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Catalytic Behavior of a Cation in a Solid Solution—An Electrostatic Potential Approach

HAROLD H. KUNG

Chemical Engineering Department, The Ipatieff Laboratory, and the Materials Research Center, Northwestern University, Evanston, Illinois 60201

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A method to calculate the electrostatic potential at a surface cation site and at an adsorbate site is described. The method is applied to evaluate the difference in the electrostatic potential at the two sites when the cation is placed in different oxide solid solutions of the same crystal structure. It is concluded that the ability of the cation to accept an electron from the adsorbate increases if the cation is in a more ionic oxide matrix, and vice versa. This conclusion appears to be consistent with published experimental data involving adsorption and catalysis on a number of solid solutions.

INTRODUCTION

Commercial transition metal oxide catalysts are almost always multicomponent. Notable examples of these include the methanol synthesis catalyst which is a mixture of Zn, Cu, Cr, or Al oxides (*1*), the water-gas shift catalyst which is a mixture of Co and Mo oxides or Zn and Cu oxides (*2*), and various selective oxidation catalysts (*3*). These mixtures of different oxides can form solid solutions with each other, new chemical compounds, physical mixtures, or a combination of these.

Even for the simplest system of a dilute solid solution of two binary oxides, it is often not trivial whether the electron affinity (or acidity) of, for example, a Ni^{2+} ion increases or decreases when it is being incorporated into a more basic and ionic matrix of MgO as compared to a matrix of NiO. The purpose of this work is to answer this question by considering the electrostatic potential at an adsorbate and at a surface cation site on this simple although restrictive class of dilute binary solutions. A binary oxide solid solution has two cations A and B of the same formal oxidation state. In principle the cations can be of the main group or transition metals. In practice, it is much more common to find true solid solutions in which one or both of the cations are transition metal ions.

Compared to the pure oxide, the properties of a cation A can be affected by the presence of a second cation B in the solid solution in a number of ways. The surface density of cation A can be very different from the bulk density with the difference depending on the degree of surface segregation of either component. The collective properties of the cations, such as magnetic exchange interactions and electron conduction can be modified. The electrostatic potential (or lattice self-potential) at the cation site is changed when the ionicity of the solid is changed. The possible change in the ionicity of the solid, as well as the possible distortion of the lattice because of different ionic radii of A and B, could also modify the property of the oxygen ion. Some or all of these effects may be manifested in changes in the surface chemistry and catalytic properties of the oxides.

This paper considers strictly the change in the adsorbate–surface cation interaction through changes in the electrostatic potential at the adsorbate and at the surface cation site when the cation is placed into a solid solution instead of the pure compound. As will be discussed in greater detail later, if the change in the electrostatic

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potential at the adsorbate site is different from that at the cation site, electron flow between the two sites can be either enhanced or retarded depending on the direction of the change. This could result in a change in the catalytic property of the cation.

In the next section, the method of calculation and the model used will be described. Using this model, quantitative results on the change in electrostatic potential are calculated for solid solutions of oxides of the rock-salt structure. From these results, general conclusions can be drawn that should be applicable to other oxides. These conclusions are then used to interpret published experimental observations on the catalytic behavior of a number of oxide solid solutions. Finally, a discussion on the model and its application will follow.

MODEL FOR SURFACE–ADSORBATE INTERACTION

Electrostatic Potentials at a Surface Cation and an Adsorbate Site

These quantities can be calculated following the method of Mark (*4–6*) for an adsorbate site at the position of the nearest neighbor to the surface cation. The method is a direct extension of the theory of intrinsic surface states of an ionic lattice (*7*). According to the model, each ion is represented by a point charge located at the lattice site. Coulombic potential (or lattice self-potential) at any point in the lattice is then a direct summation of the electrostatic potential due to all the ions in the lattice:

$$V = \sum_{i,j,k} \frac{q_{i,j,k}}{r_{i,j,k}} \equiv \sum_{i,j,k} Q \qquad (1)$$

in which $q_{i,j,k}$ is the effective charge on the ion at a distance $r_{i,j,k}$ from the point of interest. Since $r_{i,j,k}$ can be expressed as an integral multiple of some conveniently chosen distance r_0, such as the interionic distance (*8, 9*), the summation can be written as a series summation.

The electrostatic potential V_S at a surface ion site of a semi-infinite crystal can be expressed as

$$V_S = \sum_{i \geq 0,j,k} Q. \qquad (2)$$

The summation is over half-space. The index i labels planes that are parallel to the surface plane ($i = 0$), and the j and k are projected onto the surface plane. Similarly, the electrostatic potential V_a at an adsorbate site that is one nearest-neighbor distance above the surface ion site can be expressed as

$$V_a = \sum_{i<0,j,k} Q = \sum_{i>0,j,k} Q \qquad (3)$$

The value of V_S has the following significance. For a surface cation carrying a certain positive charge, a more negative V_S implies a more attractive potential for the cation. The cation is then more stable at the site. Alternatively, a more negative V_S requires a less positively charged cation to achieve the same attractive energy. The value of V_a has similar significance for the adsorbate.

Since cation–adsorbate interaction involves electrons from both centers, it depends on the relative energy levels of the electrons involved. Thus the change in this interaction because of different matrices will depend on the *relative changes* of V_S and V_a when a cation of interest A is removed from a matrix of A oxide and placed into a matrix of B oxide, as is shown in the example in Fig. 1 in which A is Ni and B is Mg. This relative change ΔV can be expressed in terms of Eqs. (2) and (3) as

$$V = (V_S - V_a)_B - (V_S - V_a)_A \qquad (4)$$

$$= \sum_{i\geq 0,j,k} (Q_B - Q_A) - \sum_{i<0,j,k} (Q_B - Q_A). \qquad (5)$$

The subscript A or B indicates that the quantity is to be evaluated in AO or BO, respectively. ΔV can be evaluated if the ionic charges and positions in both AO and

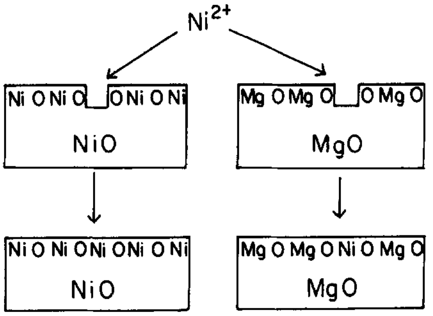


FIG. 1. Schematic representaion of the incorporation of an ion into different matrices.

BO are accurately known. In the infinitely dilute solid solution under investigation, the solution can be represented by an isolated surface cation A in a BO matrix. Then, except for the nearest and perhaps the next nearest neighbors surrounding A, all other ions are at their perfect lattice positions. Further simplification is achieved by neglecting relaxation of the surface plane which is shown to be small for oxides from low-energy electron diffraction data (*10–13*). Finally the effective charges of the surface cations and anions are assumed to be the same as those in the bulk, and the small potentials due to the surface dipoles are neglected.

Within the point charge approximation, the contributions to the potentials at a site come primarily from the long-range coulombic potential and the short-range repulsive potential. The coulombic potential is the interaction among the effective charges at the ion centers. It has an inverse dependence on distance. The repulsive potential comes from the overlap between electron clouds. Thus it is almost entirely confined to nearest-neighbor interaction, and can be approximated by a form with exponential dependence on distance. Since these two contributions have a distance and an effective charge dependence, we shall discuss the magnitude of ΔV with respect to these two parameters.

Dependence on Effective Charge

In evaluating the effect of effective charge on ΔV, the ionic positions in the pure compound and in the solid solution are assumed to be identical. While Eq. (5) is applicable to any crystal structure, we have evaluated it for divalent oxide MO of cubic structure. It can easily be shown that the conclusion thus generated applies readily to oxides of other structures and stoichiometries because the lattice self-potential of other oxides are either comparable to or larger than that of cubic MO (*4, 9, 14*). For a cubic MO, the ionic charge of the cation and the anion in the pure compound is the same, and Eq. (5) can be simplified to

$$\Delta V = (q_B - q_A)\left[\sum_{i\geq 0,j,k} \frac{1}{r_{i,j,k}} - \sum_{i<0,j,k} \frac{1}{r_{i,j,k}}\right]. \qquad (6)$$

The first bracketed expression is the difference in effective ionic charge of BO and AO, and the second bracketed expression depends only on the interionic distance r_0 and the exposed plane. For a typical r_0 of 0.2 nm, ΔV is evaluated for different effective charges (Fig. 2). The formal oxidation states of cations in common oxides range from 2 to 6. A change in the effective charge of 0.5 may not be uncommon. Such a change results in a change in ΔV of up to 5 V. Furthermore the sign of ΔV suggests that *a cation A is electrostatically more*

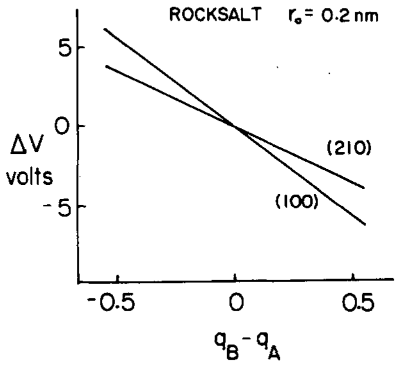


FIG. 2. The calculated ΔV as a function of the difference in the effective charges for the (100) and (210) planes of a cubic oxide.

stable in a more ionic matrix BO, and it can accept electrons more readily from the adsorbate than A in AO.

Dependence on Interionic Distance

When an ion A is placed into a matrix BO of a different interionic distance, the nearest neighbors of A relax in an attempt to accommodate the difference. The extent of relaxation, however, is usually about half of what one would expect if the ionic radii are assumed to be constant (*15, 16*). Relaxation of the second nearest neighbor is much smaller, and of those farther away is negligible. For a cubic oxide BO whose equilibrium interionic distance is 10% smaller than that of AO, relaxation would make the A–O nearest-neighbor separation 5% larger than the corresponding B–O separation, and the A–B second nearest-neighbor separation would be 1% larger than the corresponding B–B separation.

The potential at A is being affected in the following way. Consider the case in which A is larger than B. The shorter distance between A and its nearest-neighbor oxygen ions in the solid solution results in an increase in repulsive potential, but the shorter distance between ion A and all of the other ions in the lattice decreases the potential at A through stronger coulombic interaction. For an ion A placed into the (100) surface plane of BO whose interionic distance is 10% smaller than that of AO, the increase in repulsion energy due to shorter A–O distance can be estimated to be about 2.5 eV, which corresponds to a potential increase of about 1.2 V at A. This is evaluated using the exponential form for repulsive potential, $B \exp(-r/\rho)$, and a value of B of 1×10^{-9} erg, ρ of 0.033 nm, r_0 of 0.21 nm, and nominal charge of 2. These are typical values of binary cubic oxides (*17, 18*). The change in the coulombic energy at A can be calculated to be about 1 eV using Eq. (1) and the relaxed ion positions. This corresponds to a potential increase of about 0.5 V at A. Thus the total potential change ΔV at A is about 1.7 V, which is the upper limit of the potential change. The attractive potential at A due to the relaxation-induced dipoles surrounding A and the fact that ion A itself can relax from the perfect lattice position to minimize the repulsive potential will decrease ΔV.

The potential at the adsorbate site is also changed by the different ionic radii. However, because of the position of the site, repulsive interaction is not present, and changes in the coulombic potential are much smaller than that at ion A (*4–6*). Thus the contribution to ΔV from the adsorbate site is small.

It can be seen that for a very large difference in the interionic separation of 10%, there is only a modest change in ΔV of less than 1.7 V. For many solid solutions involving transition metal ions, the difference in the interionic separation is less than 5%. For example, in the rather strained solid solution of Al_2O_3–Cr_2O_3, the difference in the interionic distance is 5% (*18*). In those cases, ΔV of less than 1 V is expected. Compared to the potentially much larger changes in ΔV due to different effective charges, it can be concluded that the dependence of ΔV on interionic separation is not important.

APPLICATION TO CATALYSIS AND CHEMISORPTION

The result of the analysis above can be summarized as follows. Within the electrostatic potential consideration, the effect on chemisorption and catalysis by the formation of a solid solution can be understood in terms of the effective charge of the ions. If an active cation center is placed onto a more ionic matrix, the center becomes a better electron acceptor, that is, more acidic with respect to the adsorbate. Conversely, an active center in a less ionic matrix becomes a better electron donor, that is, more basic. In this section, we shall see if the above statement is consistent with literature observations using solid solutions.

The calculated results of Fig. 2 suggest that for a change in effective charge of 0.5, a ΔV of 5 V can be obtained. It is interesting to note that the energy of the highest-occupied molecular orbitals of π-allyl anion and π-allyl cation differ by about 13 eV (*19*). That of the π-allyl radical is presumably in between these levels. Thus for a ΔV of 5 V which corresponds to a relative change in electron orbital position of 5 eV, it is possible that an adsorbed π-allyl anion becomes a π-allyl radical when the active center is put into a solid solution.

In applying our conclusion to catalysis, it must be recognized that these calculations are ground-state calculations. Thus meaningful comparison can only be made on systems whose reaction mechanism, and thus the entire course of reaction, is the same on the pure oxide and on the solid solution. Furthermore, the electrostatic argument is essentially an energetic argument, it is most likely to be successful when it is used to understand changes in activation energies of the rate-determining step. This is because the observed rate depends also on the density of the active site which is related to the surface composition that is not being considered here.

N_2O Decomposition

Perhaps the system most suitable for application of this analysis is the N_2O decomposition reaction on Cr_2O_3–Al_2O_3 (*20, 21*) and NiO–MgO (*22*). The following mechanism appears to apply:

$$N_2O(g) + e^-(s) \rightarrow N_2O^-(ad), \qquad (I)$$

$$N_2O^-(ad) \rightarrow N_2(g) + O^-(ad), \qquad (II)$$

$$2O^-(ad) \rightarrow O_2(g) + 2e^-(s). \qquad (III)$$

The reaction is strongly inhibited by oxygen, suggesting that under steady-state conditions, step (III) is rate limiting. It is also established that the active centers involve transition metal ions.

Because N_2 is evolved in step (II), it is possible to measure the rates of steps (I) and (II) by following the evolution of N_2. Stone and co-workers performed this experiment and their results are presented in Table 1 (*20, 21*). Although experiments were conducted over the entire compositional range of Cr_2O_3–Al_2O_3, we only concentrate on the dilute solid solution limit because of the assumption of infinite dilution used in the analysis. The result shows that the activation energy for these two steps combined is higher in the solid solution than in Cr_2O_3. In terms of our model,

TABLE 1

Comparison between Solid Solution and Pure Oxide

Catalyst	$E_{act.}$ (kJ/mole)	Reaction
0.1% Cr_2O_3–Al_2O_3	33.5	$N_2O(g) + e^-(s) \rightarrow N_2O^-(ad)$ $N_2O^-(ad) \rightarrow N_2(g) + O^-(ad)$
α-Cr_2O_3	8.2	
1% Cr_2O_3–Al_2O_3	52	$N_2O(g) \rightarrow N_2(g) + O^-(ad)$ $20^-(ad) \rightarrow O_2 + 2e^-(s)$
α-Cr_2O_3	105	
1% NiO–MgO	80	
NiO	96–151	
	Rate (% conversion of butene at 325°C)	
$FeCrO_3$	50	$C_4H_8 + \frac{1}{2}O_2 \rightarrow C_4H_6 + H_2O$
Fe_2O_3	35	

step (I) involves removal of an electron from the solid. Since Al_2O_3 is more ionic than Cr_2O_3 (*23, 24*), Cr in a matrix of Al_2O_3 will less readily donate an electron to the adsorbate. Thus the activation energy for this reaction will be higher on $Cr_2O_3-Al_2O_3$ than on α-Cr_2O_3.

For the steady-state reaction, the rate-limiting step of step (III) involves extraction of an electron from the adsorbed oxygen by the solid. This process should be enhanced by a more electron accepting solid. Thus Cr in a more ionic matrix of Al_2O_3 would be energetically more favorable for this step than Cr in Cr_2O_3. This agrees with the observed lower activation energy for $Cr_2O_3-Al_2O_3$. A similar argument applies to the NiO–MgO solution. MgO is more ionic than NiO (*23, 24*). Thus it is expected that Ni in MgO will accept an electron more readily than Ni in NiO, and result in a lower activation energy for this reaction as observed. It is interesting to note that in spite of the acidic nature of Al_2O_3 and the basic nature of MgO, their effects are predicted to be the same in this model.

While we made use of only data obtained on very dilute solid solutions, it is interesting to note that the same trend was observed even for more concentrated samples.

While we interpreted the above data using the electrostatic potential argument, the effect due to changes in cooperative effect between neighboring cations should be explored. Since the steps in these reactions involve charge transfer, it would be easier for these steps to occur on clusters of transition metal ions than isolated ions because of easier charge delocalization in a cluster. While this effect may participate, it is not likely to be dominant. If this effect were dominant, one would expect that the activation energy for the dilute solid solutions should be always higher than that for the pure transition metal oxide, independent of the direction of electron transfer. This contradicts the observation.

O_2 Adsorption

Oxygen adsorbs on surfaces in a number of forms such as O^{2-}, O^-, O_2^-, or O_2. The energies of these species are within about 2 eV of each other except O^{2-} which is about 6 eV higher (*25*). Thus it is possible that the nature of adsorbed oxygen species changes as a result of the formation of solid solution.

The nature of adsorbed oxygen on the MnO–MgO system was determined by Dyrek using EPR (*26*). On samples containing 1.1% Mn or less, adsorption of oxygen resulted in the appearance of a new signal which the author interpreted as due to either O^- or O_2^-. On concentrated samples, however, adsorption of oxygen did not result in the appearance of a new signal, rather the broad EPR signal of Mn^{2+} reduced in magnitude. This was interpreted as oxygen adsorption on these samples as O^{2-} which is diamagnetic. The process oxidizes Mn^{2+} to Mn^{3+}, thus reduces the Mn^{2+} signal.

In terms of our electrostatic potential argument, the Mn center in a more ionic matrix of the MgO (*23*) does not donate electrons as readily as Mn in MnO. Thus in the dilute samples, fewer electron transfers occur and the oxygen adsorbs as O^- or O_2^-. On the concentrated samples, electron transfer takes place more readily and oxygen adsorbs as O^{2-}. Thus the argument is consistent with the observation.

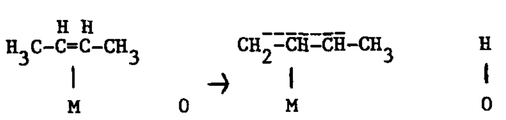
On another series of oxide solid solutions, CoO–MgO, similar observations were made (*27*). However, interpretation was complicated by the participation of Co of different coordination symmetry.

Oxidative Dehydrogenation of Butene to Butadiene

Steady-state rate data for this reaction were reported by Rennard and Kehl (*28*). Unfortunately activation energies were not reported. Thus only rates are used here for discussion. As mentioned in the beginning of this section, caution should be exercised when interpreting rates using this electrostatic potential argument.

Their reported rates on Fe_2O_3 and Fe CrO_3 are listed in Table 1 for the reaction temperature of 325°C. A similar trend was observed at 375°C. Since the reaction involves a redox mechanism, Fe is believed to be the active center (*29, 30*). Thus Fe in a Cr_2O_3 matrix is more active than Fe in Fe_2O_3.

The rate-determining step of the reaction is believed to be the hydrogen abstraction step in the formation of π-allyl from the adsorbed butene (*30, 31*):



$$\underset{M}{\underset{|}{H_3C\text{-}\overset{H}{C}{=}\overset{H}{C}\text{-}CH_3}} \quad O \rightarrow \underset{M}{\underset{|}{CH_2\text{-}CH\text{-}CH\text{-}CH_3}} \quad \underset{O}{\underset{|}{H}}$$

(IV)

There is little in the literature which suggests whether Fe_2O_3 or Cr_2O_3 is more ionic. We reason that Cr_2O_3 is more ionic because Cr_2O_3 forms CrO_3 readily in air (*32*) but cannot be readily reduced. However, Fe_2O_3 can be readily reduced to lower oxides but can hardly be oxidized. We take this as evidence that charge transfer from Cr to O takes place more readily than that from Fe to O. Thus Cr_2O_3 is more ionic.

When Fe is placed in the more ionic matrix of Cr_2O_3, the Fe center accepts electrons more readily, and it can better stabilize a more anionic adsorbate. The oxygen ions surrounding Fe are more electron rich because of the more ionic character of the matrix. Thus abstraction of H as a protonic species would take place more readily on the solid solution. The ability of the solid solution to enhance abstraction of H as proton and to stabilize the resulting allylic species by accepting the electron results in lowering of the activation barrier of this step, and thus a faster reaction rate.

The above argument can similarly be expressed in terms of surface acidity. Fe in the solid solution accepts an electron more readily. Thus the butene–Fe complex becomes more acidic. This more acidic species can give up a proton more readily than the similar yet less acidic species on pure Fe_2O_3. Thus the reaction proceeds faster on the solid solution.

DISCUSSION AND CONCLUSION

This paper explores the use of electrostatic potential argument to understand the differences in surface chemistry and catalytic behavior of a cation when the cation is placed in its own oxide or in another oxide in the form of a solid solution. Quantitative evaluation suggests that in most cases, change in the electrostatic potential is primarily due to change in the effective ionic charge of the matrix. A more ionic matrix makes the cation center more acidic and vice versa. Thus the activation energies of reaction steps involving electron transfer between the cation center and an adsorbate will be affected accordingly. This prediction appears to be consistent with published literature data.

Different approaches had been used to explain oxide catalysis. In one approach, the semiconducting properties of oxides are being used. This approach is successful toward understanding conductivity changes in adsorption and desorption, photoassisted processes, and the effect of doping on chemisorption. However, it is difficult to apply it to totally insulating materials. Another approach is the localized approach that treats a surface site as an isolated surface coordination compound with little or no communication with the rest of the solid. This approach is successful in many instances but it does not usually predict or explain the effect of the presence of a second component in a mixed oxide. The approach outlined here makes use of a localized surface active center approach but allows the center to be influenced by the rest of the solid through electrostatic interaction. Thus it can be viewed as an extended localized approach. Clearly the approach does not contain any information on the collective behavior of electrons or ions.

It cannot be used to explain magnetic or electronic exchange interactions. Fortunately, many catalytic reactions do not depend on such collective properties.

This simple electrostatic potential method also implicitly assumes that the electronic structure of the active cation center, especially the nature and the spatial orientation of the electron orbitals involved in bonding, does not depend on the matrix. Undoubtedly the degree of admixing of orbitals of the cation with surrounding oxygen ions or with other cations depends on the covalency of the solid, which differs among different matrices. For most insulating or semiconducting oxides of catalytic interest, the valence band is mostly made up of oxygen *p* orbitals, and the conduction band of the cation *sp* orbitals. The *d* band, if present is usually narrow because of poor overlap among different *d* orbitals (*33*). Because of these common features, it may be reasonable to assume that the electronic structure of the active cation is changed but little in a solid solution. This may be particularly true for the dangling bonds that are responsible for bonding with molecules because these bonds are directed spatially to have little overlap with other ions. The effect of the matrix is then to influence the energy of these dangling bond orbitals by the electrostatic potential. However, covalency still enters in the calculation through the parameter of effective charge.

The relative electrostatic potential at the active site and at the adsorbate is only one of the important properties affecting a reaction. There are other important factors. For example, the degree of surface coordination unsaturation is also important in affecting the binding of the reactants. For reactions in which the active center involves a cluster of ions, the location and the properties of all the ions involved are important. For reactions in which lattice oxygen participates, other bulk properties must be considered. Thus when using the conclusion drawn from this paper, all of these other variables should be kept constant. This is likely to be the case when an oxide is compared with its solid solution of the same crystal structure, such as in the examples discussed. In view of the apparent success of this approach, it appears to be worthwhile to further explore the concept with more sophisticated models and to test it with more complicated systems.

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