.

In order to gain an understanding of what these reasons may be it is relevant to consider the possible configurations of the *B*-site cations at the surface of $MgCr_2O_4$. It is reasonable to assume that the [100], [110] and [111] planes will be equally represented in the formation of the total surface. On the [100] plane the chromium ions will form rows of adjacent ions. These rows are separated from each other by a distance equal to twice the distance between adjacent ions due to the intervention of a row of *A*-site cations and two rows of anions. The [110] plane has two possible structures. The first ([110]*a*) consists of rows of adjacent cations separated by a distance approaching three times the adjacent cation distance due to anions and *A*-site cations. The second ([110]*b*) plane consists of lines of relatively isolated ions separated from each other by a distance of about twice the adjacent cation distance. The final plane [111] also has two possible structures. The first ([111]*a*) consists entirely of *B*-site cations in consecutive rows, every other row having alternate cations missing. The other [111] plane ([111]*b*) is similar to the [110]*b* plane. Table 3 lists the approximate relative populations of *B*-site cations due to each plane. It can be seen that on this basis the "isolated" cations amount to ~20% of the total surface cations. It is, however, unlikely that the [110]*b* and [111]*b* planes will have an equal contribution with the [110]*a* and [111]*a* planes. They will probably merely form steps on these latter planes. We can speculate, therefore, that "isolated" cations will contribute say 10–15% of the surface chromium ions in SMC.

TABLE 3
ENVIRONMENT OF THE *B*-SITE CATIONS AT THE SURFACE OF A SPINEL

Plane	*B*-Site surface cations (%) (approx)[a]	Remarks
[100]	46	Rows of adjacent ions
[110]*a*	11.5	Rows of adjacent ions
[110]*b*	11.5	"Isolated ions"
[111]*a*	23	Rows of adjacent ions
[111]*b*	8	"Isolated ions"

[a] Assumes surface is composed of equal areas of the three planes and that the [110] and [111] planes have equal areas of (*a*) and (*b*).

The postulate can now be made that even in the catalysts which have a high Cr content it is the relatively isolated surface Cr ions which are the active sites. This suggestion can be supported by the low E_A found on all samples except SMAC50. If we apply this assumption to the calculation of $k/[\mathrm{Cr}]$ for SMC we obtain a value close to that for SMAC10. This would suggest that the reasoning is not without foundation. It will be noted (Fig. 3), however, that the values of $k/[\mathrm{Cr}]$ obtained in a similar manner for SMAC50 to SMAC300 are still a factor of 10 lower than for SMAC10.

Consideration of the electronic state of the Cr ions in these samples may provide a further explanation for their lower activity. Isolated Cr ions at the surface will strive to complete their octahedral coordination by adsorption. Although crystal field stabilization energies (CFSE) would favor this, electrostatic considerations may result in this being a relatively weak adsorption. However, it seems likely that surface Cr ions, whose electrons are correlated with those of nearest neighbor Cr ions on the surface or even in the bulk, will have a reduced drive, in terms of CFSE, towards a full anion octahedron. As a result surface sites involving pairs of Cr ions will be less willing to give up electrons in adsorption and may be inactive as adsorption sites. Even Cr ions isolated on the surface will be coupled with one or more Cr ions in the bulk. This would result in a decreased activity in N_2O decomposition. This effect may well be most important for SMAC50 since here the electron exchange between the Cr ions will be strongest for two reasons; firstly, each Cr ion has only 2 or 3 Cr neighbors and superexchange between individual Cr ions will be highest, and secondly, their separation is less than in samples SMAC100 to SMC. The solid state studies (7) suggested the existence of short range order in SMAC300 and in the light of the above discussion this may explain the lower activity on this catalyst. Thus it has been suggested that the active sites for N_2O decomposition on the catalysts are predominantly isolated surface Cr ions. The variation in the activity of these sites over the catalyst series can be attributed to the varying degrees of electron correlation between the surface Cr ions and its Cr nearest neighbors. The stronger this

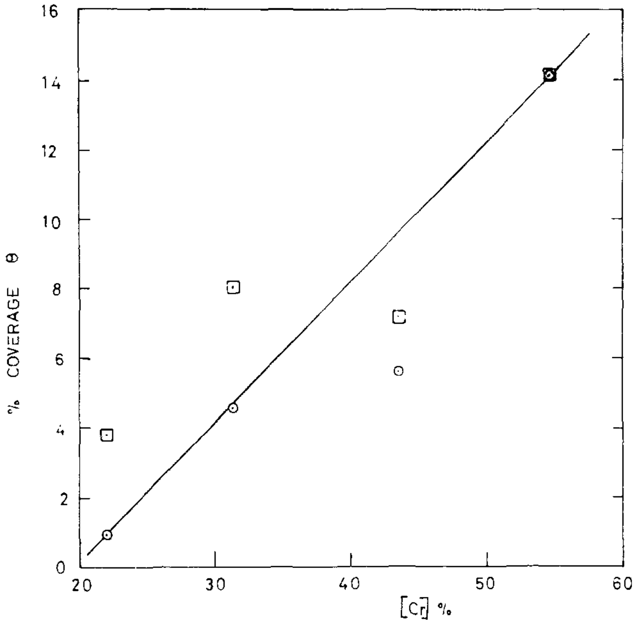

FIG. 5. The variation of oxygen adsorption with chromium content for reaction at T = 500 and = 560°C: ⊙, θ calculated with respect to all the B-site surface cations; ⊡, θ calculated with respect to the B-site surface chromium ions.

interaction is, the less active is the surface ion in N_2O decomposition.

Finally we turn to a consideration of the identity of the strong oxygen adsorption sites. Figure 5 shows that oxygen coverage varies in an approximately linear fashion with [Cr] for SMAC50, SMAC100, SMAC300, and SMC. It would appear that the site consists of a group of Cr ions whose frequency increases rapidly with [Cr]. For a [Cr] increase of 2.5 the surface coverage increases 14 times. Any suggestion as to the identity of this site is speculative; however, earlier workers (*4*) have emphasized that a site which has relatively high electron accessibility is necessary. Thus a site where clusters of Cr ions occur would seem to be most preferred. Such clusters are most abundant on the [111] plane where it is possible to envisage an oxygen ion being coordinated to three cations at once. Clearly one cannot dismiss the possibility of surface-defects and vacancies playing an important role in the adsorption but further study will be necessary to discover the extent of their influence.

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