An Interpretation of the Activity Behavior of Model Oxide Solid Solution Catalysts on the Basis of a Solid-State Polaron Hopping Mechanism

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The catalytic activity of doped oxide systems α-Al$_{2-x}$Cr$_x$O$_3$, MgAl$_{2-x}$Cr$_x$O$_4$, Mg$_{1-x}$Cu$_x$Al$_2$O$_4$, Mg$_{1-x}$Ni$_x$Al$_2$O$_4$, Mg$_{1-x}$Ni$_x$O, and Mg$_{1-x}$Co$_x$O for reactions such as N$_2$O decomposition, CO oxidation, H$_2$–D$_2$ exchange, the decomposition of isopropanol, and the oxychlorination of ethylene is not a monotonic function of doping but appears to follow a regular pattern. On doping with transition metal cations from zero up to 10 to 15% (dependent on the host solid) the catalytic activity increases, then drops and thereafter increases again. This pattern of activity is explained by using the concept of polaron formation around the impurity center in the host solid. It is suggested that in the region of 10 to 15% doping each polaron will have at least one polaron nearest neighbor, which will greatly facilitate the electron movement through the solid. This in turn restricts the desorption step for reasons connected with the Pauli principle.

INTRODUCTION

In recent years many workers have utilized oxide solid solutions as model catalysts in an attempt to understand the mechanism of operation of complex catalyst systems (*1–19*). These studies have shown that the relative importance of the host matrix on the one hand and the dopant cation, usually a *d*-transition metal ion (t.m.i.) on the other can be separated and assessed (*7*).

Typically a diamagnetic and catalytically relatively inert oxide has been used as a host matrix which forms a solid solution with the dopant atom of interest. In this way it is possible, at low dopent concentration, to isolate the active t.m.i. and to study its activity considering it as a localized center ignoring the perturbations arising from interactions with neighboring t.m.i. Alternatively these interactions may be monitored systematically by progressively increasing the dopent concentration. The catalytic systems which have been studied over the whole range of dopent concentration are α-Al$_{2-x}$Cr$_x$O$_3$ (*11*), MgAl$_{2-x}$Cr$_x$O$_4$ (*12*), Mg$_{1-x}$Cu$_x$Al$_2$O$_4$ (*9*), Mg$_{1-x}$Ni$_x$Al$_2$O$_4$ (*18*), Mg$_{1-x}$Ni$_x$O (*15*), and Mg$_{1-x}$Co$_x$O (*19*). A number of different reactions have been carried out on these systems to test their activity. The α-Al$_{2-x}$Cr$_x$O$_3$ catalysts have been tested for the decomposition of N$_2$O (*1, 2*) and the catalytic exchange of H$_2$–D$_2$ (*4, 5*); the Mg Al$_{2-x}$Cr$_x$O$_4$ catalysts for the decomposition of N$_2$O (*3*), the exchange of H$_2$–D$_2$ (*6*), and isopropanol decomposition (*10*); the Mg$_{1-x}$Cu$_x$Al$_2$O$_4$ samples for the oxychlorination of ethylene (*9*) and the oxidation of CO (*8*); the Mg$_{1-x}$Ni$_x$Al$_2$O$_4$ catalysts for the decomposition of N$_2$O (*18*); and the Mg$_{1-x}$Ni$_x$O and Mg$_{1-x}$Co$_x$O catalysts

for the decomposition of N_2O (15, 19) and the oxidation of H_2 (20, 21). Except for some of the data on H_2 oxidation (20), in all these cases the same sort of activity pattern was found; i.e., the undoped catalyst α-Al_2O_3, $MgAl_2O_4$, or MgO has a very low activity which increases rapidly with the addition of t.m.i. up to 10% substitution; at this point a fall is observed, and after that fall the activity increases again (see Figs. 1a and b, 2a–c, 3a and b, and 4a–c).

We believe that this regular pattern, despite variations in host matrices, must be due to some underlying electronic effect. The range of catalysts used and the differing reactions studied suggest that this phenomenon may well have implications for catalysis in general. In this paper we try to define its origins more precisely.

EXPERIMENTAL

The solid-state properties of all the catalysts to which we have referred have been characterized in considerable detail by the authors concerned. The concentration of t.m.i. in the host oxides at which intercation interactions become significant is fairly clear. Since, however, we are dealing with a phenomenon involving the movement of electrons, conductivity measurements on the catalysts available have now been carried out to amplify the solid-state data.

The electrical conductivity behavior of each of the solid solution series α-$Al_{2-x}Cr_xO_3$, $Mg\,Al_{2-x}Cr_xO_4$, and $Mg_{1-x}Cu_x$-Al_2O_4, was studied as follows. A pellet of the catalyst was prepared by compressing about 1 g of the powder under a pressure of 10 tons/cm². The pellet was clamped between two platinum electrodes which were connected with a cell of 1.5 V. The current passing through the pellet was measured with a Pico ammeter (V. G. Electronics) having a range of 10^{-12} to 10^{-3} A. The electrical measurements were
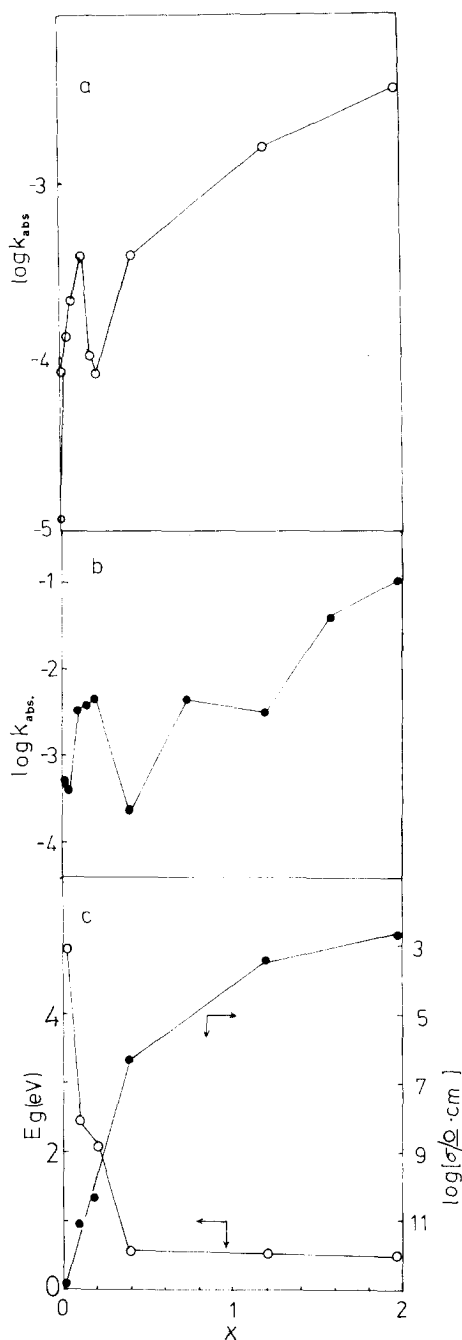

FIG. 1. Catalytic activity of α-$Al_{2-x}Cr_xO_3$ taken as log k_{abs} for (a) the decomposition of N_2O at 555 K, (b) the H_2–D_2 exchange at 625 K, (c) the conductivity of the samples at 870 K, and the variation of the activation energy of conduction, E_g, as a function of x (1, 2, 5).

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TABLE 1

Activation Energies (Kilojoules/Mole) for Some N_2O and Oxychlorination Reactions

N₂O on α-Al₂₋ₓCrₓO₃ (1,2)			N₂O on MgAl₂₋ₓCrₓO₄ (3)		Oxychlorination of C₂H₄ over Mg₁₋ₓCuₓAl₂O₄ (8)	
	h.p.[a]	l.p.[a]				
x			x		x	
0	75	41	0	136	0.01	72
0.002	—	34	0.02	115	0.05	73
0.02	78	24	0.18	95	0.10	56
0.05	—	25	0.67	124	0.25	51
0.07	64	16	1.00	88	0.50	53
0.18	75	19	1.50	101	CuAl₂O₄	54
0.40	98	11	MgCr₂O₄	97		
0.79	96	—				
1.20	86	18				
α-Cr₂O₃	119	8				

[a] h.p. and l.p. refer to high pressure (4 kN m^{-2}) and low pressure (2 N m^{-2}) reactions, respectively. No oxygen desorption occurred in the latter case.

made in a small pressure of N_2O (~5 Torr) since all the catalysts had been used for the N_2O decomposition reaction. The variation of conductivity as a function of temperature was observed to be identical whether the catalyst temperature was being raised or lowered. Changing the atmosphere to hydrogen had a small effect on the conductivity, σ, and an insignificant effect on the activation energy for conduction, E_g, as might be expected for low-surface-area powders.

Despite widespread controversy over procedures for electrical measurements on oxide powders, the measurements gave good agreement with literature values of E_g and σ for α-Cr₂O₃ (22), α-Al₂O₃ (23), and Mg Cr₂O₄ (24). Thus the data for the solid solution series are expected to be reliable, especially for internal comparisons within a given series.

RESULTS

The variation of catalytic activity as a function of x for α-Al₂₋ₓCrₓO₃ in N_2O decomposition at $T = 555$ K and the H_2–D_2 exchange at $T = 625$ K are shown in Figs. 1a and b. The characteristic pattern

of activity is evident in each case. The variation of conductivity and the activation energy for conduction, E_g, as a function of x is also shown in Fig. 1c for comparison. Activation energies are given in Table 1.

The variation of catalytic activity for MgAl₂₋ₓCrₓO₄ as a function of x in N_2O decomposition at 833 K, in H_2–D_2 exchange at 625 K, and in isopropanol decomposition at 573 K is shown in Figs. 2a–c. In Fig. 2d conductivity data are displayed.

Figures 3a and b indicate the same activity pattern for the system MgCuₓAl₂O₄ in the oxychlorination of ethylene at 473 K and the oxidation of CO at 493 and 583 K. Again the conductivity data are shown (Fig. 3c). In all cases there is a correlation between the minimum of activity and a sharp change in the conductivity plot. The pattern of the catalytic activity of Mg₁₋ₓNiₓAl₂O₄ is markedly influenced by the fact that the x = 0.25 and x = 0.50 samples have an inversion parameter $\alpha = 0.11$ as compared to 0.20 for the other catalyst samples of this spinel series. The observed activity of these two samples may be normalized to that expected if α were 0.20. Cimino and Schiavello (7, 18)
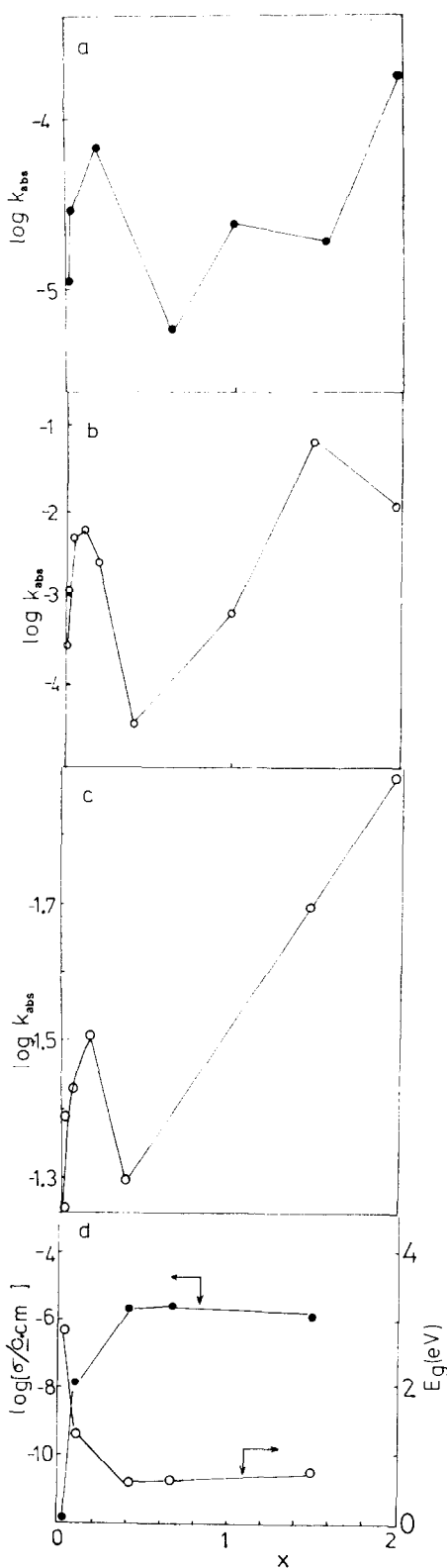
suggest that a 3–4% inversion from the tetrahedral to octahedral occupation yields an increase of log k of $\sim$0.5 at $1000/T$ = 1.5. Thus the increase of 10% in octahedral preference observed in those two samples would be expected to increase log k by *at least 0.5*. Thus the activity for these catalysts for $\alpha = 0.20$ will be lowered by $\Delta \log k = 0.5$. Figure 4 shows the results of this correction. The dotted line reproduces the activity data of Cimino and Schiavello (*18*) for the so-called SAMN (1000) samples at $1000/T = 1.5$, i.e., at 666 K. The solid line is the expected activity of the catalysts at a constant inversion parameter $\alpha = 0.20$.

Furthermore in Figs. 4 b and c we present the catalytic activity for $Mg_{1-x}Ni_xO$ and $Mg_{1-x}Co_xO$ for the decomposition of N_2O. The data were obtained from the relevant papers of Cimino et al. (*15*, 17).

It can be seen that in all cases the variation in activity is similar showing the rise and fall followed by a final rise. This behavior is even more marked when the activities of each catalyst are normalized to a unit t.m.i. concentration. Figures 5 a and b show the situation obtained in the case of N_2O decomposition and H_2–D_2 exchange over α-$Al_{2-x}Cr_xO_3$.

In Figs. 5 b and c the data of Boreskov et al. (*20*) and Gerasimova et al. (*21*) for the oxidation of H_2 over $Mg_{1-x}Co_xO$ and $Mg_{1-x}Ni_xO$ are presented. These are also normalized to unit t.m.i. concentration. It is significant to note that Boreskov has suggested that the $Mg_{1-x}Co_xO$ activity does not follow the trends presented above (*20*). However, the results of Gerasimova et al. on $Mg_{1-x}Co_xO$ at high temperature *do* seem to follow the familiar trend. The

FIG. 2. Catalytic activity over $Mg\,Al_{2-x}Cr_xO_4$ for (a) N_2O decomposition at 833 K, (b) H_2–D_2 exchange at 625 K, and (c) decomposition of isopropanol at 573 K. (d) The conductivity of the samples at 870 K and the activation energy of conduction, E_g, is also shown for comparison (*3, 6, 10*).
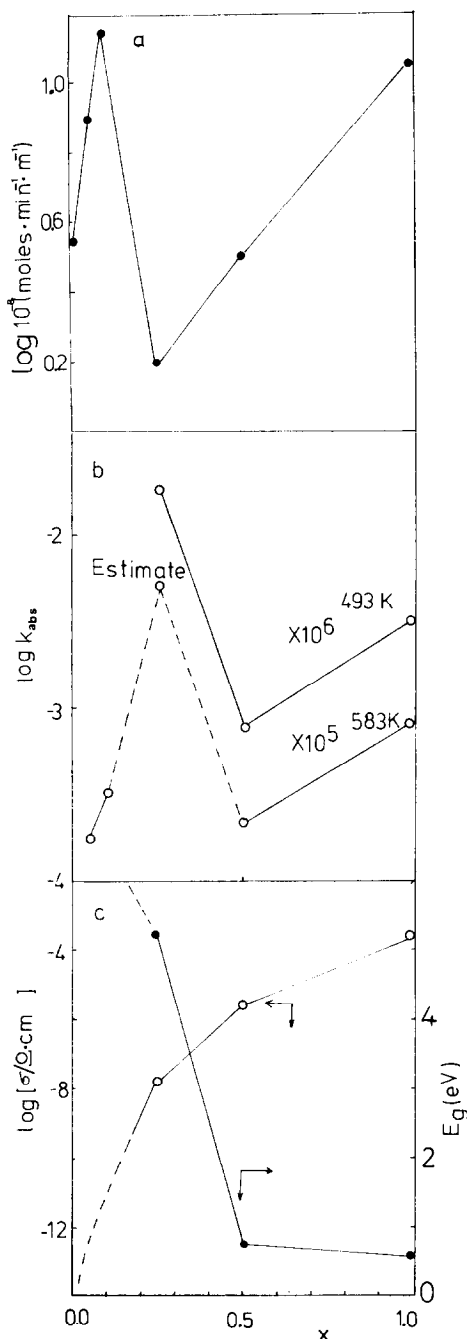
FIG. 3. Catalytic activity over $Mg_{1-x}Cu_xAl_2O_4$ for (a) ethylene oxychlorination at 473 K and (b) CO oxidation at 493 and 583 K. (c) The conductivity at 870 K and the variation of the activation energy of conduction, E_g, is also shown (8, 10).

reason for the apparent conflict of data may well lie in the differing procedures adopted for pretreating the catalysts.

Boreskov et al. outgassed the catalysts with a rotary pump at 400°C and then heated them in oxygen at 400°C for 4 hr. Gerasimova et al., however, activated their catalysts at 600°C for 2 hr under high vacuum and then heated in oxygen for 1 hr at 600°C. They claim that this procedure was necessary to completely regenerate the catalyst because traces of water vapor left on the catalyst could inhibit activity. Certainly this latter procedure is much closer to that generally applied in activating solid solution catalysts. Furthermore the fact that the high-temperature data on $Mg_{1-x}Co_xO$ do follow the expected trend suggests that product water may also inhibit activity at low temperatures.

DISCUSSION

It is clear from the activity patterns presented above that a drop in the catalytic activity occurs in the region of 10–15% doping of the inert matrix with t.m.i. This type of behavior has been observed elsewhere in the past. Oxide catalysts dilute in t.m.i. have been shown to be more active in a number of classes of simple catalytic reactions (1–3 and 13–19). It is tempting to suggest that the mechanism operating in these model oxide catalysts could be generalized to less well-defined catalysts. The explanation offered in earlier work was that electronic interactions between t.m.i. result in a decrease in activity. We shall try here to clarify more precisely the mechanism of those interactions and to define their effect in the adsorption–catalysis–desorption process.

A t.m.i. having a d^n electronic structure introduced into a material like $\alpha\text{-}Al_2O_3$, $MgAl_2O_4$, or MgO will be affected by, and will itself affect, its environment. In the language of solid-state physics this is known as polaron formation. A polaron consists of a d-electron (in this case) and its polarized region in the crystal. The conductivity behavior of a number of transition metal oxides has been interpreted
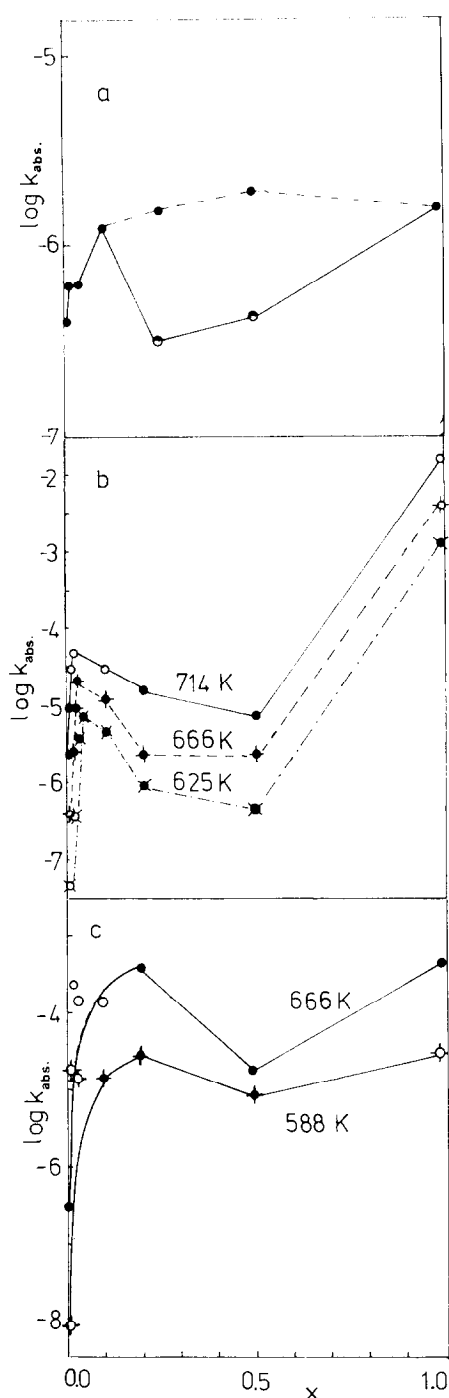
FIG. 4. Catalytic activity for N_2O decomposition over (a) $Mg_{1-x}Ni_xAl_2O_4$, (b) $Mg_{1-x}Ni_xO$, and (c) $Mg_{1-x}Co_xO$. The empty circles in (b) and (c) represent extrapolated values of activity from the Arrhenius plots. Data from (18), (15), and (19) for (a), (b), and (c), respectively; see text.

in terms of a polaron hopping mechanism (25). The strong probability that the charge transfer process in these oxide solid solutions proceeds by a similar mechanism forms the basis of the ensuing treatment.

Around the electron the field set up in the crystal, and with which it interacts, has a potential energy function given by

$$V = -e^2/\kappa_p r, \quad \text{for } r > r_p$$

and (1)

$$V = -e^2/\kappa_p r_p, \quad \text{for } r < r_p,$$

where r_p is the polaron radius and

$$1/\kappa_p = (1/\kappa_\infty) - (1/\kappa), \quad (2)$$

where κ_∞ and κ are the high-frequency and static dielectric constants of the host.

In determining r_p there are two limiting approximations:

(i) The effective mass, m^*, of the electron is so high that the kinetic energy of the electron, $h^2\pi^2/m^*r_p^2$, localized by the potential, V, is negligible. In this case, which is usual in transition metal oxides, r_p will be somewhat less than the interionic radius. The polaron is called a "small polaron." Its energy is made up as follows: (a) the energy required to polarize the host lattice, $\frac{1}{2}e^2/\kappa_p r_p$, and (b) the lowering of the potential energy of the electron, $-e^2/\kappa_p r_p$.

Thus the polaron energy $-W_p$ is given by

$$-W_p = -\tfrac{1}{2}e^2/\kappa_p r_p. \quad (3)$$

(ii) The other extreme is the "large polaron" which occurs when m^* is not large. Here the kinetic energy term $h^2\pi^2/2m^*r_p^2$ must be added to (3), so that

$$-W_p = -\tfrac{1}{2}e^2/\kappa_p r_p + h^2\pi^2/2m^*r_p^2. \quad (4)$$

The situation in transition metal oxides usually approximates to the small polaron case. The effective mass, m^*, of the electrons is usually large because the d-bands are very narrow.

The small polarons generally move by hopping from one polarization well to the next. Figure 6 illustrates the mechanism. In Fig. 6a there is a small polaron with an
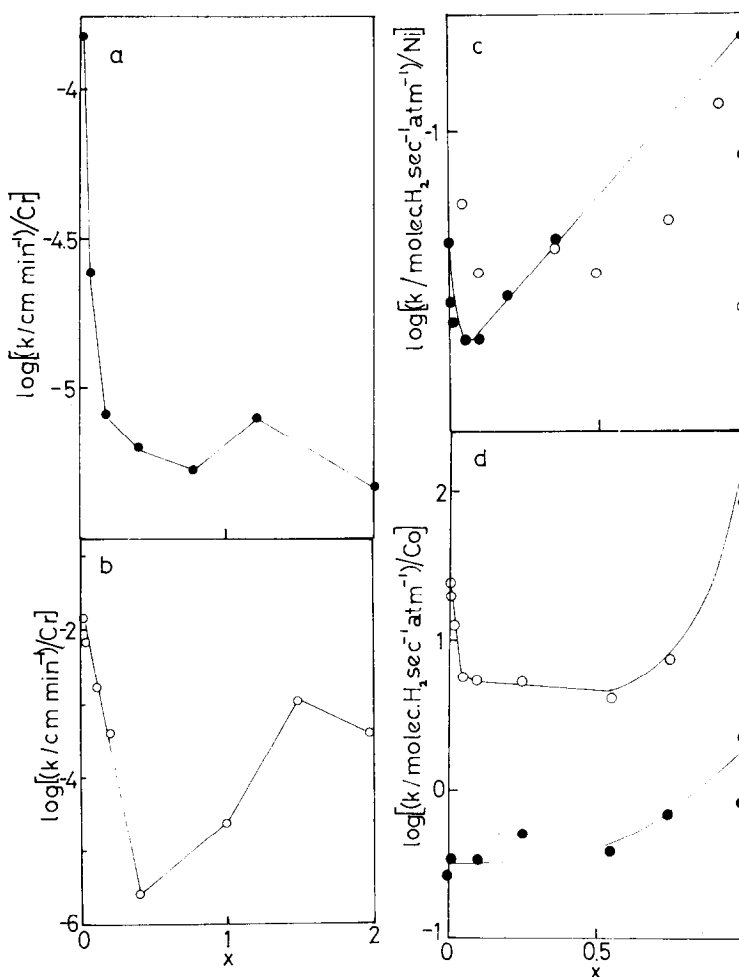
FIG. 5. Variation of activity (a) *per Cr ion* for N_2O decomposition and (b) *per Cr ion* for H_2-D_2 exchange, over α-$Al_{2-x}Cr_xO_3$ catalysts; (c) *per Ni ion* for hydrogen oxidation over $Mg_{1-x}Ni_xO$ at 683 K, comparing the data of Popovski *et al.* (20a), ○ ; and Gerasimova *et al.* (21), ● ; (d) *per Co ion* for hydrogen oxidation over $Mg_{1-x}Co_xO$ at 740 K, ● ; and 823 K, ○ .

electron localized in its potential well at equilibrium. If the electron is to be transferred, thermal fluctuations must ensure that the energies of the adjacent wells are equal as in Fig. 6b. It is clear that the smallest activation energy which can produce this situation is when both wells have half the original depth. When the atoms are so far apart that the charge clouds do not overlap appreciably, then the activation energy for hopping is given by

$$W_H = \tfrac{1}{2}W_p. \tag{5}$$

If the charge clouds do overlap, the energy becomes

$$W_H = \tfrac{1}{4}e^2/\kappa_p([1/r_p] - [1/R]), \tag{6}$$

where R is the distance from one polaron site to the next.

Thus the frequency of hopping will be given by
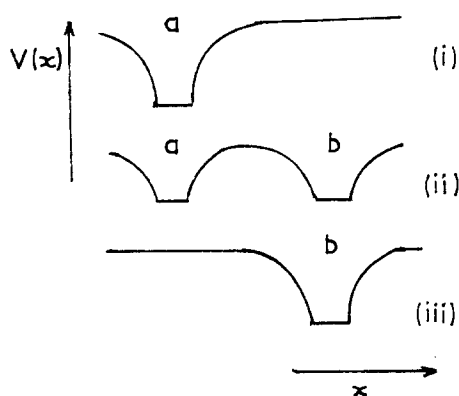
$$w = w_0 \exp (- W_H/kT). \tag{7}$$

FIG. 6. Potential wells on a pair of ions a and b during the hopping process: (i) before hopping; (ii) thermally activated state when electrons can move; and (iii) after hopping.

Polaron theory has been extensively applied to semiconducting transition metal oxides (25). Here a d-electron is thought to move from one metal ion to another via the 2p orbitals of the oxygen ions. (Examples are the movement of Ni^{3+} centers through NiO, or Ti^{3+} through TiO_2.) Clearly in the case of d-electrons, the spin of the hopping electron will also be a significant factor in the transfer process. This effect, however, will not be introduced here since it does not affect the basic argument.

Austin and Mott emphasize (25) that the concept of the polaron is valid only if the number of carriers (n) is considerably less than the number of lattice sites (N), so that there are enough sites around a carrier to be polarized. If $n/N > 0.1$ then two polarons will compete for the same site.

In the case of the solid solution catalysts where d^n cations like Cr^{3+}, Ni^{3+}, and Cu^{2+} are incorporated into lattices such as α-Al_2O_3, MgO, and $MgAl_2O_4$, polaron formation will be expected around these cations. Initially the polarons are far apart, and direct hopping from one t.m.i. to another via oxygen 2p orbitals will not be possible. The hopping electron will have to hop *over* a number of non-t.m.i. cations such as Al^{3+} or Mg^{2+}. Mott met this

situation in discussing the conductivity of ferrites where two types of sites, A and B, are present. Conduction occurs via the A sites. Thus electrons have to pass from one A site over a B site to arrive at the next A site. An energy term $\Delta\mu(\gg kT)$ has to be added to the activation energy of conduction, thus

$$\sigma = \sigma_0 \exp - (\Delta\mu + W_H)/kT \quad (8)$$

At high dilution of t.m.i., $\Delta\mu$ will be large because the electron will have to traverse many non-t.m.i. cations. As the doping increases $\Delta\mu$ would be expected to fall eventually to zero when each t.m.i. has at least one t.m.i. nearest neighbor.

In the case of some oxides further incorporation of t.m.i. can result in direct d-orbital overlap between the t.m.i. cations on the lattice and metallic conduction results when

$$n^{\frac{1}{3}}\alpha_0\kappa \sim 0.45, \quad (9)$$

where α_0 is the hydrogenic Bohr radius. This does not occur with the solids under consideration, but this situation will be dealt with in later papers.

Examination of the conductivity data, particularly the activation energies of conduction in Figs. 1–4 shows that there is a fall from high values (~5 eV) at low doping levels to a constant value of ~0.5–0.8 eV between ~15 and 10% t.m.i. addition. Initially the t.m.i. are essentially isolated, and the electrons are localized on the polaron because large energies are required (~4.0 eV) to transfer the electrons to distant t.m.i. With increasing addition of t.m.i. to the host, eventually a point is reached when each t.m.i. has at least *one* t.m.i. nearest neighbor and $\Delta\mu \to 0$; the hopping of the polarons is relatively easy, and we can say that the electrons have become "nonlocalized." The critical concentration at which this occurs will be called the localized–nonlocalized or LNL point. In Table 2 these critical points have been estimated for each of the host struc-

TABLE 2

Localized to Nonlocalized (LNL) Changes in Oxide Solid Solutions

Host oxide	Transition metal ion (t.m.i.) in solution	Critical concentration for LNL point		Supporting data for LNL point
		Predicted	Observed from conductivity data	
MgO	Ni²⁺ Co²⁺	~8%	~6.5%	
α-Al₂O₃	Cr³⁺	~14%	>10% (x = 0.18) <25% (x = 0.40)	Reflectance spectra EPR Magnetic data (11)
MgAl₂O₄	Cr³⁺	~16% (only on B sites)	~13% (x = 0.40)	Reflectance spectra EPR Magnetic data (12)
	Cu²⁺	(a) ~16% of B (b) ~14% of B + ~16% of A (c) All of A + 8% of B	>9.5% of B 6% of A (x = 0.25) <14% of B 21% of A (x = 0.50)	EPR Magnetic data ESCA (8)

tures of interest by calculating the fraction of cations which would have to be t.m.i. in order that each t.m.i. would have one neighboring t.m.i. coordinated directly to it via at least one oxygen anion. It can be seen that there is good agreement between the predicted concentrations for the transition from localized centers to more nonlocalized electronic behavior and the observed solid-state data. These transitions have been observed using a number of techniques (8, 11, 12), but they are highlighted here by the conductivity data. In each case there is a fairly sharp transition of several orders in the conductivity at the expected dopent concentration. The MgO catalysts were not available to us, but it is reported that a sharp transition in conductivity occurs at 6% Ni²⁺ concentration (26).

Thus it has been established that before the LNL point electron transfer between t.m.i. is difficult, and the electrons are essentially localized. After the LNL point electrons on dopent atoms are less localized, and the electrons are much freer to move and interact with each other. It is these features which are significant in our discussion of the catalytic mechanism.

The decomposition of N₂O will be used as a model reaction to discuss the mechanisms of catalysis. This will be done for two reasons. First the reaction has been studied extensively in the past, and its mechanism is well known. Second it has been used to test all the catalysts referred to in this paper and so provides a uniform approach to the problems. The successive steps of this reaction are as follows (7):

Step 1: Adsorption

$$N_2O_{(gas)} + K_{(cat)} \rightarrow N_2O^-_{(ads)} + K^+_{(cat)}$$
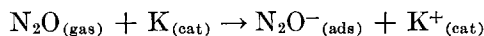
where $K_{(cat)}$ is a site on the surface. The gas molecule is adsorbed by transfer of an electron, *completely* or *partially*, to the molecule while a vacant site or hole K^+ is left behind in the catalyst. (In this discussion complete transfer of the electron is assumed but it is recognized that partial transfer is often more likely.)

Step 2: Reaction

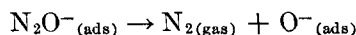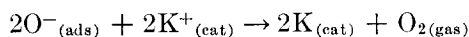This involves the breaking up of certain chemical bonds and creation of others:

$$N_2O^-_{(ads)} \rightarrow N_{2(gas)} + O^-_{(ads)}$$

TABLE 3

Activation Energy of Desorption of Oxygen (2)

Catalyst	E_d (eV)
α-Al$_2$O$_3$	0.34
0.02*	0.54
0.07	0.48
0.18	0.56
0.40	0.88
0.79	0.83
1.20	0.67
α-Cr$_2$O$_3$	1.09

* x in α-Al$_{2-x}$Co$_x$O$_3$.

Step 3: Desorption

$$2O^-_{(ads)} + 2K^+_{(cat)} \rightarrow 2K_{(cat)} + O_{2(gas)}$$

or

$$O^-_{(ads)} + K^+_{(cat)} + N_2O \rightarrow K_{(cat)}$$
$$+ N_{2(gas)} + O_{2(gas)}$$
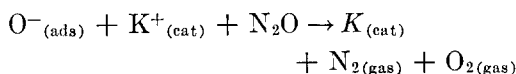
The electron transferred to the adsorbed species is moved back to the solid and reoccupies the vacant site. Until desorption there is a high probability that the site will remain deficient in electron charge *if* the movement of the electrons to the site from the catalyst bulk is restricted, and this will be so before LNL. After LNL the probability of filling the vacant site with a bulk electron will become much greater, and this will affect desorption.

The empty orbital on the catalyst site can be filled in one of two ways: An electron can be gained from the adsorbed species *or* from the bulk. The electron which will move to the empty orbital will be the one with lower activation barrier to overcome. The activation energy E_b required to move a bulk electron from one site to another will be given by the activation energy of polaron conduction $(\Delta\mu + W_H)$. The activation barrier for the return of the electron from the adsorbed species to the surface is given by E_d, which should be proportional to the activation energy of desorption *before* LNL. Thus when (a) $E_b > E_d$, the empty site will be filled with an electron from the adsorbed

species; this will be the situation before the LNL point, where $E_b \sim (\Delta\mu + W_H) > 1$ eV and $E_d < 1$ eV [as evidenced by the activation energies for desorption of oxygen from α-Al$_{2-x}$Cr$_x$O$_3$ catalysts (2), Table 3]; (b) $E_b \rightarrow E_d$, the two paths will start competing with each other; this will occur near or at the LNL point when $\Delta\mu \sim 0$; (c) $E_b < E_d$, a bulk electron will tend to fill the empty orbital.

As a result of (c) after the LNL point the desorption process (step 3) may involve an electron–electron collision; otherwise the molecule will remain adsorbed. The process should obey the Pauli exclusion principle. Thus no two electrons can occupy the same site or orbital unless they differ by at least one quantum number. In our case an electron has been transferred to the oxygen atom adsorbed on the catalytic site, and the hole left behind may be filled by an electron from the bulk. This bulk electron will thus be in a potential well. Thermal oscillations may, however, enable the electron to move elsewhere thus vacating the orbital again and enabling it to accept back the electron from the adsorbed species. Thus a further activated step has been introduced into the desorption process [Table 3 shows that the activation energy of desorption of O$_2$ over α-Al$_{2-x}$Cr$_x$O$_3$ (2) increases substantially after the LNL point] which would be expected to lower the rate of desorption and hence the overall activity, as is observed.

Finally, beyond the LNL point the activity rises again with further doping. In some reactions such as N$_2$O decomposition and ethylene oxychlorination the activity rise is monotonic with t.m.i. incorporation indicating that the number of active sites in the surface is directly related to the concentration of t.m.i. in the catalyst, and consequently activity per t.m.i. is constant. This is also reflected in the Arrhenius parameters. There is a steady rise in A, the preexponential factor,

while the activation energies are fairly constant. The situation is different for other reactions such as H_2–D_2 exchange and hydrogen oxidation where there is a much more rapid rise of activity with t.m.i. content. Such behavior probably reflects either a change of mechanism or the use of multication sites. It is quite likely that both factors will operate simultaneously in these reactions.

CONCLUSIONS

This discussion seems to provide a satisfactory electronic explanation for the drop in catalytic activity for simple catalytic reactions at the point where a transition from electronically isolated centers to nonlocalized centers occurs as a result of doping a diamagnetic insulator host. The implications of this discussion are that a *good catalyst* for simple reactions, involving electron acceptor molecules which adsorb on one catalytic site (a t.m.i.), will be that catalyst whose active sites are far enough apart that orbital overlap is unlikely and electron hopping between them is very difficult. The critical concentration for this localized site situation to break down seems to be around 10 to 15% substitution depending on the host lattice structure. The active surface site then becomes part of a complex electron transfer system within the bulk of the solid. No longer is it simply involved with a one-electron transfer with an adsorbed molecule at the surface. Electron interaction with adsorbed species has to compete with electron interaction with the other centers in the bulk, and as a result surface catalytic activity falls.

Although it is thought that these conclusions are of general applicability, it is clear that the problem of catalyst selectivity has not been considered. This will be the subject of a subsequent paper. Furthermore, we have not considered possible two or more site reactions such as

the isobutane dehydrogenation reactions studied by Marcilly and Delmon (27) over similar solid solutions. Clearly here at least different spatial/statistical constraints will operate.

There are a number of mixed oxide catalytic studies in the literature which do not show exactly similar behavior to those reviewed here. Many do not claim to be studies on solid solutions, but in a sense this is not relevant. Our conclusion is that isolate sites are very active; electronic interaction can depress this activity whether it occurs uniformly through a homogeneous solid, or in high concentration patches or islands in the surface.

ACKNOWLEDGMENT

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