A MODEL CLUSTER STUDY OF THE ACID–BASE PROPERTIES OF PHOSPHATE CATALYSTS

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Summary

Various model clusters have been chosen to simulate the surfaces of phosphate catalysts (phosphoric acid, boron phosphate, aluminum phosphate and silicon phosphate). Semi-empirical CNDO/2 calculations have been performed, and the calculated electronic parameters are utilized to predict the surface acid–base characteristics of these catalysts and the effect of water adsorption. The order of acidity and basicity of these catalysts as predicted from the calculated values of HOMO and LUMO energy levels is in semi-quantitative agreement with experimental observation.

Introduction

Phosphates have been found to catalyze a variety of reactions such as isomerization, polymerization, partial oxidation and ammoxidation of olefins, dehydration and dehydrogenation of alcohols and alkylation of hydrocarbons [1]. Phosphoric acid and metal phosphates are polar catalysts possessing both acidic and basic surface properties. The existence of acid–base sites on the surface of phosphate catalysts has been probed through the use of a number of experimental procedures involving the chemisorption of gases, electron spin resonance, nuclear magnetic resonance and infrared spectroscopy of chemisorbed species, isotopic exchange, liquid-phase titrations with Hammett indicators, and the study of catalytic reactions promoted by such sites.

However, relatively little work has been reported on either the source and nature of these acid–base sites, or their dependence on the cation [2].

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However, the σ and π bonding of the orthophosphate ion has been analyzed by Urch [3] using atomic absorption spectral data. Johansen [4] has reported *ab initio* calculations on the orthophosphate ion for the purpose of comparison with other oxyanions. Hojer *et al.* [5] have compared the results from CNDO calculations on the orthophosphate ion with those found from *ab initio* calculations. The present studies have been initiated to compare acid—base sites on alumina, silica, silica—alumina and the phosphates of boron, aluminum and silicon.

Method

The results of theoretical studies of a large number of solid surfaces and chemisorbed species with a variety of computational techniques have been reported, and a number of excellent reviews are available [6, 7]. The semi-empirical CNDO/2 method has been used to perform the cluster calculation [8]. While *ab initio* techniques have a number of advantages, particularly for atoms containing a relatively small number of electrons, semi-empirical techniques involve a smaller commitment of computer time. Although values of the quantities calculated by the latter methods may differ considerably from the expected values, nevertheless evidence exists for the validity of these values on a relative basis [6, 7]. Application of the CNDO/2 method to clusters representing zeolites has recently been reported [9].

Phosphoric acid and orthophosphates of cations (T) such as boron, aluminum and silicon exist in polymorphous silica structure. In this structure both phosphorus and the cation T (where T = B, Al or Si) are tetrahedrally coordinated to four oxygen atoms. Alternate tetrahedra of PO_4 and TO_4 are bridged by oxygen atoms to form a continuous three-dimensional array.

In the present calculation, a cluster model with two tetrahedral units is chosen to simulate the surface of phosphate catalysts. The tetrahedral arrays are terminated by attaching hydrogen to the oxygen atoms, which will represent the ideal situation occurring on the surface, where surface hydroxyl groups exist due to the presence of water in the atmosphere. The bond parameters (Table 1) used in these calculations are values reported by

TABLE 1

Values of bond parameters used for the model calculations

Cluster	Bond lengths (nm)			Bond angles
	P—O	T—O[a]	O—H	all T—O—T and T—O—H[a]
P_2	0.1516	—	0.0980	109° 29'
BP	0.1540	0.1440	0.0980	109° 29'
AlP	0.1516	0.1700	0.0980	109° 29'
SiP	0.1516	0.1700	0.0980	109° 29'

[a]T = B, Al, Si.

Moffat [1]. The values of the calculated parameters, such as binding energy, position of molecular energy levels and electronic charge densities on various atoms of the cluster, are employed to provide indications of the acid–base character.

Results

Alumina, silica and phosphoric acid clusters

The clusters chosen to represent alumina (a), silica (b) and phosphoric acid (c) and the calculated charge distribution on various atoms of the cluster are shown in Fig. 1. The comparison of charge densities is shown in Table 2. It is apparent that the cations with maximum positive charge are the Lewis acidic sites, while the bridging oxygen atoms with maximum negative charge are the Lewis basic sites. The protons of the hydroxyl groups must be acting as the Bronsted acid sites.

Silica–alumina and phosphate clusters

Clusters representing silica–alumina (a), boron phosphate (b), aluminum phosphate (c) and silicon phosphate (d) and their charge densities are
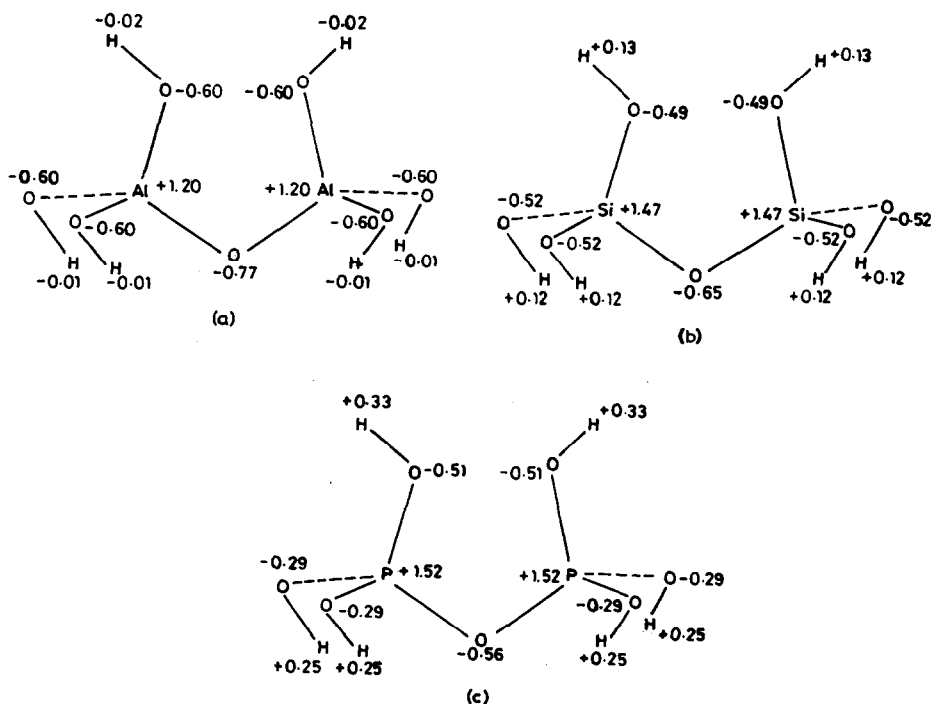
Fig. 1. Calculated charge densities for the clusters representing (a) alumina, (b) silica and (c) phosphoric acid.

TABLE 2

Electronic charges on various atoms of clusters (see Fig. 1)

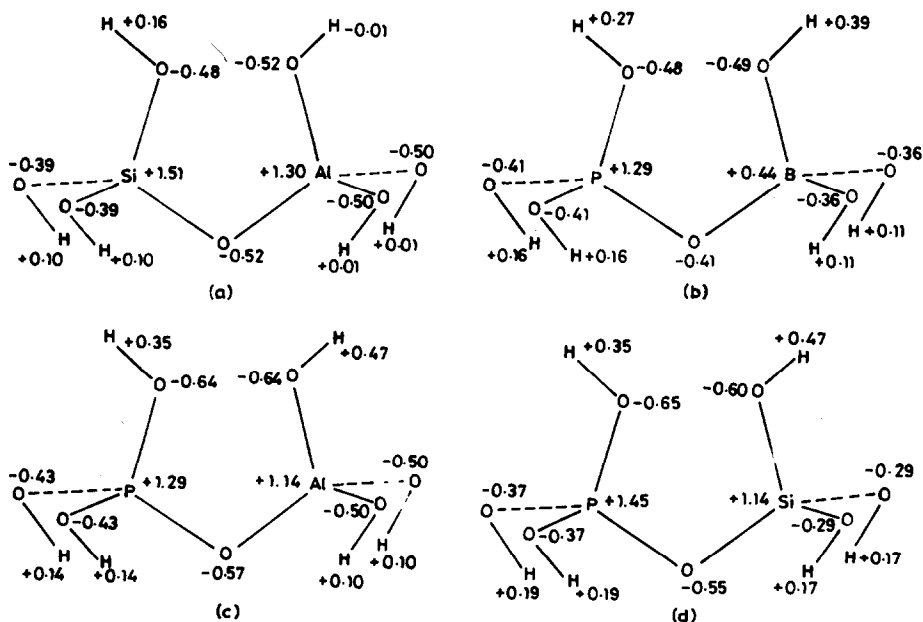| Clusters Atoms	Al_2	Si_2	P_2
cations	+1.20	+1.47	+1.52
bridging O_2 (O_b)	−0.77	−0.65	−0.56
exposed O_2 (O_e)	−0.60	−0.49	−0.51
tetrahedral O_2 (O_{td})	−0.60	−0.52	−0.29
H of O_e	−0.02	+0.13	+0.33
H of O_{td}	−0.01	+0.12	+0.25

Fig. 2. Calculated charge densities for the clusters representing (a) silica–alumina, (b) boron phosphate, (c) aluminum phosphate and (d) silicon phosphate.

shown in Fig. 2. The electronic charge densities on various atoms of these clusters are summarized in Table 3. The exposed oxygen atoms are found to have the maximum electronic density and hence function as Lewis basic sites. On the basis of the magnitude of positive charge on cations, it is inferred that the silicon atoms function as acidic sites in silica–alumina and phosphorus atoms function as the acidic site in boron phosphate, aluminum phosphate and silicon phosphate. Bronsted acidity of these catalysts is due to protons attached to exposed oxygen, since these possess maximum positive charge.

TABLE 3

Electronic charges on various atoms of clusters (Fig. 2)

Atoms[a]		Clusters	SiAl	BP	AlP	SiP
cations	(i)		+1.51	+1.29	+1.29	+1.45
	(ii)		+1.30	+0.44	+1.14	+1.14
bridging O_2 (O_b)			−0.52	−0.41	−0.57	−0.55
exposed O_2 (O_e)	(i)		−0.48	−0.48	−0.64	−0.65
	(ii)		−0.52	−0.49	−0.64	−0.60
tetrahedral O_2 (O_{td})	(i)		−0.39	−0.41	−0.43	−0.37
	(ii)		−0.50	−0.36	−0.50	−0.29
H of O_e	(i)		+0.16	+0.27	+0.35	+0.35
	(ii)		−0.01	+0.39	+0.47	+0.47
H of O_{td}	(i)		+0.10	+0.16	+0.14	+0.19
	(ii)		+0.01	+0.11	+0.10	+0.17

[a] Atom (i) refers to silicon in aluminum silicate and phosphorus in phosphates; atom (ii) refers to aluminum in aluminum silicate and the other cations T (where T = B, Al and Si) in phosphates.

Effect of water adsorption on phosphate catalysts

The surface hydroxyl groups found in these catalysts result from the dissociation of adsorbed water. In addition, water is often a product in reactions catalyzed by these solids. Since water plays a vital role in controlling the activity of these catalysts, the effect of the adsorption of water vapour on these catalysts has been studied by various experimental techniques [10]. The presence of water in small amounts has been shown to be essential for the observed catalytic activity. However, water in larger amounts alters the surface and bulk properties and eventually the activity of the catalyst [11].

The electronic interaction between water and the catalyst and the effect of water on the charge distribution of the cluster may be analyzed from the results of the present calculations. It may reasonably be assumed that the water molecule is bonded to cations through its lone pair of oxygen electrons. The energetically most favourable adsorption of water follows a path directed toward the cation and centered between the three nearest oxygen atoms forming the tetrahedral base (Figs. 3 and 4). The possibility of the adsorption of water on either the phosphorus atom or on the other cation T (where T = B, Al or Si) has been examined. The configurations considered and their charge distributions are shown in Figs. 3 and 4. While the magnitudes of the charges are somewhat altered, the acidic and basic characteristics of the catalysts remain unchanged. The charge densities on
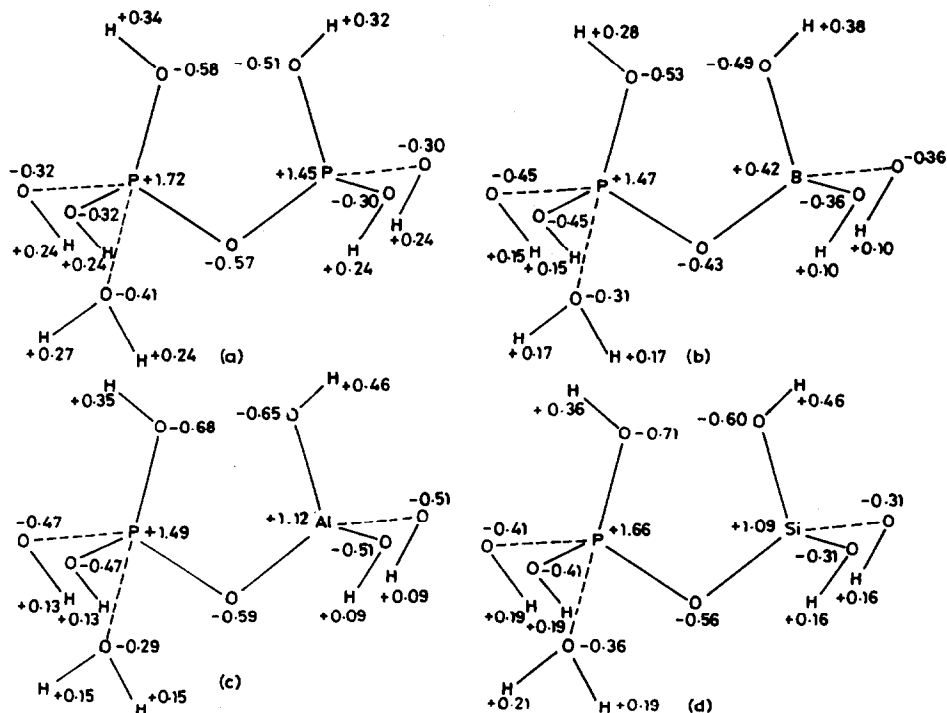
Fig. 3. Calculated charge densities for the adsorption of water on the phosphorus atom of various phosphates: (a) phosphoric acid, (b) boron phosphate, (c) aluminum phosphate and (d) silicon phosphate.

some of the atoms in the cluster before and after adsorption of water are given in Tables 4 and 5.

The energy values of the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) are indications of the electron pair-donating and electron pair-accepting capabilities of these catalysts. The Lewis acidic and basic sites may be identified by noting the atoms providing the major contributions to the HOMO and LUMO wavefunctions (Table 6).

Discussion

Alumina, silica and phosphoric acid clusters

In clusters representing alumina, silica and phosphoric acid (Fig. 1), the positive charge on the cations increased in the order Al < Si < P, which is the order of the Lewis acidity. The bridged oxygen can be seen to have the largest magnitude of negative charge of all oxygen atoms present, and must presumably be the Lewis basic site. The magnitude of the negative charge on the bridging oxygen atoms, which is indicative of the Lewis basicity, increases in the reverse order to that observed for the Lewis acidity. The values of the energies of the HOMO and LUMO of these clusters, shown in Table 6,
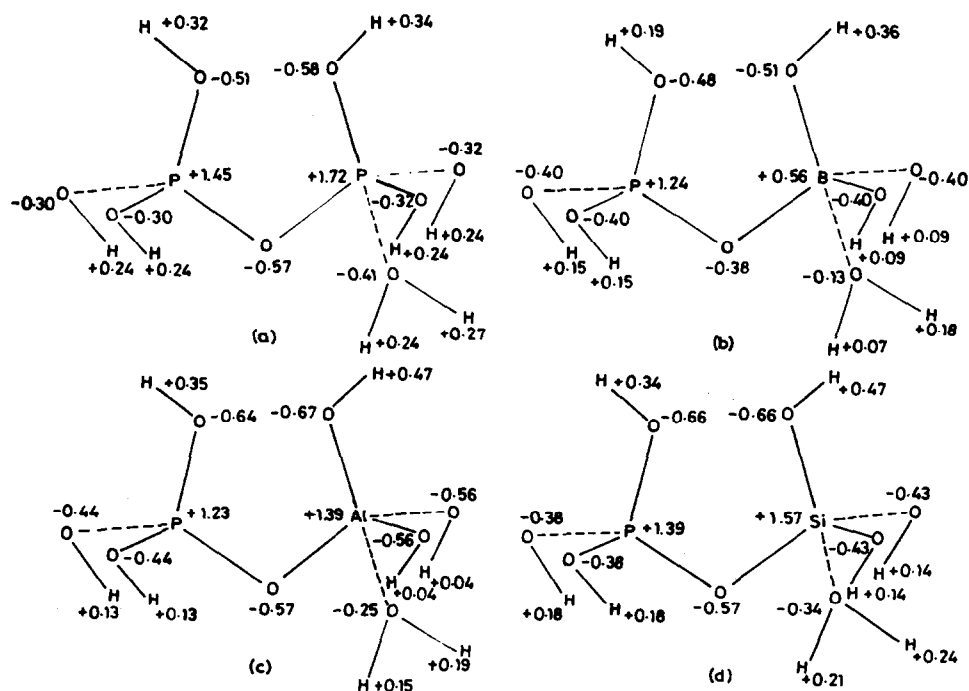
Fig. 4. Calculated charge densities for the adsorption of water on the cation T of various phosphates (T = B, Al, Si): (a) phosphoric acid, (b) boron phosphate, (c) aluminum phosphate and (d) silicon phosphate.

TABLE 4

Electronic charge on various atoms of clusters before and after adsorption of water molecule on phosphorus atom

Atoms	Clusters	PP	PB	PAl	PSi
phosphorus	before	+1.52	+1.29	+1.29	+1.45
	after	+1.72	+1.47	+1.49	+1.66
T^a	before	+1.52	+0.44	+1.14	+1.14
	after	+1.45	+0.42	+1.12	+1.09
exposed O_2 (O_e)	before	−0.51	−0.48	−0.64	−0.65
	after	−0.58	−0.53	−0.68	−0.71
tetrahedral O_2 (O_{td})	before	−0.29	−0.41	−0.43	−0.37
	after	−0.32	−0.45	−0.47	−0.41
H of O_e	before	+0.33	+0.39	+0.47	+0.47
	after	+0.32	+0.38	+0.46	+0.46
H of O_{td}	before	+0.25	+0.11	+0.10	+0.17
	after	+0.24	+0.10	+0.09	+0.16
H_2O	oxygen	−0.41	−0.31	−0.29	−0.36
	H pointing towards O_{td}	+0.27	+0.17	+0.15	+0.21
	H pointing away from O_{td}	+0.24	+0.17	+0.15	+0.19

^{a}T = B, Al, Si.

TABLE 5

Electronic charges on various atoms of clusters before and after adsorption of water molecule on the cation T^a

Atoms	Clusters	PB	PAl	PSi
phosphorus	before	+1.29	+1.29	+1.45
	after	+1.24	+1.23	+1.39
T^a	before	+0.44	+1.14	+1.14
	after	+0.56	+1.39	+1.57
exposed O_2 (O_e)	before	−0.49	−0.64	−0.60
	after	−0.51	−0.67	−0.66
tetrahedral O_2 (O_{td})	before	−0.36	−0.50	−0.29
	after	−0.40	−0.56	−0.43
H of O_e	before	+0.27	+0.35	+0.35
	after	+0.19	+0.35	+0.34
II of O_{td}	before	+0.11	+0.10	+0.17
	after	+0.09	+0.04	+0.14
H_2O	oxygen	−0.13	−0.25	−0.34
	H pointing towards O_{td}	+0.18	+0.19	+0.24
	H pointing away from O_d	+0.07	+0.15	+0.21

[a]T = B, Al, Si.

also predict the same trend. The order of Bronsted acidity as related to the charge on the hydrogen is Al < Si < P.

The results of these calculations predict that phosphoric acid is predominantly acidic, alumina is predominantly basic and silica is intermediate in acid–base characteristics. This is in accord with the well-known experimental observation that phosphoric acid catalyzes dehydration and hydrolysis reactions which require acidic sites, while reactions such as aldol condensations are promoted by alumina. Silica is found to be a mild catalyst with both acidic and basic sites [12].

Silica–alumina and various phosphate clusters

In silica–alumina, the charge density on the bridging oxygen (bonded to both Si and Al) is comparable to that on exposed oxygen (bonded to a cation and hydrogen). However, in phosphates the exposed oxygen has a higher charge density than the bridging oxygen, and the wave function of the HOMO has maximum contribution from 2s and 2p orbitals of exposed oxygen. This may be due to the larger difference in the electronegativity of the cations in various phosphates, and also due to varying P—O and T—O distances in phosphates (while in silica-alumina both Si—O and Al—O distances are the same (1.65 Å)). The polarity in the cluster, and consequently

TABLE 6

Values of Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) and the main atoms contributing to these levels

Structure	Clusters	HOMO (a.u.)	Contributing atoms[a]	LUMO (a.u.)	Contributing atoms
1(a)	AlAl	−0.002	O_b	+0.487	Al
1(b)	SiSi	−0.508	O_b	+0.020	Si
1(c)	PP	−0.903	O_e	−0.496	P
2(a)	SiAl	−0.388	O_b	−0.089	Si
2(b)	BP	−0.412	O_e of B[b] and P	−0.050	P and B
2(c)	AlP	−0.386	O_e of Al and P	−0.022	P and Al
2(d)	SiP	−0.612	O_e of Si and P	−0.268	P and Si
3(a)	PP—H_2O	−0.863	O_e of P	−0.476	P
3(b)	BP—H_2O	−0.385	O_e of B[b] and P	−0.036	P
3(c)	AlP—H_2O	−0.359	O_e of Al and P	−0.018	P and Al
3(d)	SiP—H_2O	−0.583	O_e of Si and P	−0.252	P and Si[b]
4(a)	PP—H_2O	−0.863	O_e of P	−0.476	P
4(b)	PB—H_2O	−0.381	O_e of B	−0.027	P
4(c)	PAl—H_2O	−0.368	O_e of Al	+0.007	P
4(d)	PSi—H_2O	−0.595	O_e of Si and P[b]	−0.219	P[b] and Si

[a]For notation refer to Table 2.
[b]Atoms contributing major components for the formation of MO.

the electronic charge distribution, is primarily dependent on the oxygen–metal distances and the electronegativity of the cations. The present calculations indicate that the Lewis acidity of silica–alumina is stronger than that of phosphates, while the Bronsted acidity is higher in the latter where the protons have greater positive charge. In the phosphates the order of Lewis acidic strength is BP ≈ AlP < SiP, while the order of Bronsted acidity is BP < AlP ≈ SiP and the Lewis basicity order is BP < AlP ≈ SiP.

Effect of water adsorption on phosphate catalysts

It is evident from the results of the calculations that the effect of the adsorption of water is primarily restricted to a change in the charge densities within the tetrahedron to which water becomes adsorbed (Tables 4 and 5). Since the water molecule apparently adsorbed on the cation, the latter is effectively eliminated as a Lewis acid site. In addition, the magnitude of the positive charge on the cation of the adjacent tetrahedron, as well as that of the hydrogen atoms of the substrate, is reduced. The values calculated for the overlap suggest that the hydrogen bonding between the oxygen of the water molecule and the hydrogen atoms attached to the tetrahedral oxygen atoms is relatively weak. The increase in the charge densities on the exposed oxygen atoms may account for the Lewis basicity.

Conclusions

It is evident from the present work that simple semi-empirical calculations, while no doubt in considerable error on an absolute basis, are of value in predicting the relative acid–base properties of polar solids. With the present catalysts, the cations are found to be the Lewis acid sites, the oxygen atoms are Lewis basic sites and the protons of the surface hydroxyl group are responsible for the Bronsted acidity. Small amounts of water are apparently required to generate Bronsted acidity, while water in larger quantities acts as a poison by decreasing the positive charge on the hydrogen atoms and by blocking the Lewis acid sites.

Further studies on larger clusters should facilitate the inclusion of effects due to changes in the relative amounts of cations and phosphorus on both the electron distribution and the catalytic activity. Discrimination of the acidic strength of various possible surface hydroxyl protons may then be possible.

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