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# The Significance for Oxide Catalysis of Electronic Properties and Structure*

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The reasons why the application of band theory as a basis for understanding catalysis by oxide semiconductors has met with limited success are reviewed. They include the limitations of the theory itself, the complexity of crystal imperfections in oxides, and the extreme versatility of oxide surfaces to form with any given molecule a variety of chemisorbed species. It is pointed out, however, that certain important concepts survive, notably charge transfer adsorption and the control of valence and stoichiometry.

The band theory approach has been superseded by developments emphasizing crystal structure, with chemisorption viewed as a process for restoring, either partially or completely, the interruption of structure brought about by the formation of a surface. Models for chemisorption and catalysis stemming from this concept of coordinative unsaturation are more easily able to incorporate chemical knowledge of bonding and molecular structure.

The review concludes by referring to current researches on oxides which emphasize the role of localized centers for catalysis. Special attention is given to oxide solid solutions prepared by dissolving a transition metal oxide in an insulating diamagnetic oxide as matrix. This enables catalysis to be studied with control over the electronic interaction between the active transition metal ions. Catalytic activity develops strongly even in dilute solutions, and it is possible to assess for particular reaction types the extent to which electronic interaction between transition metal ions is harmful or beneficial.

The use of oxides as catalysts is already widespread, and their importance in this chemical field of application is continuously growing. The energy crisis and the increasing concern with the problems of pollution demand that oil and coal should be used less for direct combustion and more for controlled chemical conversion to useful materials. These developments are among many in current technology which call increasingly on heterogeneous catalysis, and on the resources of science in improving our understanding of the action of catalysts.

Electronic properties feature in this because heterogeneous catalysis involves the formation of chemical bonds between reactant molecules and solid surface. The bonds at oxide surfaces are subject to the same wide variations in electron distribution as the chemical bonds *within* oxides which in the final reckoning control the fine detail of optical, magnetic, and electron transport properties, so that in principle there need be no difference in the way the problems are handled. In practice, however, there has to be a difference, because the electronic theory of solids is approximate. The shortcomings are intensified when the relatively high symmetry of internal crystal structure is interrupted by introducing a surface and by placing on it a variety of foreign chemical species. In this review our aim is to discuss general approaches to these problems and highlight some of the researches which appear most relevant to them.

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## Band Theory and Oxide Catalysis

The early attempts to formulate an electronic basis for oxide catalysis were not deterred by the limitations of solid state theory. Chemisorption on a semiconducting oxide was treated as a boundary layer problem in which electrons were donated or accepted by the solid, thereby charging the adsorbed species (*1–3*). By postulating chemical reaction between oppositely charged species, followed by desorption, a mechanism for catalysis was provided (*4–6*). The bare essentials are shown schematically in Fig. 1 for a reaction between a molecule $X$ of low ionization energy and a molecule $Y$ of high electron affinity.

This model stimulated a great deal of interest in adsorption and catalysis on oxides. It rationalized a number of known effects, such as the changes of conductivity observed during chemisorption, and it afforded a framework within which to discuss existing data on oxide catalysis and to plan new studies. Inasmuch as the principal function of the oxide was to act as a source and sink for electrons, with properties defined by the height of the Fermi level $E_F$, the catalytic activity could be expected to change by doping oxides with altervalent ions, or by sustained illumination with sufficiently energetic quanta. Effects of this kind were observed, and a number of reviews treated the subject in detail (*7–9*).

The experimental evidence, however, frequently failed to support in detail the precept of a direct relationship between semiconductor theory and oxide catalysis. Let us examine the factors which have contributed to this situation.

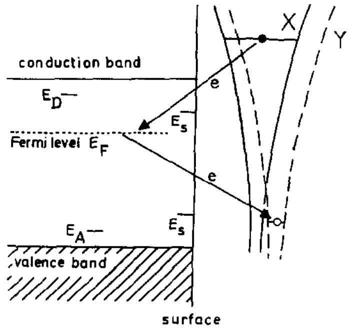

FIG. 1. The reaction $X + Y \rightarrow XY$ over an oxide catalyst. Step 1: $X(g) \rightarrow X^+(\text{ads}) + e$ (to catalyst); Step 2: $Y(g) + e$ (from catalyst) $\rightarrow Y^-(\text{ads})$; Step 3: $X^+(\text{ads}) + Y^-(\text{ads}) \rightarrow XY(g)$.

In the first place the nature of the imperfections in oxides has proved to be much more complex than had been supposed. Individual point defects have been observed by EPR to show appreciable mutual interaction, and also combination, with the result that localized donor and acceptor states ($E_D$ and $E_A$, Fig. 1) must be spread in reality over a wide range of energy. The detailed X-ray studies initiated on molybdenum oxide (*10*) and widened to include titanium, vanadium, tungsten, and other oxides (*11*) have shown that 'extended' defects occur at least in the oxygen-deficient nonstoichiometric phases of these materials, the crystallographic shear planes (essentially *arrays* of adjacent point defects) being readily observable by high resolution electron microscopy (*12*). The complications for the energy level structure are considerable. The problems of incomplete dispersion of defects have also clouded the issue in respect of the catalytic studies on the effect of altervalent dopents, as in the catalysis of CO oxidation by doped nickel oxide (*9, 13*).

In the second place there is the clear evidence from transport studies and theoretical work that a simple band model is not appropriate for oxides such as the 3*d* oxides which feature so often as active catalysts. The warning was first given by Morin (*14*) some 20 years ago, and the dialogue of how best to describe the energy level structure of NiO, for instance, still continues (*15*). Linked also with the theoretical developments, and of special relevance for chemisorption and catalysis, is the work on surface states (*16*). Here again, the effect is to introduce localized levels in the band gap, schematically denoted as $E_s$ in Fig. 1, one corresponding to the surface cation and the other to the surface anion.

These considerations, then, all contrive to generate levels within the band gap, and some of them, notably the overlap of *d*-orbitals such as is held to occur in $V_2O_3$ and $Ti_2O_3$ (*17*), and presumably therefore in the *CS* planes of substoichiometric rutile, will lead to this multiplicity of states, and all can play a part in determining the height of the Fermi level, the one 'rounded' parameter that describes the properties of the oxide in the boundary-layer theory. It is scarcely surprising that activity patterns in catalysis, necessarily invoking studies with different oxides, fail to match the expectations of theory.

However, this is not all, for we have yet to consider the model from the standpoint of the reactants. The most important consideration from this side is the ability of many molecules to be held on the surface of an oxide in more than one chemisorbed form. The clearest evidence for different chemisorbed forms comes from ir spectroscopy. Many oxides have now been studied (*18*), and the recurrent theme (as with metal surfaces) is the production of several distinct ir bands as a result of adsorbing any one gas on a given oxide. A recent and illustrative example is the work of Cerruti et al. (*19*), who have observed 14 bands to develop when nitric oxide is adsorbed on MgO. The authors have tentatively assigned all these bands, and they attribute them by analogy with known ir spectra to the adsorbed species $NO^-$, $NO_2{}^-$ (or $NO_2^{2-}$, since the ir data cannot distinguish the charge absolutely) and the dimer $N_2O_2^{2-}$. Exact assignments will have to await studies by other techniques, but it is certainly clear that several chemisorbed forms are coexisting. The heat of this adsorption, determined calorimetrically, is 18 kcal mole$^{-1}$ (*20*). Nitric oxide on MgO is a case where the molecule does not break up on chemisorption. However, chemisorption frequently occurs both nondissociatively *and* dissociatively. For $H_2O$ adsorbed on rutile, for instance, the O–H stretching frequencies of intact $H_2O$ and dissociated $H_2O$ are readily distinguished, and can be correlated with the two principal adsorption types revealed by temperature programmed desorption (*21*). The dissociative chemisorption amounts to a reaction with an oxygen ion of the surface ($O_s^{2-}$):

$$O_s^{2-} + H_2O \rightarrow OH_s{}^- + OH_{ads}^-.$$

A similar situation must occur with the NO adsorption described above to account for the observed $NO_2{}^-$ (or $NO_2^{2-}$) spectra. In that case a clear distinction can be made between two $NO_2^{n-}$ modes, in one of which the O atom of the originating NO molecule is directed *away* from the surface and in the other of which it is bonded *to* the surface.

The consequences of these observations and many others from ir spectra studies that could have been cited are that the energy levels of a chemisorbed molecule are manifestly different from those of a free molecule. On interacting from the physically adsorbed layer, a molecule suffers a severe perturbation of its electronic states and its effective ionization energy and electron affinity, the quantities of interest in a boundary layer treatment, are not only altered, but are changed differently according to the conformation adopted in the interaction (cf. $NO_2^{n-}$ above). The molecule may behave as if in an excited state. Moreover, we should note that processes of the type

$$O_s^{2-} + H_2O \rightarrow OH_s{}^- + OH_{ads}^-$$

do not require charge transfer from *distant* species. It is not the Fermi level of the bulk semiconductor which is involved, but rather a surface state $E_s$.

A final point to be made with reference to the scheme in Fig. 1 is that, as with any reaction made up of a sequence of steps, the rate of the overall catalysis will be the rate of the slowest step. Thus, even when processes such as Step 1 or Step 2 (Fig. 1) afford adequate descriptions of chemisorption the reaction on the surface (Step 3) may still control the overall rate, in which case no correlation of catalytic activity with the concentration of free carriers or electron transfer energies will occur. An example from the recent literature is the work of McArthur, Bliss, and Butt (*22*) on the catalysis of ethanol dehydrogenation by ZnO. Ethanol chemisorption produces an increase in conductivity of ZnO, which implies that, ZnO being *n*-type (high Fermi level), the adsorption is of the type $X \rightarrow X_{ads}^+ + e$ (Fig. 1). The electronic nature of this step was confirmed by the fact that application of an electric field (5 kV) promoted instant desorption of ethanol. The rate of the dehydrogenation reaction, however, was unaffected by the application of the field. Thus, either the surface reaction controls the overall rate or the catalysis is proceeding via an uncharged species insensitive to the height of the Fermi level.

The formulation and application of an electronic theory of catalysis on metal oxides is therefore faced with a succession of formidable obstacles when it comes to matching theory with experiment. In summary we have: (i) the localized energy states of a solid oxide are numerous and widely distributed; (ii) the appropriate electron affinities and ionization energies of reactant molecules are not unique quantities and may not even be those of the ground state; (iii) reaction on the surface does not necessarily involve species charged overall in opposite directions; (iv) kinetic control of catalysis may reside entirely in a configurational activation of mobile species already chemisorbed. The problems which we have highlighted have been recognized in many quarters for a long time, but hitherto they do not appear to have been reviewed together. However, it deserves to be more widely acknowledged that the most refined of the theoretical efforts to link electron theory of solids with catalysis, namely the work of Wolkenstein (*8*), has gone a long way to providing at least a formal solution to the limitations which beset the simple theory. It remains very doubtful, however, whether the mechanistic secrets of oxide catalysis are going to be unlocked by this approach, as the number of disposable parameters is so great.

## The Surviving Concepts

If progress on the basis of the band theory is blocked, let us take stock of the concepts stemming from the early work which rightly persist.

### *1. Charge Transfer Adsorption*

Originally proposed on the basis of resistance changes observed during adsorption on semiconducting oxides (*23*), the occurrence of charge transfer has become unequivocally established through EPR studies of adsorption on oxides (*24*). Three paramagnetic ion radicals of oxygen ($O^-$, $O_2^-$ and $O_3^-$) have all been identified on oxide surfaces (*25–28*), and there is now proof that $O^-_{ads}$ is indeed generated by decomposition of $N_2O$ on oxides (*29*), as long supposed (*30*). Molecules with high electron affinity (tetracyanoethylene, trinitrobenzene) have naturally attracted close attention, and EPR work shows that they readily form anions when adsorbed on oxides. Cationic species identified by EPR on oxides include benzene, anthracene, and perylene (Pe). Perylene ($Pe^+_{ads}$) has often been thought to occur simultaneously with $O^-_{2ads}$ (*31*), reminiscent of Steps 1 and 2 in Fig. 1, but the isolated electron transfer from Pe to solid is also known, for instance on supported $MoO_3$, where the electron can be shown to be trapped in the empty *d* levels of the molybdenum ion (*32*). Related to this is the now well-authenticated evidence for photo-adsorption, photodesorption and photocatalysis (*33–36*). The studies here have been mainly confined to ZnO and fully oxidized $TiO_2$, which have the merit of a simple absorption spectrum uncomplicated by *d–d* transitions. Photocatalysis of a variety of oxidation reactions has been reported, and the common experience is that activation matches closely with absorption in the fundamental band, albeit being greatest near the absorption edge. The chain of processes, taking the example of $TiO_2$, must presumably begin with the sequence:

$$\begin{aligned} TiO_2 + h\nu &\rightleftharpoons ep\ (\text{exciton}) \rightarrow e + p \\ p + M_s &\rightarrow M_s^+ \\ e + O_2(g) &\rightarrow O^-_{2_{ads}}, \end{aligned}$$

where $M_s$ is a trap for the positive hole ($p$) either on the surface or in the interior. The relevance for the present review is that photo-effects strongly support the concept of charge transfer as one mode of catalytic activation on oxides.

### *2. Controlled Valency*

The second concept to survive is *controlled valency*. The original work by Verwey et al. (*37*) showed that monovalent $Li^+$ ions introduced in solid solution in the divalent oxide NiO served to generate positive holes ($Ni^{3+}$ ions). This principle of doping with an altervalent ion to control the valency of the transition metal ion, and hence to control the electron transport properties, was very widely applied to semiconducting oxides used in catalytic studies (*7*). The significance of adding a foreign ion of one valency to generate in an oxide a charge-balanced valency which would otherwise be present only adventitiously, is still important outside the context of relationships between semiconductivity and catalysis. The presence of a transition metal ion in a particular valency in a matrix is extremely relevant to correlations of catalytic activity with *d*-electron number, such as with the twin-peaked activity patterns discussed by Dowden (*38*). Valency control is important, too, in systems where overreduction or overoxidation has to be prevented, as in selective oxidation catalysis (*39*). An example of valency control put to advantage in a specific catalytic study is in the system $Li_xMn_yMg_{1-x-y}O$ investigated by Cimino et al. (*40*). Earlier work (*41*) had suggested that $Mn_2O_3$ was among the most active of oxides for $N_2O$ decomposition, but the oxidation state of manganese oxides is notoriously difficult to control. Cimino et al. sought to examine whether $Mn^{3+}$ or $Mn^{4+}$ was the more active oxidation state for $N_2O$ decomposition by coincorporation of lithium and manganese in solid solution in MgO, $Li^+$ and $Mg^{2+}$ being relatively inactive. The composition of valency in the solid solution is accordingly $Li_xMn^{3+}_{2y-x}Mn^{4+}_{x-y}Mg_{1-x-y}O$, so it was possible to study the catalysis over a series of oxides of differing $Mn^{3+}$ and $Mn^{4+}$ content by varying the $x/y$ ratio between 1 and 2. The results showed clearly that $Mn^{3+}$ ions are more active than $Mn^{4+}$ ions for catalysis of $N_2O$ decomposition.

### *3. Stoichiometry Control*

Related to valency control, though to be distinguished from it, is *stoichiometry control* and its influence in oxide catalysis. The original themes here were those of transitions between *p*-type and *n*-type behavior (e.g., in copper oxide or in chromia) or between *n*-type and degenerate behavior (e.g., in ZnO) as systems were reduced. The complication of a foreign ion in the oxide (as in the controlled valency principle described above) is absent in this case, but very much present is the problem of uncertainty over the ionic disorder, viz interstitials, vacancies, and extended defects. Mechanisms of catalysis invoking a decisive role played by changes in stoichiometry are accordingly tenuous, but there is recurring evidence that in oxidation reactions, for example, control of stoichiometry can be important. Wise et al. (*42*) have shown in recent years that the catalytic activity of $Cu_2O$ for selective oxidation is preserved only so long as $Cu_2O$ is Cu-rich, the O-rich region of nonstoichiometry leading to a predominance of deeper oxidation. For bismuth molybdate (*43*), it has been established by kinetic studies and by isotopic labelling experiments that selective oxidation of olefins proceeds by a mechanism which involves extraction of oxygen from the oxide structure (*44*). In the scheelite phase of $PbMoO_4$, substitution of $3Pb^{2+}$ by $2Bi^{3+}$ and a cation vacancy generates catalytic activity for selective oxidation of propylene (*45*). These examples are a reminder that the more subtle kinds of oxidation catalysis may demand structures able to withstand lattice imperfection.

## **Crystal Structure and Surface Coordination**

The deviation from stoichiometry to which reference has just been made is but one of many aspects which underline the need to take into account the variations in crystal structure shown by oxides when discussing their catalytic properties.

We have already alluded to the crystallographic shear structures which account for the nonstoichiometry of rutile and $ReO_3$-related structures ($MoO_3$, $V_2O_5$, $WO_3$). In the latter structures *CS* planes develop when the coordination of some of the constituent $MO_6$ octahedra changes from corner-sharing to edge-sharing. Each such unit change of coordination releases one oxygen atom. A reducing agent present at the site where such an extended defect intersects the surface could accordingly acquire *one* oxygen atom. Batist et al. (*46*) have observed that with bismuth molybdates, which occur in several phases depending on Bi/Mo ratio, there is catalytic activity for the *selective* oxidation of olefins only when the structure contains corner-shared $MoO_6$ octahedra. It is natural to speculate whether shearing of octahedra is the mechanism by which oxygen is selectively made available to the organic reactant. Transition metal oxides such as the simple 3*d* monoxides (NiO, CoO, etc.) with the rock-salt structure catalyze only the total oxidation of olefins.

The reaction of isotopic oxygen exchange and equilibration at oxide surfaces is worthy of discussion, because it has been systematically studied over about 50 different oxides (*47–49*) and is the simplest catalytic reaction involving oxygen gas. The following three processes may be distinguished (*50*).

Single exchange:

$$R' \quad {}^{18}O_2 + {}^{16}O_s = {}^{18}O^{16}O + {}^{18}O_s.$$

Multiple exchange:

$$R'' \quad {}^{18}O_2 + 2{}^{16}O_s = {}^{16}O_2 + 2{}^{18}O_s.$$

Equilibration:

$$R \quad {}^{18}O_2 + {}^{16}O_2 = 2{}^{18}O^{16}O.$$

$O_s$ signifies an oxide ion of the catalyst, and ${}^{18}O_2$, ${}^{18}O^{16}O$ and ${}^{16}O_2$ denote the three distinguishable gaseous oxygen species.

Most oxides simultaneously exhibit two of these reactions, and some like ZnO exhibit all three. For the full details reference should be made to the review by Novakova (*50*), but to obtain an overall impression one may classify the activities on the basis of the predominating mechanism, and this is done for a dozen oxides of widely differing types in Table I. Mechanism *R'* is the most common of the three, being exhibited to some degree by the majority of the 50 oxides studied, but among them those with close-packed structures are well represented. The oxides exhibiting predominantly the *R''* multiple exchange mechanism are mostly those without close-packed structures, and moreover they exchange virtually all of their oxygen with oxygen gas. It is logical to link the incidence of this mechanism for $V_2O_5$, $MoO_3$, and $WO_3$ with the speciality of these oxides in being able to switch $MO_6$ octahedra from corner-sharing to edge-sharing, as described earlier. This affords a straightforward mechanism for releasing a second oxygen atom to supplement the single exchange characteristic of close-packed oxides. Moreover, we know that these oxides are affected in depth at the shear plane: just as nonstoichiometry over a wide range can be generated and restored, so oxygen transport in the bulk of the solid is facilitated. Other oxides which exhibit the *R''* mechanism are $Bi_2O_3$, PbO, CuO, AgO, and PdO. Both $Bi_2O_3$ and PbO have a structural similarity in that they are derived from the fluorite structure by extracting anions, which again may presage high oxygen mobility. As for CuO, AgO and PdO, these are a cognate set of oxides with $d^9$ cations that exhibit coplanar $MO_4$ coordination. The structure of CuO can be thought of as made up of $MO_6$ octahedra in which Jahn–Teller distortion has removed one axial pair to a large separation. The weakening of the M–O bonding in the axial direction may be responsible for the easy oxygen release during the exchange reaction. The *R* process is uncommon; however, when it does occur it is remarkably efficient (*51*) and gives rise to isotopic mixing at low temperatures, even −196°C (*34*). It now seems likely that the $O^-_{3\,ads}$ species is an intermediate in the *R* process occurring at low temperatures. To sum up, however, the main conclusion to be drawn is that the type of coordination exhibited by the catalyst is evidently very significant in steering the course of these exchange reactions. In line with this, Winter (*47*) has shown that the activation energy for the common *R'* exchange correlates with crystal dimensions within a given crystal structure class.

TABLE I

PREDOMINATING MECHANISMS OF OXYGEN ISOTOPE EXCHANGE

| | |
|---|---|
| *R* | $\gamma$-$Al_2O_3$, ZnO (if well outgassed) |
| *R'* | MgO,* NiO,* ZnO,* $Cr_2O_3$,* $TiO_2$* |
| *R''* | $V_2O_5$,** $MoO_3$,** $WO_3$,** $Bi_2O_3$,** PbO,** CuO* |

* Only a very few layers of the oxide exchange.

** Many layers (possibly all) of the oxide exchange.

Let us now turn our attention to the actual chemisorption sites on oxides. It has been confirmed by LEED that the atomic arrangements at surfaces are primarily determined by the same structural principles which define the arrangement in the bulk. Thus it is realistic to consider the chemisorption sites as being characterized to a good approximation by the geometry which the crystal structure of the solid prescribes. Now a surface necessarily contains atoms whose coordination is lower than in the bulk. Chemisorption can accordingly be regarded as a process by which the coordination characteristic of the bulk is partially or completely restored.

The adsorption of oxygen on the nickel ions of nickel oxide can serve as an example (*52*, *53*). In the bulk, $Ni^{2+}$ ions are in six-fold octahedral coordination, but in the surfaces of the three main cleavage planes, viz (100), (110) and (111), the coordination of $Ni^{2+}$ is reduced from $NiO_6$ to $NiO_5$, $NiO_4$, and $NiO_3$, respectively. The variations of coordinations ($NiO_5$, $NiO_4$, and $NiO_3$) will all occur on the (100) plane alone if one admits the presence of occasional anion vacancies ($NiO_4$), steps ($NiO_4$), and kinks in steps ($NiO_3$). Dissociative chemisorption of oxygen on these sites enables the variously exposed nickel ions to recover the sixfold coordination characteristic of the bulk.

In Fig. 2 the chemisorption sites $NiO_5$, $NiO_4$, and $NiO_3$ are shown symbolically as *a*, *b* and *c* respectively, where *M* indicates the cation and *X* the anion. As Burwell et al. (*54*) have pointed out, oxide surfaces will contain coordinately unsaturated (*cus*) anions as well as *cus* cations, and chemisorption will frequently involve both simultaneously. Thus, structure *a* can give heterolytic adsorption of hydrogen (Fig. 2d), or bidentate adsorption of CO or NO (Fig 2e), the latter being one of the likely structures for $NO^{n-}_{2ads}$ discussed earlier. Structure *b* permits adsorption of two different modes involving the same metal ion, as postulated in Fig. 2f for $CO_2$ adsorption (*55*). These simple models prove very useful in discussing ir spectra of chemisorbed molecules. The structures *a*, *b*, and *c* (and especially *a* and *b*) will be very common on oxide surfaces since so many oxides have octahedral coordination in the bulk.

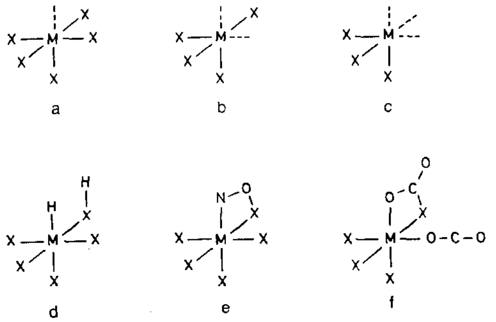

FIG. 2. Coordinatively unsaturated (*cus*) surfaces (*a*, *b*, *c*) and some modes of chemisorption (*d*, *e*, *f*).

## Catalytic Centers: The Localized Approach

The *cus* sites in Fig. 2 afford immediate scope for formulating catalytic mechanisms, and the classic example is the Arlman–Cossee mechanism for the $TiCl_3$-catalyzed polymerization of propylene (*56*). The analogy with reactions occurring in coordination complexes is close (*57*).

The essential point about these models is that they stress the *localized* nature of the processes. When transition metal ions are present, the possibility exists of electronic interaction between metal ions in adjacent polyhedra, and of electron transfer. The question arises as to how relevant these effects are for catalysis at the oxide surface. It is a very fundamental question.

It is possible to investigate it by using as catalysts solid solutions of transition metal ions in an insulating, diamagnetic oxide as solvent. By forming randomized solid solutions containing the transition metal ion at different concentrations, one may study the properties of the system in chemisorption and catalysis with control over the electronic interactions between the ions. More specifically one may explore:

(i) The catalytic activity of the transition metal ion (*T* ion) as the solid changes from insulating and paramagnetic behavior (very dilute solution) to semiconducting and usually antiferromagnetic behavior (dilute or concentrated solution);

(ii) The effect of *d* electron population, by comparing the activity of one *T* ion ($d^n$) with another ($d^m$) in the *same* inert matrix at the *same* concentration;

(iii) The influence of the crystal field, by comparing the activity of the *same* *T* ion in two inert matrices of differing cation site symmetry.

To these effects can be added the permutation that for a catalytic system capable of reacting in more than one way (e.g., dehydrogenation vs dehydration, partial oxidation vs total oxidation), one may explore the changes in the catalyst not only in respect of total activity but also in respect of *selectivity*.

A program of research to study these effects has been in progress during the last ten years in the laboratories of Professor A. Cimino and of the author. The work involves both solid state chemistry and surface chemistry, since the solid solutions have to be well characterized. The scope of the catalytic part of the studies is summarized in Fig. 3. The results for many of these systems, beginning with $N_2O$ decomposition on NiO–MgO (*58*) and including recent reviews (*59*, *60*), are already published and other work is still in progress. The researches on $\alpha$-$Cr_2O_3$-$Al_2O_3$ are described in a series of papers beginning in 1969 (*61*) and also including recent publications (*62*, *63*).

The principal results so far can be summarized as follows.

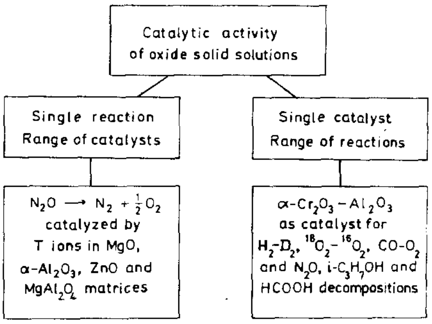

FIG. 3. Catalytic reactions investigated over oxide solutions.

(i) Catalytic activity develops strongly already in very dilute solutions (e.g., 1 *T* ion per $10^2$ cations).

(ii) The activity induced per *T* ion is *not* a constant quantity, but shows variations of great intrinsic interest across the concentration range to pure *T* oxide.

(iii) The activity is a function of the symmetry of the solvent matrix.

(iv) *T* ions act specifically, i.e., $T(d^n)$ and $T(d^m)$ activities vary widely, as do those of $T_1$ and $T_2$ ions of the same $d^n$.

(v) The *selectivity* varies with *T* ion concentration.

Figures 4–6 illustrate some examples, and for fuller details and interpretations reference can be made to the original articles. Figure 4 shows the activities in $N_2O$ decomposition of $Cr^{3+}$ ions in $\alpha$-$Al_2O_3$ (*62*) and $MgAl_2O_4$ (*64*) as a function of concentration, illustrating (i), (ii) and (iii) above, Fig. 5 a comparison of activities in $N_2O$ decomposition for *T* ions of the 3*d* series when dispersed at 1 % overall concentration in MgO as matrix (*60*), illustrating (i) and (iv), and Fig. 6 the selectivity of $\alpha$-$Cr_xAl_{2-x}O_3$ for the decomposition of isopropanol, illustrating (v) (*65*).

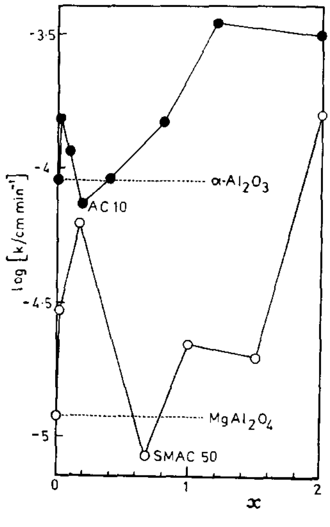

FIG. 4. The activity of $\alpha$-$Cr_xAl_{2-x}O_3$ (●) and $MgCr_xAl_{2-x}O_4$ (○) catalysts for $N_2O$ decomposition at 560°C (*62*, *64*).

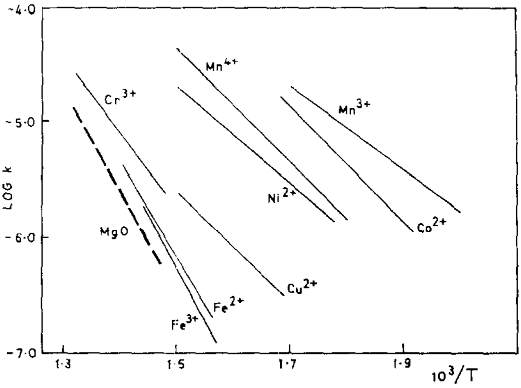

FIG. 5. The relative activities of 3*d* transition metal ions for $N_2O$ decomposition, illustrated as Arrhenius plots, and referred in each case to a 1 at % solid solution of the ions in MgO (*60*).

There are side effects to be borne in mind, such as that the *matrix* ions may develop activity in the presence of *T* ions, or that clustering of *T* ions may occur (perhaps on the surface preferentially), but these are more in the nature of perturbations than primary effects and can usually be sufficiently controlled not to invalidate the main analysis. The "spill-over" effect (to borrow a term from metal catalysis), whereby *T* ions initiate activation and reactive species migrate over the matrix, is of considerable interest per se.

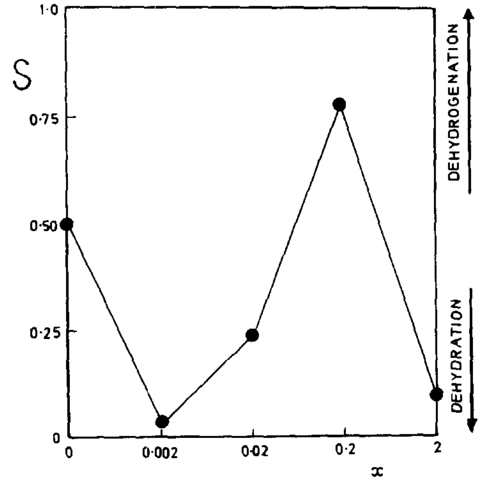

FIG. 6. The selectivity towards dehydrogenation and dehydration in the decomposition of isopropanol at 350°C over $\alpha$-$Cr_xAl_{2-x}O_3$ solid solutions preoutgassed at 850°C (*65*).

A second theme in investigating the localized approach, somewhat closer to solid state physics, is to study the uv spectroscopy of interactions between chemisorbed molecules and surface states. We have recently begun studies on high surface area MgO, where the "erosion" of absorption attributable to surface excitons can be followed and, in favorable cases, observed simultaneously with the production of new absorption bands in the chemisorbed species (*66*), a manifestation of the localized electron transfer to which reference was made earlier. This work is being extended to a comparison of MgO, CaO, SrO, and BaO, since these oxides are isostructural but show a gradation of charge transfer energy ($M^{2+}O^{2-} \rightarrow M^{+}O^{-}$) that narrows the band gap and which, should allow one to study variations in electron delocalization on to chemisorbed species.

Finally, a brief reference should be made to molecular sieve zeolites. These have the advantage of extensive surfaces, which are not *coordinatively* unsaturated but *electrostatically* unsaturated. Charge-balancing metal cations normally preserve overall neutrality, but protons or organic ions can partially or even completely replace them. Extremely effective catalytic centers for acid-catalyzed reactions can be generated (*67*). In addition to reactions of carbonium ion-type (cracking, isomerization, etc.), it now seems likely that reactions specific to transition metal ions can be initiated (*68*). These zeolite systems represent another family of oxide catalysts which require a localized approach for interpretation of properties, and one may hope that their study will provide the key to interpreting in precise structural terms the acidity and basicity of oxide surfaces. This would be the means to achieve complementarity in the understanding of the broad compass of chemical reactions known to be catalyzed by metallic oxides.

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