NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Technical Report 32-949

Surface Adsorption in Magnesium Oxide

T. H. Nielsen
M. H. Leipold

FACILITY FORM 602

N66 33769	
(ACCESSION NUMBER)	(THRU)
23	1
(PAGES)	(CODE)
CR-77167	06
(NASA CR OR TMX OR AD NUMBER)	(CATEGORY)

GPO PRICE $ ____________

CFSTI PRICE(S) $ ____________

Hard copy (HC) 1.00

Microfiche (MF) .50

ff 653 July 65

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

June 1, 1966

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Technical Report No. 32-949

Surface Adsorption in Magnesium Oxide

T. H. Nielsen
M. H. Leipold

C. E. Levoe, Manager
Materials Section

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

June 1, 1966

Prepared Under Contract No. NAS 7-100
National Aeronautics & Space Administration

CONTENTS

Appendixes

TABLES

FIGURES

ABSTRACT

33769

Calculations are presented for approximating the adsorption energies of argon and helium atoms, and hydroxyl ions on magnesium oxide (MgO) surfaces, with consideration being given to abnormal, highly active sites. Results indicate extremely high ($>$100 kcal/mole) adsorption energies for these species (in certain active sites) that are unlikely to be removed in thermal treatment. The number of such active sites is calculated, the ease of determination of impurities located in such active sites is evaluated, and methods of reducing such contamination by adsorption are discussed. Findings indicate that rearrangement of surface structure is unlikely in MgO and that adsorption of gas is the most likely mechanism by which MgO can lower its surface free energy.

I. INTRODUCTION

Considerable emphasis in ceramic research has been placed on the quantity and distribution of impurities in polycrystalline magnesium oxide (MgO). However, the quantity of one of the more common contaminants, the hydroxyl ion (OH^-), is seldom reported. More detailed chemical analysis of MgO indicated OH^- to be present in atomic amounts from 100 to 1000 ppm in fabricated specimens and to remain in those specimens that were heated to as high as 2200°C. Since a likely source of OH^- in dense MgO would be from surface adsorption of water on the particles from which the specimens are made, this study of the subject was undertaken. Some consideration was given to adsorption of species other than OH^- to avoid ignoring other contaminants and to develop possible replacements for OH^- contamination that would be more easily removed.

In the author's review of the literature, a great deal of empirical data was found on surface behavior of MgO, however, thorough treatment of the theoretical calculation of such data was lacking. One comprehensive article (Ref. 1) on such theory was noted that, although it did not treat MgO in any detail, provided a basis for the application of existing surface theory to MgO.

II. SURFACE ENERGY

Magnesium oxide, an ionically bonded compound, is considered to exist structurally of a three-dimensional array of positive and negative ions. Each Mg^{++} is surrounded by six $O^{=}$ ions, and each oxygen ion is surrounded by six magnesium ions; the bonding energy is equal in all six directions. However, at the surface of a MgO crystallite, the periodic array ends, and the coordination number of the surface ions is less than six; here, the bonding energy is distributed in fewer directions than in the bulk of the material. Because of the lower coordination in the surface, the residual bonding energy of the ions that is not directed to neighboring ions is manifest as the surface energy of the solid. The surface energy is, thus, some fraction of the bonding energy.

The surface energy of any substance is defined as the free-energy change in bringing an atom or an ion from within the bulk of the substance into the surface layer; expressed in ergs/cm^2, it is the free energy required to increase the surface area by 1 cm^2. Every system tends to move toward a position in which state the surface free energy and the bulk free energy have minimum values.

The surface free energy can be lowered intrinsically either by reducing the surface area or by adjusting the surface composition so that the component of least energy is present in the outermost layer. This adjustment, referred to as the Gibbs adsorption process, is the rearranging of the surface composition so that the larger ions are present in the surface layer in excess of the stoichiometric amount, thereby lowering surface energy of the substance. Polarization of the larger ion in the surface will further reduce the surface energy, and polarization will be greater for large ions having small charges.

When applied to the surface of an *oxide,* these principles suggest that the presence of *cations* at the surface contribute to a higher free energy. This free energy may be lowered intrinsically in an oxide by either (Ref. 2) of two processes: (1) the retraction of the surface cations so that anions, only, are predominantly present in the surface layer or (2) the polarization of surface anions.

The efficiency of the surface cation retraction mechanism depends on three structural properties: (1) the presence of more anions than cations, (2) a low cation/anion radius ratio, i.e., < 0.5, and (3) a low melting point. If surface ions are to rearrange their lattice positions to form a low-energy surface, movement of these ions must take place. In high melting point substances, the activation energy for this motion is high, and hence, a low-energy surface can be formed only at high temperature. The existence of such a surface also implies the existence of cations in disordered position just below the surface; this position may, by raising the bulk free energy, offset any decrease in surface energy. In very small particles, any change in bulk free energy as a result of the above described process represents a large fraction of the total bulk free energy. Thus *small particles* cannot exist with disordered surface layers since this tends toward a totally disordered and, hence, unstable lattice. There is evidence to indicate that small particles cannot exist with disordered structures (Refs. 3 and 4). With *larger particles,* however, a disordered layer in the surface can be tolerated, since any change in bulk free energy is then a small fraction of the total bulk free energy. Consequently, even though the cation/anion radius ratio for MgO is relatively low (0.47), the other criteria for this model to exist are not optimum. Therefore, this model probably is not valid for MgO.

Lowering surface energy in MgO by polarization of surface anions has not proved likely. The surface oxygen ions are not strongly polarized by divalent cations unless the cation size is low—an example is the case of beryllium ($r_{Be^{++}} = 0.31$ Å). The polarization influence should be noticeable. Indeed, beryllium does show covalent properties in bonding and a coordination number of 4. In the class of oxides of magnesium to barium (radius > 0.47 Å), with coordination number of 6 and little covalency, the small polarizing power of these cations is not expected to affect the surface energy markedly as a result of polarization of the oxygen ion.

Thus, MgO cannot lower its surface energy by either of these processes—submergence of surface cations or polarization. Therefore, adsorption of gas remains as the most likely mechanism by which MgO can lower its surface free energy. The process is likely to be the more important at low temperatures when ions are immobile for such high melting-point substances as MgO, which has a melting point of 2800°C. Further, the process is of even greater importance for any such oxides having either a high cation/anion ratio or a high cation/anion-radius ratio, since each of these states makes it difficult to shield the cations.

The amount of surface energy of MgO produced by these unshielded cations has been determined by Gilman (Ref. 5), using cleavage measurements, to be 1200 ergs/cm^2. Solution by heat measurements gave values of 1040 ergs/cm^2, and by atomic theory gave values of 1300 to 1440 ergs/cm^2. Nicolson (Ref. 6) calculated the surface tension of MgO and verified his results with lattice parameter measurements. Nicolson took into account various forces—Coulomb energy, van der Waals forces, repulsion, ion-dipole, like-dipole and unlike-dipole forces—and calculated a value of 6573 erg/cm^2 for surface tension, a value about 5 times greater than the surface energy which is not unreasonable for ionic solids. These atoms, molecules, or ions are not held by the surface energy, as such, even though their presence is a result of surface energy; they are held by interactions of electron movement, electron exchange, and by induced polarization of the surface. If an inert gas were to interact with the surface of MgO to a degree of satisfying the surface energy, only, and did not enter into any complexed interactions, we could, by using Nicolson's calculated value for surface tension, determine the maximum binding force of such an adsorbed molecule. Such a calculation is presented in Section III.

III. BINDING ENERGY RESULTING FROM SURFACE

There are no special adsorption forces. The forces that hold a visiting molecule at a surface are exactly the same as the forces that form molecules from atoms, crystals from molecules, etc. The forces involved in binding a crystal together can be calculated in many cases to any desired degree of accuracy. However, adsorption energy is difficult to calculate because little is known about three conditions: the real structure of the surface, magnitude of the repulsion forces, and real distance of adsorbed atom from the surface.

Despite these unknowns, the nature of adsorption forces and the approximate magnitude of adsorption energies can be determined for some species on some structures.

The Nicolson value for surface tension is used to calculate the binding energy of adsorbed atoms as a result of surface energy on a 100 Å particle:

$$\text{Tension} \times \frac{\text{surface area}}{\text{mole}} = \text{binding energy}$$

$$\frac{6500\ \text{erg}}{\text{cm}^2} \times \frac{7.52 \times 10^7\ \text{cm}^2}{\text{mole}} = \frac{4.88 \times 10^{11}\ \text{erg}}{\text{mole}}$$

Then conversion of units gives

$$\frac{4.88 \times 10^{11}\ \text{erg}}{\text{mole}} \times \frac{\text{J}}{10^7\ \text{ergs}} \times \frac{\text{cal}}{4.18\ \text{J}} = \frac{11.65\ \text{kcal}}{\text{mole}}$$

A value of 11.65 kcal/mole is not unreasonable for the total energy in the physical adsorption of a gas on an ionic solid. However, the adsorption of a gas varies with the amount of surface covered and the number of layers of gas adsorbed. If we assume an exponential distribution such that

$$11.65\ \text{kcal/mole} = \int_0^x e^x dx = e^x - 1$$

$$x = 2.53\ \text{kcal/mole}$$

The value 2.53 kcal/mole would then represent the strongest bonding available derivable from the surface energy. This, again, is not unreasonable when considering physically adsorbed gases. But as stated previously, surface energy is not the only factor; other forces can be involved in the bonding of a gas molecule to the surface. The magnitude of these other forces may be 10 to 100 times the magnitude of the forces from the surface energy alone.

The detailed calculation of the forces involved for the many combinations of adsorbed sites, adsorption process, and adsorbed gases involves approximately 2000 combinations. Thus, some selection and interpretation were necessitated during the calculation. The calculations that were made, and their interpretation, are listed in Appendix A.

IV. BINDING ENERGY RESULTING FROM INTERACTION OF ATOMIC FORCES

The various adsorption forces calculated in the appendix are summed to give a total adsorption energy. Tables 1 through 5 list the various forces for hydroxyl, argon, and helium species adsorbed at various sites on the surface of MgO. It is interesting to note that, for the different adsorbed molecule-surface combinations considered, all

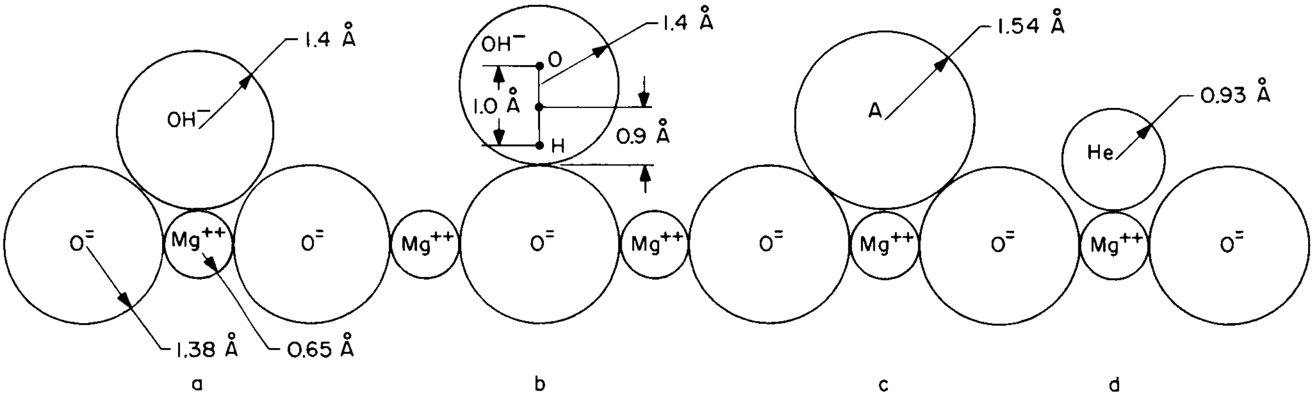

Fig. 1. Surface structure models for surface adsorption calculation

Table 1. Adsorption energy of hydroxyl ion over magnesium ion (Fig. 1a)

Force	Adsorption energy, kcal/mole				
	Face	Edge	Active corner	End	Hole
Coulomb	−11	−14	−39	−138	−11
Polar van der Waals, dipole	Lacking	Lacking	Lacking	Lacking	Lacking
Polar van der Waals, ion	−29	−29	−23	Negligible	<−29
Electrostatic polarization	−13	−16	−43	−149	Negligible
Dispersion	−16	−16	−12	−40	−31
Total	−69	−75	−117	−327	<−71

Table 2. Adsorption energy of hydroxyl ion over oxygen ion (Fig. 1b without regard to dipole)

Force	Adsorption energy, kcal/mole				
	Face	Edge	Active corner	End	Hole
Coulomb	+7	+10	+28	+97	+7
Polar van der Waals, dipole	Lacking	Lacking	Lacking	Lacking	Lacking
Polar van der Waals, ion	−20	−19	−16	Negligible	<−20
Electrostatic polarization	−3	−4	−10	−36	Negligible
Dispersion	−7	−7	−6	−14	−14
Total	−23	−20	−4	+47	<−27

Table 3. Adsorption energy of hydroxyl dipole over oxygen ion (Fig. 1b)

Force	Adsorption energy, kcal/mole				
	Face	Edge	Active corner	End	Hole
Coulomb	Lacking	Lacking	Lacking	Lacking	Lacking
Polar van der Waals, dipole	−14	−15	−19	−36	>−14
Polar van der Waals, ion	Lacking	Lacking	Lacking	Lacking	Lacking
Electrostatic polarization	−3	−4	−10	−36	Negligible
Dispersion	−7	−7	−6	−14	−14
Total	−24	−26	−35	−86	>−28

Table 4. Adsorption energy of argon atom over magnesium (Fig. 1c)

Force	Adsorption energy, kcal/mole				
	Face	Edge	Active corner	End	Hole
Coulomb	Lacking	Lacking	Lacking	Lacking	Lacking
Polar van der Waals, dipole	Lacking	Lacking	Lacking	Lacking	Lacking
Polar van der Waals, ion	Lacking	Lacking	Lacking	Lacking	Lacking
Electrostatic polarization	−9	−10	−19	−55	Negligible
Dispersion	−9	−9	−7	−22	−19
Total	−18	−19	−26	−77	−19

Table 5. Adsorption energy of helium atom over magnesium ion (Fig. 1d)

Force	Adsorption energy, kcal/mole				
	Face	Edge	Active corner	End	Hole
Coulomb	Lacking	Lacking	Lacking	Lacking	Lacking
Polar van der Waals, dipole	Lacking	Lacking	Lacking	Lacking	Lacking
Polar van der Waals, ion	Lacking	Lacking	Lacking	Lacking	Lacking
Electrostatic polarization	<−2	−3	−7	−24	Negligible
Dispersion	Negligible	Lacking	Lacking	Negligible	Negligible
Total	<−2	−3	−7	−24	Negligible

of the sites that constitute the majority of those available for adsorption in a powder (i.e., face, edge, holes due to overlapping particles) have approximately the same adsorption energy. Active sites, such as corner and end sites (where crystal growth stops on a face), although limited in number, show adsorption energies from 2 to 4 times the energy of the other sites considered in the case of OH^- on a Mg^{++} site. If this relative magnitude of the adsorption energy is approximately correct, molecules absorbed at active corner and end sites would be very difficult to remove.

In comparing the adsorption energies of the different molecules, the inert gases argon and helium should desorb more easily from all surface sites—including the most strongly bonded end sites—than would the hydroxyl ions adsorbed on the surface. When comparing the adsorption of hydroxyl at different positions, the magnitude of the forces indicated that the hydroxyl ion would be preferentially adsorbed over a magnesium ion on the surface.

These energy considerations demonstrate the strong bonding to be expected with OH^- in certain active sites in MgO. Also of concern is the quantity of OH^- to be introduced by such sites. Geometric calculations of such quantities are summarized in Fig. 2. The detailed calculations for the number of such sites are contained in Appendix B. The face sites are listed for partial coverage, since experimental (Ref. 7) evidence indicates this to be the lower limit of hydroxyl detection by IR spectroscopy.

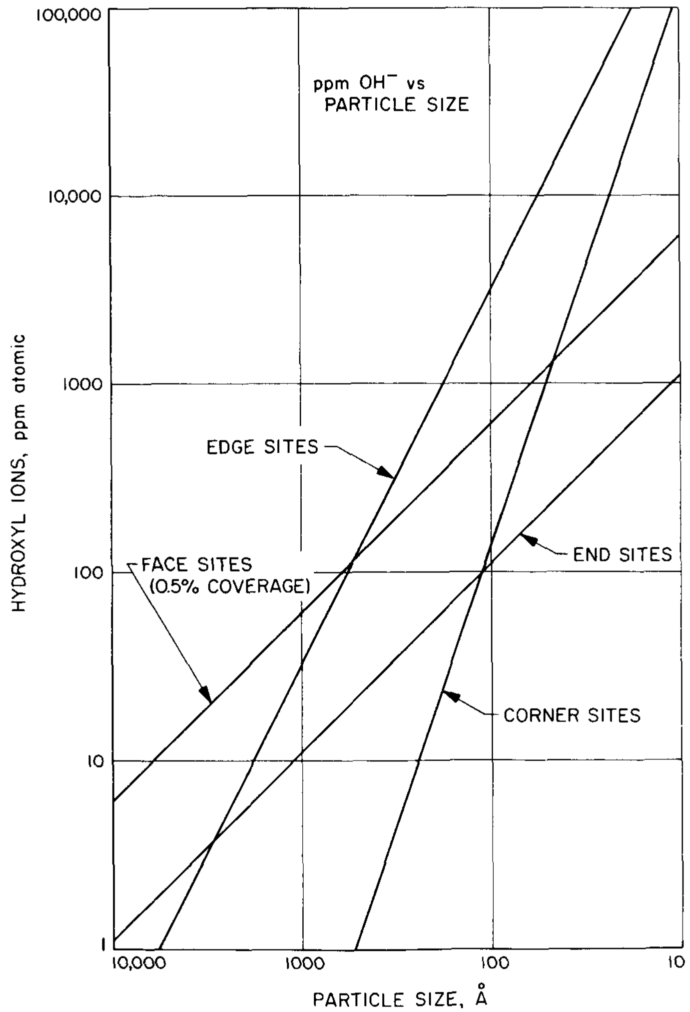

Fig. 2. Hydroxyl concentration vs particle size, assuming occupancy of various sites on a cube

V. DISCUSSION

A. Surface Adsorption

When the basic carbonate, $3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$, that is produced at JPL is calcined at approximately 700°C, the resulting crystallite size is about 150 Å. From other observations (Ref. 8), the oxide probably consists of a spongy aggregate, relics of the parent crystals, Electron microscope observations (Ref. 9) of air-calcined basic carbonate show the MgO aggregate to be made up of rectangular overlapping plates. The MgO crystallites in this configuration would offer sites for strong bonding by processes discussed in Appendix A. Since it has been indicated that the likely way in which MgO can lower its surface free energy at moderate temperatures is by gas adsorption, this process will occur. If the adsorbed gas were bonded to the surface to the extent of the maximum value of the surface tension, only, then these gases might be desorbed easily. But these gases, particularly those forming the first layer, interact with the electrostatic forces at the surface of the MgO crystallite and form strong combinations of chemical and physical bonds with varying strengths. Thus, the surface energy is lowered by the adsorption of gases, but the quantitative decrease in energy does not represent the force that bonds the gas molecules to the surface.

The calculated approximations for the adsorption forces of gases on the surface of MgO (in Tables 1 through 5) show that the magnitude of the forces between the adsorbed species and the surface depends on both the *location* of the adsorbed species on the surface and the *type of interaction* between the species and the surface. For hydroxyls adsorbed on the MgO surface, the magnitude of the bond force is highest when the hydroxyl molecule is located at an active site. The decomposition temperature for molecules so located cannot be calculated thermodynamically, because only a few molecules are being considered; however, the high adsorption energies suggest that high temperatures would be required for thermal desorption. Experimental evidence (Ref. 7) shows that hydroxyl present in normal face sites is completely removed only by temperature of the order of 900°C. Energies calculated here are far higher than that for normal face sites.

Other experimental investigations that might have revealed the presence of these OH^- ions held in active sites have suffered because of lack of sensitivity for the small amounts of OH^- involved. For example, in studies by Anderson et al., (Ref. 7) in which the presence of OH^- surface layer on MgO was correlated with extent of decomposition, it is likely that hydroxyls strongly bonded at active sites could not be detected by the techniques used. A-75 Å particle (the size used by Anderson et al.) has approximately 6800 ppm edge sites and approximately 450 ppm corner and end sites. For the configurations used by Anderson, et al., the limit of IR detectability is approximately 1300 ppm atomic of OH^- (see Appendix C for calculations). Hydroxyl ions at edge sites are just above the limit of IR detectability, and the corner and end site hydroxyls can escape detection of both IR and volumetric analysis. Hydroxyl ion impurities may remain in MgO to the heat treatment temperatures (~2200°C) used at this Laboratory. This finding would be consistent with mass spectrographic data obtained here that shows 300 to 1000 ppm hydroxyl ions existing in MgO at JPL that have undergone various heat treatments.

The fact that OH^- can exist on the surface of the JPL material at the temperatures and pressures involved, leads to analysis of the residence of this OH^- as the material is sintered and the grains grow. The OH^- fits the MgO lattice, as it is almost the same size as an $O^{=}$ Electrical neutrality may be preserved, since Konklin, et al., (Ref. 10) using nuclear double resonance techniques, have shown unambiguously that the OH^- ion fits in the lattice next to a magnesium ion vacancy. Since there is a higher density of vacancies at the grain boundary, the OH^- should likely be concentrated there. The facts that the OH^- ion is strongly bonded to MgO and that it can be accommodated by the lattice suggest that moderate thermal treatment will not reduce the OH^- to the low ppm range. Such limits may be reached only by fusion-purification or oxidation without the presence of OH^-.

There are ways in which the OH^- content in MgO produced by precipitation and thermal decomposition may be kept low. The alcohol wash used in the JPL material handling procedure is one way. The CH_3CH_2OH has a dipole moment of the same order as the OH^-. In addition, the CH_3CH_2 group will be bonded by nonpolar van der Waals forces of nearly the same value as the dipole bonding. Thus, the CH_3CH_2OH may exchange for H_2O adsorbed on the MgO, and the excess CH_3CH_2OH may dissolve the displaced H_2O. Since the CH_3CH_2 is a larger molecule than the OH^- ion, it probably shields a number of sites from readsorbing OH^-. Also, when the hydroxyl is attached to a molecule, as with alcohol, the total adsorption energy is less than when it is adsorbed as a free radical. The IR spectroscopy data taken here at JPL, showing lower OH^- peaks in MgO that had been washed with alcohol prior to fabrication, are consistent with this hypothesis.

The OH^- adsorption might also be reduced by introducing helium or argon to the surface before exposing it to OH^-. Helium and argon will be strongly bonded to the MgO surface at active sites by electrostatic polarization. The bond energies are -24.2 kcal/mole for helium and -54.8 kcal/mole for argon at active end sites. Helium would appear to be the best, since it has a lower total adsorption energy (see Table 5) because of its lower polarizability; and, if entrapped during densification, will diffuse out faster because of its smaller radius (Ref. 11).

B. Decomposition Reaction

Thermodynamic studies of the decomposition reaction directed to defining an optimum calcining temperature showed that, while native magnesite (Ref. 12) and $Mg(OH)_2$ (Ref. 13) showed a maximum in activity and surface area with decreasing calcining temperature, the basic carbonate used here does not. The surface area of the basic carbonate falls off rapidly from ~ 200 m^2/g to about 20 to 30 m^2/g in the temperature range of 400 to 800°C. Thus, lower calcining temperatures should produce more active powders and, in turn, enhance pressure sintering.

VI. CONCLUSIONS

In spite of the lack of extensive data and satisfactory theory for the composition and structure of the surface of MgO, some significant conclusions may be drawn. The nature of the surface of MgO does not permit surface rearrangement; therefore, gas adsorption will occur to reduce surface energy. The presence of hydroxyl ions as the adsorbed specie is very likely because of the high adsorption energies (>100 kcal/mole) and the existence of hydroxyl in the MgO production process. The high adsorption energies also indicate that thermal treatment would not be effective in removing hydroxyl ions from active sites.

It is also concluded that the quantity of active sites is sufficient to account for the amount of hydroxyl observed in MgO. Finally, it is suggested that, after thermal treatment, the hydroxyl impurities are most likely to reside at the grain boundaries.

APPENDIX A

Calculation of Adsorption Forces

An excellent treatise on the nature of adsorption forces has been published by de Boer (Ref. 1). The bulk of the calculations in this report summarize methods and assumptions developed by him, but the application in this case is to particular species not formerly treated in detail in other literature.

The calculations for the adsorption of He, A, and OH^- and various available sites on the surface of MgO cubes were developed with consideration of the following forces:

1. *Coulomb attraction:* Electrostatic attraction resulting from exchange of an electron
2. *Polar van der Waals:* Force resulting from Coulombic attraction between one end of dipole and surface field
3. *Surface polarization:* Force resulting from polarization of dielectric surface by change of adsorbed ion and Coulombic attraction
4. *Adsorbed specie polarization:* Force resulting from polarization of adsorbed specie by surface field and subsequent Coulombic attraction
5. *Dispersion:* Interaction of electronic field of adsorbed specie with that of surface

Also considered were the magnitude of these forces at Mg^{++} and $O^=$ normal face sites and other-than-normal face sites (e.g., corners, edges).

1. Coulomb Interaction

When an ion approaches the surface of an ionic compound, there is a Coulomb force interaction. In general, for a lattice of NaCl type, the energy contribution of the Coulomb forces takes the following form (Ref. 1):

$$E_c = k_1 \frac{\epsilon^2}{r_c} \tag{A-1}$$

where

ϵ = electron charge, statcoulombs

r_c = minimum adsorbed ion-surface ion

k_1 = proportionality constant depending on site

The equation above applies to an ion absorbed over an Mg^{++} ion on a {100} face with $k_1 = 0.0662$. A different situation exists with respect to edge, corner, and end (where crystal growth stops on a face) positions occurring on freshly formed crystal faces. These crystallographic locations, because of reduced effect of surrounding repulsive forces, are extremely *active* spots for adsorption by electrostatic attraction. Here $k_1 = -0.0903$, -0.2470, and -0.8737, respectively, for edge, corner, and end positions. Healing, sintering, and grain growth tend to reduce the number and activity of such active spots. Also, other crystallographic faces that generally do not occur in well developed crystals may exercise stronger forces than do normal faces. For example, adsorption energy on a rhombic dodecahedron face of an alkali halide is $k_1 = -0.2082$. For an OH^- ion adsorbed over a Mg^{++} ion as shown in Fig. 1a, the energy decrease due to Coulomb interaction can be estimated by use of Eq. (A-1).

$$E_{c_{\{100\}\text{face}}} = \frac{-0.66 \times 10^{-12}\ \text{ergs}}{\text{atom}}$$

In kcal/mole, the values for Coulomb attraction are −11.5 for a face site, −14.3 for edge, −39.1 for corner and −138 for an end site. The values for adsorption on corners and end sites illustrates the high binding energy involved in Coulombic interactions at highly active sites. The formulas used above for attraction can also be used to estimate repulsion energy when an ion approaches a surface ion of like charge. In repulsion, the energy contribution is positive.

2. Polar van der Waals Force

Molecules that have a permanent dipole will interact with the electrostatic field that emanates from the surface of ionic solids. For the adsorption energy to be significant, two criteria must be satisfied: (1) the negative ions must form the outer layer, and (2) the dipole must be situated in the polar molecule in such a way that it can be very close to the surface. The surface of MgO probably does not satisfy the first condition, but it is of interest to consider dipole interactions.

The OH^- ion satisfies the second condition since the H atom is very near the periphery of the molecule.

Figure 1b shows the position of an OH^- over an $O^=$. The center of the dipole molecule at the closest approach to an oxygen ion ($r = 1.4$Å) is at a distance of 2.28Å from the center of the oxygen ion.

The adsorption energy contribution from dipole interaction may be approximated (Ref. 1) by the expression

$$E_\mu = -F\mu \qquad \text{(A-2)}$$

where μ is the dipole moment and F denotes the electrostatic field of the surface, estimated (Ref. 1) by

$$F = K\frac{8\pi\epsilon}{r_c^2}\exp\left(-\pi\sqrt{2}\frac{r}{r_c}\right) \qquad \text{(A-3)}$$

where

$r_c = r = 2.28$Å

$\epsilon = 4.803 \times 10^{-10}$ ESU

$K =$ dyne cm^2/statcoulomb^2

then, by substitution,

$$F = \frac{5.82 \times 10^6 \text{ dyne}}{\text{ESU}}$$

If 1.7×10^{-18} ESU is the value for the dipole moment of OH^-, $E\mu$ is -14.25 kcal/mole. This value is probably slightly higher for MgO, since the oxygen does not completely screen the magnesium ion and there is a resultant reduced effective charge. At active sites, the energy from dipole moment is increased because of reduced repulsion by the surrounding magnesium ions. The magnitude of the increase at active sites is less than that for the Coulombic interaction and has been estimated at approximately 2.5 for an end position.

$$E_{\text{end}} = 2.5\,E_{\text{face}} = -\frac{36.4\text{ kcal}}{\text{mole}} \qquad \text{(A-4)}$$

The energy at edge and corner sites can be estimated by considering the increase in repulsion from surrounding magnesium ions to be in the same proportion as Coulomb interaction; thus, the values are -14.8 kcal/mole for edge and -19.1 kcal/mole for corner sites.

3. Polarization of a Dielectric Surface by an Adsorbed Ion

When an ion is adsorbed on the surface of a dielectric, there is a shifting of the electrons in the surface atoms caused by the polarizing effect of the ion. With dielectrics, the polarization of the electrons is restricted to the atoms of the dielectric or to a group of atoms to which the electrons belong. An ion close to a surface will induce a dipole moment in the neighboring surface atoms. The energy needed to separate the charges in forming the dipole and the energy gained by the mutual attraction of the ion and the dipole are accounted for when the binding energy for the ion and the atom in the surface is given (Ref. 1) by:

$$E_{\epsilon\alpha} = \frac{-\alpha\epsilon^2}{2\,r_0^4} \qquad \text{(A-5)}$$

where

$r_0 =$ distance between atom and surface, cm

$\alpha =$ polarizability, cm^3 (Table A-1)

$\epsilon =$ electron charge, statcoulombs

The adsorption energy of the nearest atom, only, is considered in the above equation. The fact that surrounding atoms also contribute to this energy requires a complicated summation process to include all contributions. A more satisfactory value for the adsorption energy caused by electrostatic induction energy resulting from electrostatic induction for the system of an OH^- ion adsorbed on the surface of MgO is

$$E_{\epsilon\alpha} = \frac{-\epsilon^2}{4\,r_0}\frac{(K-1)}{(K+2)} \qquad \text{(A-6)}$$

where K is the dielectric constant.

The dielectric constant K for MgO is 9.65. Thus, $E_{\epsilon\alpha}$ for a hydroxyl adsorbed over an Mg^{++} ion in MgO (Fig. 1a) is 29 kcal/mole. On active sites, such as corners and edges, the magnitude is less; and at crystal-end positions, it is negligible. At active sites created by lattice disturbances and holes, the magnitude will be higher.

Table A-1

	Polarizability (Ref. 14)
He	0.201×10^{-24} cm^3
A	1.68×10^{-24} cm^3
Mg^{++}	0.094×10^{-24} cm^3
$O^=$	3.88×10^{-24} cm^3
F^-	1.04×10^{-24} cm^3
OH^-	[a]3.83×10^{-24} cm^3

[a]Calculated from dipole moment.

4. Electrostatic Polarization of an Adsorbed Molecule

The energy contribution by electrostatic polarization of the adsorbed molecule or atom permits adsorption of species that do not possess permanent dipoles—for example, inert gases are induced to have the same behavior as molecules with permanent dipoles. The ratio between adsorption on a face to that at an active spot is nearly the same as in the case of adsorption of ions and far greater than in the case of dipole interactions described earlier. The electrostatic polarization contribution to adsorption may be estimated by the de Boer equation:

$$E_\alpha = -F^2 \frac{\alpha}{2} \qquad \text{(A-7)}$$

where

F = value described in Eq. (A-3)

α = polarizability (Table A-1)

For argon over Mg^{++} (Fig. 1c), $E_\alpha = -4.8$ kcal/mole.

At active sites, the contribution by electrostatic polarization, which is very high, is estimated to be as high as 11.5/1 for an end position. An equation of the form of Eq. (A-4) is satisfactory for estimation of active site adsorption. Thus, for argon over Mg^{++}, the energy in an end position is -54.8 kcal/mole. Use of the same ratio as Coulombic interaction, the energy is determined to be -19.1 kcal/mole for a corner site, and -9.6 kcal/mole for an edge.

Because of the unhomogeneity of the electrostatic field of an ionic surface, it has been recommended (Ref. 1) that the argon atom be divided into volume elements and used an integral to evaluate the adsorption energy. The adsorption energy for argon adsorbed over a potassium ion in KCl is computed as -0.45 kcal/mole by Lenel's method and -0.25 kcal/mole by Eq. (A-7). The Lenel method for evaluating argon adsorption over a magnesium ion in MgO would suggest an energy value of -8.56 kcal/mole.

The contributions to adsorption energy were found for helium and hydroxyl by use of Eq. (A-7).

Helium over an Mg^{++} (Fig. 1d)

$E_{\alpha_{\text{face}}} = -2.1$ kcal/mole

$E_{\alpha_{\text{edge}}} = -2.6$ kcal/mole

$E_{\alpha_{\text{corner}}} = -6.9$ kcal/mole

$E_{\alpha_{\text{end}}} = -24.2$ kcal/mole

Hydroxyl over an Mg^{++} (Fig. 1a)

$E_{\alpha_{\text{face}}} = -13$ kcal/mole

$E_{\alpha_{\text{edge}}} = -15.9$ kcal/mole

$E_{\alpha_{\text{corner}}} = -42.8$ kcal/mole

$E_{\alpha_{\text{end}}} = -149$ kcal/mole

Hydroxyl over $O^{=}$ (Fig. 1b)

$E_{\alpha_{\text{face}}} = -3.2$ kcal/mole

$E_{\alpha_{\text{edge}}} = -3.9$ kcal/mole

$E_{\alpha_{\text{corner}}} = -10.5$ kcal/mole

$E_{\alpha_{\text{end}}} = -36.5$ kcal/mole

5. Dispersion Force

Dispersion forces are always present in *any* combination of molecule and surface, and they always lead to attraction. Dispersion forces result from the polarization of each one of the participating molecules of any pair by the continuously changing field that arises from the electronic movements in the other partner. Various equations have been developed for the calculation of the appropriate force, the majority of which yield reasonable results. Selection here was based on availability of applicable data.

$$E = -\frac{3\epsilon h}{4\pi r^6 m^{1/2}} \left[\frac{\alpha_1 \alpha_2}{\left(\frac{\alpha_1}{n_1}\right)^{1/2} + \left(\frac{\alpha_2}{n_2}\right)^{1/2}} \right] = -\frac{k_3}{r^6} \qquad \text{(A-8)}$$

k_3 = constant based on particular species

E = adsorption energy, ergs/atom

h = Planck's constant

r = approach distance

ϵ = electron charge

α = polarizability (see Table A-1)

m = electronic mass

n = number of electrons outer shell

In Eq. (A-8), k_3 may be evaluated for the interaction of various adsorbed gases in various locations on the surface using the appropriate polarizabilities from Table 5. The adsorption energy E is then determined from the spacing between the adsorbed atom and each of various nearest neighbors r until the interaction becomes negligible. Summation of the interactions then yields the appropriate dispersion energy. In the case of OH^- over a magnesium site, a 40% reduction (Ref. 1) was used to approximate the effect of repulsion force of the second nearest neighbors, in this case, the $O^=$ ions.

The exact location of the adsorbed atom on the surface affects the calculated energy. Ions would be adsorbed over sites of opposite charge because of Coulomb attraction; however, uncharged atoms are reported (Ref. 14) to reside over interstitial sites. The approximate sites were used in these calculations of dispersion energy.

APPENDIX B

Calculation of Number of Active Sites

The number of sites may be calculated from the geometry and size of cubes.

1. Number of Surface Sites

For a minimum detectable surface coverage of 0.5%,

$$v_p = \ell_p^3$$

$$N_p = \frac{v_m}{v_p}$$

$$a_p = 6\,\ell_p^2$$

$$a_m = a_p \times N_p$$

$$N_{OH^-} = \frac{a_m}{a_{OH^-}}$$

$$\text{Number fraction } OH^- = \frac{N_{OH^-}}{N}$$

where

ℓ_p = length of cube edge, Å

v_p = volume of particle, Å^3

v_m = molar volume = 11.25 cm^3/mole for MgO

N_p = number of particles/mole

a_p = surface area/particle, Å^2

a_m = surface area/mole, Å^2

N_{OH^-} = number of OH^-/mole

a_{OH^-} = area covered by OH^- = 9.1 Å^2 (Ref. 7)

Surface ppm atomic OH^- @ 0.5% monolayer

$$= 5 \times 10^{-3} \times 10^{-6} \times \frac{N_{OH^-}}{N}$$

$$= \frac{6.1 \times 10^{-3}}{\ell_p}$$

2. Number of Active Edge Sites for OH^-

$$L_m = 6\,\ell_p N_p$$

$$N_{OH^-} = \frac{L_m}{\ell_{OH^-}}$$

$$\text{Number fraction } OH^- = \frac{N_{OH^-}}{N}$$

$$\text{edge ppm atomic} = 10^6 \frac{N_{OH^-}}{N} = \frac{3.2 \times 10^7}{\ell_p}$$

where

L_m = total edge length/mole (Å)

$\ell_{\mathrm{OH^-}}$ = length of OH⁻ = $(9.1\ \text{Å}^2)^{1/2}$

= 3.05 Å

3. Number of Active Corner Sites for OH^-

$$N_{\mathrm{OH^-}} = n_c\, N_p$$

$$\text{Number fraction OH}^- = \frac{N_{\mathrm{OH^-}}}{N}$$

$$\text{corner ppm atomic} = 10^6\, \frac{N_{\mathrm{OH^-}}}{N} = \frac{1.48 \times 10^{-16}}{\ell_p^3}$$

where n_c = number of corners/particle = 8

4. Number of Active End Sites for OH^-

$$N_{\mathrm{OH^-}} = n_e\, a_m$$

$$\text{Number fraction OH}^- = \frac{N_{\mathrm{OH^-}}}{N}$$

$$\text{end ppm atomic} = 10^6\, \frac{N_{\mathrm{OH^-}}}{N} = \frac{1.12 \times 10^4}{\ell_p}$$

where n_E = number of ends/particle — not directly known, estimate at 1 end/10^{-12} cm^2 of surface area. (The calculation shows that for the number of these sites to be equal to the 0.5% monolayer, there would need to be an end located about every 10 atomic distances).

APPENDIX C

Theoretical Sensitivity of IR Spectroscopy for OH^-

With adsorption in 10-cm length of H_2O vapor and 1-cm^2 beam, the detection limit is approximately 1-mm pressure.

$$m = \frac{VP}{M} = \frac{10}{22{,}400 \times 760} = 5.86 \times 10^{-5}\ \text{moles}$$

Atomic sensitivity OH⁻

$$= mN = 3.54 \times 10^{17}\ \text{molecules}$$

where

N = Avogadro's number

m = gas moles in sample

V = sample volume = 10 cu^3

M = molar volume 22.4 l/mole

p = pressure = 1/760

For a typical MgO sample, 50% dense and 0.1-mm thick, in a 1-cm^2 beam, we have 4.5×10^{-4} moles or 2.7×10^{20} atoms. Sensitivity for OH⁻ in this size sample is expressed as

$$\text{Sensitivity ppm atomic OH}^- = 10^6\, \frac{3.54 \times 10^{17}}{2.7 \times 10^{20}} = 1300$$

REFERENCES

1. de Boer, J. H., "Atomic Forces and Adsorption," *Advances in Colloid Science, Volume III,* edited by H. Mark and J. Verney, Interscience, New York, 1950, pp. 1–63.
2. Livey, D. T., and Murray, P., "Surface Energies of Solid Oxides and Carbides," *Journal of the American Ceramic Society,* Vol. 39, No. 11, November 1, 1956, pp. 363–72.
3. Rosenthal, D., and Kaufman, K., "X-Ray Line Broadening of Plastically Deformed Marble," *Journal of Applied Physics,* Vol. 23, 1952, pp. 600–1.
4. Thomas, D., and Baker, T. W., "X-Ray Diffraction Studies of Active Magnesium Oxide," *Proceedings of the Physical Society* (London), Vol. 74, 1959, p. 6.
5. Gilman, J., "Direct Measurements of the Surface Energies of Crystals," *Journal of Applied Physics,* Vol. 31, No. 12, December 1960.
6. Nicolson, M. M., "Surface Tension in Ionic Crystals," *Proceedings of the Royal Society* (London), Series A, Vol. 228, 1955, pp. 490–510.
7. Anderson, P. J., Horlock, R. F., and Oliver, J. F., "Interaction of Water with Magnesium Oxide Surface," *Transactions of the Faraday Society,* Vol. 61, No. 516, Part 12, December 1965.
8. Eubank, W. R., "Calcination Studies of Magnesium Oxide," *Journal of the American Ceramic Society,* Vol. 34, No. 8, August 1951, p. 225.
9. Meyer, J. W., and Yang, C. S., "Some Observations in the System $MgO–H_2O$," *American Journal of Science,* Vol. 260, 1962, pp. 707–717.
10. Konklin, P. W., Auzins, R., and Wertz, J. E., "A Hydrogen-Containing Trapped Hole Center in Magnesium Oxide," *Journal of the Physics and Chemistry of Solids,* Vol. 26, 1965, pp. 1067–74.
11. Coble, R. L., "Sintering Alumina: Effects of Atmosphere," *Journal of the American Ceramic Society,* Vol. 45, No. 3, 1962, pp. 123–7.
12. Rayouk, R. I., and Mikhail, R. H., "Surface Properties of MgO II," *Journal of Physical* Chemistry, Vol. 63, 1959, pp. 1050–53.
13. Gregg, S. J., and Pacher, R. K., "The Production of Active Solids by Thermal Decomposition," Part VI: The Calcination of $Mg(OH)_2$," *Journal of the Chemical Society* (London), Vol. 51, 1955, pp. 51–5.
14. Orr, W. J. C., "Calculation of the Adsorption Behavior of Argon in Alkali Halide Crystals," *Transactions of the Faraday Society,* Vol. 35, 1939, p. 1247.