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Formation of New Acid Sites in Dilute Oxide Solid Solutions: A Predictive Model

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A predictive model for the formation of new acid sites in a dilute solid solution of two component oxides is being developed by examining the electrostatic potential at the substituting cation site and the changes in the matrix necessary to balance the stoichiometry. When the prediction was used to compare with experimental results, the satisfactory comparison suggests that the electrostatic potential and the balance of stoichiometry are the two dominant factors in new acid site formation. The implications of this are discussed.

Introduction

A dilute solid solution of one oxide in another is perhaps the simplest class of mixed oxides amenable to simple analysis. Indeed, dilute solid solutions of two oxides of the same crystal structure and stoichiometry have been analyzed to predict the surface enrichment of one component (*1*), and to understand the difference in activation energy of a reaction catalyzed by a pure oxide versus a solid solution (*2*).

It is logical to attempt to extend the analysis to dilute solid solutions of oxides of different crystal structures and stoichiometries. Mixed oxides formed from oxides of different stoichiometries often develop strong acidity not present in the component oxides (*3*). It is a result of the effects such as the formation of new surface defects, and a change in the energy level of the surface cations. The former results from the need to balance the overall stoichiometry of the solid, and the latter results from the different number and position of neighboring oxygens around the cation as well as from the different electrostatic potential at the cation in the solid solution as compared to the pure component. Toward better understanding of these systems, we explore the consequences of balance of stoichiometry, and of the change in the electrostatic potential.

The Model

A dilute solid solution is assumed to be formed from an oxide of stoichiometry AO_y and an oxide BO_z by substituting a small amount of A into the B site. It is referred to as a substituting ion A in a matrix BO_z. For generality, y and z do not have to be integers. The solid solution is so dilute that adjacent A ions are very far apart such that in the calculation of electrostatic potential, the system is approximated by a single A ion in

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the BO_z matrix. Two situations are possible. When $y = z$, the component oxides are of the same stoichiometry and the substitution can be achieved with minimal effect on the matrix. Thus any new acidity formed would be associated directly with the electrostatic potential at the substituting ion site. When y is not equal to z, new acidic sites formed would be associated with the electrostatic potential at the substituting ion site as well as other changes necessary in the matrix to preserve the overall stoichiometry of the solid solution. These two effects are discussed separately below.

Electrostatic potential at the substituting cation site. The difference in the electrostatic potential, ΔV, experienced by a cation A in the matrix BO_z and AO_y is given by

$$\Delta V = \sum_i (q_i/r_i)_{BO} - \sum_i (q_i/r_i)_{AO} \quad (1)$$

where q_i is the charge of the ion at a distance r_i from the A site. The subscripts BO and AO denote the matrices BO_z and AO_y, respectively. If the A site is in a three-dimensionally infinite solid, and q_i is taken as the formal charge q_i^F, the summations in Eq. (1) are the lattice self-potentials V^F at the substituting cation site. Values of the lattice self-potential at the cation sites for a number of oxides are listed in Table I (*4*, *5*). Equation (1) can be rewritten as

$$\Delta V = (V^F q_i/q_i^F)_{BO} - (V^F q_i/q_i^F)_{AO} \quad (2)$$

When ΔV is negative, ion A in matrix BO_z experiences a more negative potential than in AO_y. It will be electrostatically more stable and can accept electrons more readily. It will act as a Lewis acid site. When ΔV is positive, A is less readily in accepting electrons in matrix BO_z than in matrix AO_y. From Eq. (2), it can be seen that when the ratio q_i/q_i^F is about the same in the two matrices, the sign of ΔV is determined by the relative magnitudes of V^F for BO_z and AO_y.

TABLE I

LATTICE SELF-POTENTIAL AT THE CATION SITE OF OXIDES[a]

	Compound	Potential (V)		Compound		Potential (V)
MO			M_2O_3			
	MgO	−23.9		α-Cr_2O_3		−34.9
	CaO	−20.9		α-Fe_2O_3		−34.8
	SrO	−19.5		α-Al_2O_3		−36.6
	BaO	−18.2		V_2O_3		−33.4
	MnO	−22.7		Ti_2O_3		−33.6
	FeO	−23.3		Ga_2O_3		−35.0
	CoO	−23.6				
	NiO	−24.2		Rh_2O_3		−34.1
	CdO	−21.4				
	CuO	−24.3		Pb_2O_3	Pb(1)	−32.8
	ZnO	−24.0			Pb(2)	−28.1
	PbO	−20.5				
				Nd_2O_3		−29.7
MO_2				La_2O_3		−29.0
	TiO_2	−44.7	MO_3			
	SnO_2	−42.9		CrO_3		−58.5
	SiO_2	−46.4 to −50.6[b]		MoO_3		−58.5
				WO_3		−64.5
	CrO_2	−46.2				
	ZrO_2	−42.3				

[a] Most of the values are taken from Refs. (*4*, *5*); others are calculated in this work.

[b] Value depends on the crystal structure.

Some true ion charges, q, that can be used in Eq. (2) have been derived from XPS and X-ray diffraction measurements. They are listed in Table II. The values derived from X-ray diffraction were calculated from the electron density maps and the boundaries of the ions were assumed to correspond to the point of minimum (local minimum) of electron density. The values derived from XPS were obtained using the method of Bagus and Broughton (*4*, *6*, *7*). The reliability of these values suffered from the approximation used in evaluating the final state effect, and the accuracy of the calculated binding energies of the gas phase ions (*8*). For some chromium compounds, the values of Dickinson *et al.* were reported (*9*). Finally, the ion charges provided by some theoretical cluster calculations were also included.

Changes in the matrix. When the stoichiometries of the component oxides are different, the overall stoichiometry of the

TABLE II

TRUE CATION CHARGE OF OXIDES

Compound		True cation charge[a]			
		XPS[b]	X-Ray		Calculation
MgO		1.25–1.75		1.9(*19*),1.85(*20*),1.5(*21*)	
CaO				1.8(*21*)	
SrO				2(*21*)	
BaO				2(*21*)	
VO				0–1(*22*)	0.66(*11*)
MnO		1.5		1.4(*19*),1.51(*20*)	
CoO		1–1.5		1.2(*19*),1.4(*20*)	
NiO		1–1.5		0.7(*19*),0.9(*20*)	1.2–1.8(*12*)
CuO		2			
ZnO		1.2–1.7,1.11[c](*14*)			
CdO		1.05[c](*14*)			
AgO	Ag(I)	0.53[c](*14*)			
	Ag(III)	1.87[c](*14*)			
α-Fe_2O_3		2.7			
α-Cr_2O_3		0.15(*9*),2.6			
α-Al_2O_3		2–2.5(*18*)			
TiO_2		2.8			
SiO_2		4, 2[c](*13*)		1.0(*10*)	
CrO_2		0.38[d](*9*)			
ZrO_2		1.2			
CrO_3		0.46[d](*9*)			
MoO_3		1.5–2			
WO_3		1.5			
Ag_2O		0.48[c](*14*)			
$Mg_2Si_2O_6$	(Mg ion)		(M1)	1.84(*20*)	
			(M2)	1.79(*20*)	
$LiAlSi_2O_6$	(Li ion)			0.7(*20*)	
	(Al ion)			2.4(*20*)	
$CaMgSi_2O_6$	(Mg ion)			1.44(*20*)	
	(Ca ion)			1.39(*20*)	
Mn_2SiO_4	(Mn ion)		(M1)	1.21(*20*)	
			(M2)	1.49(*20*)	

[a] Reference numbers appear in parentheses.

[b] Unless noted, the charges are calculated as in Ref. (*4*). The XPS data are from Refs. (*16, 17*) except when indicated.

[c] The final state extra-atomic relaxation of the cation has been included in calculating these values.

[d] These are taken directly from Ref. (*9*).

solid will be conserved by a change in the matrix. Two possibilities exist: a substituting cation *A* of a lower formal oxidation state than the matrix cation *B*, $y < z$, and the reverse case of *A* of a higher formal oxidation state than *B*, $y > z$.

When $y < z$, a simple substitution of *B* ion by *A* ion would result in a solid with excess oxygen. This excess can be balanced by (1) development of anion vacancies; (2) adsorption of protons on the surface; or (3) development of interstitial cation defects. (1) and (2) are intimately related if the solid is prepared by aqueous precipitation such that the surface is hydroxylated. If the surface stays hydroxylated, the protons present to balance the excess oxygen will act as new Brönsted acid sites not present in the component oxides. On heating, some of these protons may be removed as water which is formed with the concurrent formation of an anion vacancy. Thus the anion vacancy site could act as a new acid site once hydrated. The effect of (3) is less obvious to predict. It could be important for solids that have open structures. In most common binary oxides, however, the concentration of interstitial defects is limited. Whether these defects lead to the formation of acid sites is likely to depend on the nature of the cation.

When $y > z$, simple substitution of B ion by A ion would result in a deficiency of oxygen. The deficiency can be removed by (1) adsorption of negatively charged oxygen species onto the A ion; (2) adsorption of OH^- onto the A ion; or (3) presence of cation vacancies. When (1) or (2) operates, the consequence of electrostatic potential change at the A ion is removed because the coordination unsaturation of A is satisfied by the adsorbed oxygen or OH^-. Since it is not likely that adsorbed oxygen or OH^- acts as an acid site, new acidity is predicted not to develop. When (3) operates, new Lewis acid site could appear because cation vacancies are electron deficient.

Discussion

In the above model, the possibility of forming new acid sites is discussed with respect to the electrostatic potential at the substituting ion and the effect of the matrix in preserving overall stoichiometry. With respect to the former, the effect at the substituting ion depends on the sign and the magnitude of ΔV in Eq. (2), which in turn depend on the relative magnitudes of lattice self-potential and the ratio q/q^F. The values of q/q^F for most oxides are about 1/2. As to the lattice self-potential, the values in Table I reveals an interesting generalization: for compounds of the same stoichiometry, the magnitudes of the lattice self-potential are about the same and are different from other stoichiometries. In general, they are about −20 to −24 V for MO, −33 to −36 V for M_2O_3, −42 to −46 V for MO_2, and −60 V for MO_3. Thus when an oxide of a lower oxidation state is mixed into a matrix of a higher oxidation state, new Lewis acid sites are likely to develop at the substituting ion position unless there is a large difference in their ionicity (i.e., q/q^F). This observation then leads to the simplified conclusions summarized in Table III that are based on the oxide stoichiometries only.

When these conclusions are applied to mixed oxides, a comparison of the predicted and experimental results can be made. This is shown in Tables IV and V. Table IV shows the comparisons in which the predictions based on Table III are either affirmative or negative. Of the 24 oxide pairs compared, agreement between observed results and prediction were found for all but two pairs. Table V shows the experimental observations for oxide pairs

TABLE III

FORMATION OF NEW ACID SITES PREDICTED FROM STOICHIOMETRY OF THE SUBSTITUTING OXIDE AO_y AND MATRIX BO_z[a]

	Formation of new acid site		
	At substituting ion	In matrix	
Case	Lewis acid	Brönsted acid	Lewis acid
$y < z$	Yes	Yes	May be
$y = z$	Yes if BO_z more ionic	No	No
$y > z$	No	No	May be

[a] When the ionicity of the two oxides are very different, stoichiometry alone is not sufficient for prediction.

TABLE IV

COMPARISON OF EXPERIMENT AND PREDICTED FORMATION OF NEW ACID SITES

Matrix oxide, BO_z	Substituting oxide, AO_y	New acid site	
		Predicted[a]	Experiment[b]
TiO_2	CuO	+	+
	MgO	+	+
	ZnO	+	+
	CdO	+	+
	Al_2O_3	+	+
	SiO_2	+	+
	PbO	+	+
	Bi_2O_3	+	+
	Fe_2O_3	+	+
ZnO	MgO	−	+
	PbO	−	−
Al_2O_3	MgO	+	+
	B_2O_3	−	+
	Sb_2O_3	−	−
	Bi_2O_3	−	−
SiO_2	BeO	+	+
	MgO	+	+
	CaO	+	+
	SrO	+	?
	BaO	+	?
	Ga_2O_3	+	+
	Al_2O_3	+	+
	Y_2O_3	+	+
	La_2O_3	+	+
	ZrO_2	+	+
ZrO_2	CdO	+	+

[a] The + means affirmative, − means negative.

[b] All experimental data are taken from Ref. (*3*).

for which the prediction by this model is inconclusive. Of the 12 pairs, eight show new acid sites formed, four do not. Results in these two tables strongly suggest that although electrostatic potential and the balance of stoichiometry are not the only considerations, they are likely the dominant factors in new acid site formation. Only when considerations based on these two factors are inconclusive, consideration of the otherwise minor factors needs to be made.

There is available another predictive model by Tanabe *et al.* (*3*) which is a localized approach that examines the change in the coordination number of the substituting ions. In their model, formation of new acid sites is predicted by examining the difference of the ratio q^F/C for the substituting ion and the surrounding oxygen ion, where C is the coordination number. Since the ratio q^F/C is the same, except for a sign change, for the cation and the anion in a given compound (in which all cations and all anions are equivalent), this difference is the same as that between the cations of the two component oxides.

Tanabe's method and the most simplified conclusion of this method of comparing stoichiometries bear some similarities. Although the stoichiometry and the q^F/C ratio do not have a fixed relationship, q^F/C is the same for most oxides of the same stoichiometry. Thus either method gives the same prediction in most cases. While they may yield similar results, there are important differences between them. As mentioned before, Tanabe's method is a localized approach such that any new acid sites formed are at the substituting cation site. In this method, the effect of matrix is emphasized. Thus new acid sites can be formed on the matrix surface far away from the substitution site as well as at the site. The matrix affects the substituting cation through long

TABLE V

EXPERIMENTAL RESULTS OF NEW ACID SITE FORMATIONS ON OXIDE PAIRS FOR WHICH THE PREDICTION BY THE MODEL IS INCONCLUSIVE

Matrix oxide, BO_z	Substituting oxide, AO_y	Experimental results[a]
TiO_2	ZrO_2	+
	WO_3	+
ZnO	Al_2O_3	+
	SiO_2	+
	ZrO_2	−
	Sb_2O_3	−
	Bi_2O_3	−
Al_2O_3	ZrO_2	+
	WO_3	+
SiO_2	WO_3	+
ZrO_2	WO_3	+
MgO	WO_3	−

[a] Data are taken from Ref. (*3*) except for those involving WO_3 which are taken from Ref. (*15*).

range electrostatic interaction. The coordination immediately around the substituting cation is not explicitly considered although it strongly determines the lattice self-potential. Finally, ionicity is being taken into consideration.

This approach can be improved upon in several ways. The inclusion of the effect of coordination symmetry on the direction, energy and occupation of the dangling orbitals of the substituting ion and its neighbors, the use of surface lattice self-potential instead of the bulk values, the incorporation of the detailed knowledge of the properties of anion and cation vacancy defects on the matrix, and a treatment that applies to concentrated solid solutions would lead to more quantitative and interesting results.

In conclusion, this paper describes a simple and easy-to-apply method to predict the formation of new acid sites in dilute solid solutions. While the treatment is crude in most instances, the predictions agree with experimental observations. Its success points out that in most instances, electrostatic potential and balance of stoichiometry are the two most dominant factors in new acid site formation.

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References

1. G. Liu and H. H. Kung, *Surf. Sci.* **110,** 504 (1981).
2. H. H. Kung, *J. Catal.* **37,** 387 (1982).
3. K. Tanabe, T. Sumiyoshi, K. Shibata, T. Kiyoura, and J. Kitagawa, *Bull. Chem. Soc. Jpn.* **47,** 1064 (1974).
4. J. Q. Broughton and P. S. Bagus, *J. Electron Spectrosc. Relat. Phenom.* **20,** 261 (1980).
5. W. Van Gool and A. G. Piken, *J. Mater. Sci.* **4,** 95 (1969).
6. K. Sieghban, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johannson, T. Bergmark, S. E. Karlsson, I. Lundgtren, and B. Lingberg, "ESCA: Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy," Nova Acta Regiae Soc. Sci. Upsaliensis Ser. IV (1967).
7. P. H. Citrin and T. D. Thomas, *J. Chem. Phys.* **57,** 4446 (1972).
8. J. Q. Broughton and P. S. Bagus, *J. Electron Spectrosc. Relat. Phenom.* **20,** 127 (1980).
9. T. Dickinson, A. F. Povey, and P. M. A. Sherwood, *J. Chem. Soc. Faraday Trans. I* **72,** 686 (1976).
10. R. F. Stewart, M. A. Whitehead, and G. Donnay, *Amer. Mineral.* **65,** 324 (1980).
11. V. A. Gubanov, B. G. Kasimov, and E. Z. Kurmaev, *J. Phys. Chem. Solids* **36,** 861 (1975).
12. A. B. Anderson, *Chem. Phys. Lett.* **72,** 514 (1980).
13. F. Bechstedt, *Phys. Status Solidi B* **91,** 167 (1979).
14. S. W. Gaarenstroom and N. Winograd, *J. Chem. Phys.* **67,** 3500 (1977).
15. T. Yamaguchi, Y. Tanaka, and K. Tanabe, *J. Catal.* **65,** 442 (1980).
16. C. N. R. Rao, D. D. Sarma, S. Vasudevan, and M. S. Hegde, *Proc. Roy. Soc. London Ser. A* **367,** 239 (1979).
17. D. D. Sarma and C. N. R. Rao, *J. Electron Spectrosc. Relat. Phenom.* **20,** 25 (1980).
18. V. I. Nefedov, D. Gati, B. F. Dzhurinskii, N. P. Sergushin, and Ya. V. Salyn, *J. Inorg. Chem. (USSR)* **20,** 1279 (1975).
19. S. Sasaki, K. Fujino, and Y. Takeuchi, *Proc. Jpn. Acad. Ser. B* **55,** 43 (1979).
20. S. Sasaki, K. Fujino, Y. Takeuchi, and R. Sadanaga, *Acta Crystallogr. Sect. A* **36,** 904 (1980).
21. G. Vidal-Valat, J. P. Vidal, and K. Kurki-Suonio, *Acta Crystallogr. Sect. A* **34,** 594 (1978).
22. M. Morinaga and J. B. Cohen, *Acta Crystallogr. Sect. A* **32,** 387 (1976).