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Quantum Chemical Study of Acid–Base Properties of Metal Oxides. I

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Molecular orbital calculations (CNDO/2) on cluster models have been performed to elucidate the acid–base properties of several acids and bases such as silica, metal ion-exchanged silicas, and silica–alumina. Charge densities calculated as well as highest occupied and lowest unoccupied molecular orbitals are in reasonable agreement with the trends in the acid and base strength deduced from experimental observations. The calculations confirmed that Li- or Na-exchange of a silica surface enhances the basicity and Mg ion-exchange creates strong Lewis acidity. A proton linked to an oxygen interconnecting SiO_4 and AlO_4 tetrahedra in silica–alumina is a very strong acid, while a proton of silica is weakly acidic.

INTRODUCTION

Recently, quantum chemical study of solid surface and catalysis has made significant progress (*1*). The progress seems to have been made possible by the development of physicochemical measurement of the solid surface (*2*) and the success in the synthesis of small metal clusters (*3*). However, so far most efforts have been devoted to metal catalysts, and now, although a few attempts have been already made (*4*), further investigations are necessary for metal oxide systems.

It is very important to use proper models and to choose appropriate problems, since quantum chemistry has obvious deficiencies when applied to solid catalysts. Further, the conclusions, which often are of qualitative nature, should be examined in light of reliable experimental results. We have studied from the quantum chemical viewpoint the influence of basic center on the olefin isomerization mechanism (*5*), and we have been able to rationalize the experimental results. In the present work, we focus our attention on the catalyst itself. We have attempted to describe the acid–base properties of typical metal oxides, often used in catalytic processes, i.e., silica, metal ion-exchanged silicas, and silica–alumina, by using small cluster models. In these compounds, metal–oxygen bonds have a covalent character and, therefore, small cluster models of oxides may be less deficient in the simulation of an infinite solid lattice, as compared to metal catalysts.

The acidity or basicity of catalysts is important in determining the catalytic activity and selectivity, not only in typical acid–base reactions (*6, 7*), but also in oxidation processes as well (*8*). Acid–base properties of metal ion dispersed on a silica surface have already been studied by several investigators (*9*). We recently found that in dehydrohalogenation of haloalkanes there is a good correlation between the catalyst's acid–base properties and its activity, as well as the selectivity and stereochemistry of the reaction (*10*). Silicas treated with bivalent metal ion are acidic and their catalytic activity increases with the increasing acid strength. On the other hand, in the case of alkali ion-exchanged silica, the activity increases with base strength. The steric course of the reaction also exhibits a remarkable contrast: anti elimination over basic catalysts and the syn mode over

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acidic ones in dehydrobromination of 2-bromobutane. Therefore, these silicas are good models with which to start the study.

Silica–alumina is a well-known and important catalyst. Moreover, it is expected that the quantum-chemical description of both acidic and basic properties could be extended to other mixed oxides whose acidities can be evaluated as has been demonstrated by Thomas (*11*), Tanabe *et al.* (*12*), and Seiyama *et al.* (*13*).

METHOD AND MODELS OF CALCULATION

The procedures for the molecular orbital calculation (CNDO/2) and the partition of energies into two-center terms are the same as described in the previous papers (*5*). The fundamental fragment adopted in the models for calculation is a silicic acid, where a silicon atom is located at the center of a tetrahedron of oxygen atoms. Each oxygen is saturated by a hydrogen atom. When one or two hydrogens is substituted for the $-OSi(OH)_3$ moiety, dimeric or trimeric silicic acid is produced. The geometrical data adopted are given in Table 1. Some typical models are shown in Fig. 1. Calculations with monomeric, dimeric, and trimeric (linear and triangle) silicic acid showed no substantial differences in the charge density of terminal OH group and central Si atoms. Therefore, although the models are simple, results obtained are meaningful for the purpose of the present calculation. The calculations were mainly performed on dimers. Silica–alumina was simulated by substituting one or two silicon fragment(s) for corresponding alumina one(s). To compensate the charge a proton(s) is added.

TABLE 1

The Geometry of Models

Si–O	1.65 Å
∠O–Si–O	109°
O–H	0.98 Å
∠Si–O–H	113°
O–Al	1.65 Å
∠O–Al–O	109°
O–Li[a]	1.95 Å
O–Na[a]	2.50 Å
O–Mg	2.05 Å

[a] All alkali atoms are on the symmetry line, above O_b atom.

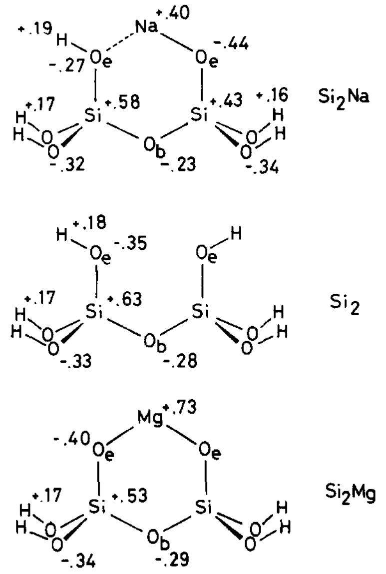


FIG. 1. Cluster models and calculated charge densities of silica (Si_2) and metal ion-exchanged silicas (Si_2M).

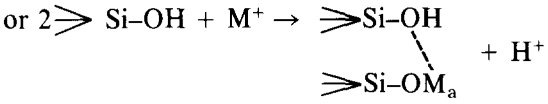
RESULTS AND DISCUSSION

Metal-Ion Exchanged Silica

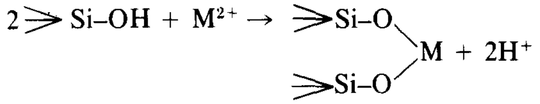
Charges gathered on atoms in silica derivatives are shown in Fig. 1 and representative data are collected in Table 2. The results for silicic acid are almost the same as reported previously (*14a*), although slightly different geometry was used. The charge density of hydrogen atom suggests that this compound is a weak protonic acid, which is in agreement with experimental observations. Considerable change was found when an alkali metal replaces a hydrogen atom.

The positions (or coordination numbers) of metal ions introduced were chosen as shown in Fig. 1 and Table 1, to a first approximation. Essential process in the ion-exchange on silica surface may be represented as given below (Ref. *10* and references therein)

$$\geqslant\text{Si–OH} + \text{M}^+ \rightarrow \geqslant\text{Si–OM} + \text{H}^+ \qquad (1a)$$



$$\text{or } 2\geqslant\text{Si–OH} + \text{M}^+ \rightarrow \begin{matrix}\geqslant\text{Si–OH}\\ \diagdown\\ \geqslant\text{Si–OM}_a\end{matrix} + \text{H}^+ \qquad (1b)$$



$$2\geqslant\text{Si–OH} + \text{M}^{2+} \rightarrow \begin{matrix}\geqslant\text{Si–O}\diagdown\\ \quad\text{M}\\ \geqslant\text{Si–O}\diagup\end{matrix} + 2\text{H}^+ \qquad (2)$$

Although the coordination number of metal ion introduced may actually be higher than above, the additional coordinations must be much weaker. In fact, the calculated charge on O_e changed by only 0.01, when Na was placed outside as in the Si_2 model (coordination number = 1). Positive charge on Na increased by about 0.1 with the decrease of coordination number from 2 to 1. Therefore, the present model is reliable as for the basicity. Even for the acidity, as far as the similar coordination models are chosen, the comparison among metal ions may be meaningful.

As shown in Fig. 1, the introduction of Na gives rise to the negative charge collected on the oxygen linked with the alkali (from −0.35 to −0.44), while the bridging oxygen (O_b) remains practically unchanged. No significant difference was found between Li and Na. In such a way the basicity of the exposed oxygen is pronounced. Charge densities on them can be compared with those calculated for NaOH and LiOH (Li, Na: +0.45 ~ +0.52, O: −0.45 ~ −0.53, depending on the M–O–H bond angle). The increased catalytic activity of alkali doped or exchanged silica was actually found in several reactions, e.g., dehydrohalogenation of haloalkanes (*10*) and aldol condensation (*15*). These activities were experimentally proved to be due to the rise in basicity.

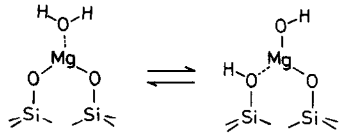
TABLE 2

Charges and O–H Bond Strength in Several Models of Solid Acids and Bases

Model[a]	Charge density			$E^b_{O_e-H}$
	Most positive hydrogen	Metal	Most negative oxygen	
Si_2	+0.18	—	−0.35	−0.723
Si_2Li	+0.19	+0.38(Li)	−0.44	−0.704
Si_2Na	+0.19	+0.40(Na)	−0.44	−0.696
Si_2Mg	+0.17	+0.73(Mg)	−0.40	—
SiAl	+0.31	+0.19(Al)	−0.36	−0.643
Si_2Al[c]	+0.30	—	−0.36	−0.646
$SiAl_2$[c]	+0.30	—	−0.36	−0.646

[a] See Fig. 1.
[b] Two-center energy (a. u.).
[c] Triangular trimer.

Remarkable is the large positive charge on Mg (+0.73), indicating strong Lewis acidity. The catalytic activity is expected to be caused by the Lewis acidity of the metal ion, in this case. The presence of two bare oxygen atoms associated with exposed Lewis acid may produce the activation of a water or similar molecules in the same way as proposed previously for Li salt (*14*).



Highest Occupied and Lowest Unoccupied Molecular Orbitals (HOMO and LUMO)

Basicity and acidity, or donor ability and electron affinity, can also be discussed in terms of the levels of HOMO and LUMO. If the HOMO levels are taken as a criterion for the donor ability, the basicity of silica derivatives should increase in the following order (HOMO levels calculated are given in parentheses in atomic unit):

$$Si_2(-0.561) < Si_2Mg(-0.516) < Si_2Li(-0.477) \lesssim Si_2Na(-0.457)$$

This order is parallel to the ionization potentials of metals or hydrogen involved in the models. The charge density on an oxygen bonded directly to the metal increases in essentially the same manner, as described above. The trend is also in reasonable agreement with the optical scale of basicity, in which sodium glass is more basic than lithium glass (*16*).

Those HOMOs of Si_2M mainly comprises p_x orbitals of O_e's which are not directly bonded to a proton (x axis is taken perpendicular to the Si–O–Si plane, and y and z axes are in the Si–Si and O_b–M directions, respectively). Just below the HOMO, there are MOs composed mainly of p_y and p_z of the same O_e's. Therefore, three MOs which are concentrated on O_e and directed away from surface may be able to interact with a reactant and exhibit basic character. The basic character of these HOMOs has previously been discussed (*14b*).

Lewis acidity can be similarly estimated. The LUMO levels exhibit the following order of increasing electron affinity for silica derivatives and this is again in agreement with that expected from the charge density.

$$Si_2(0.211) \gg Si_2Li(0.11) > Si_2Na(-0.014) \gg Si_2Mg(-0.069)$$

where the LUMO levels are given in parentheses in atomic unit.

The LUMOs of Si_2M are concentrated on metal ions introduced. This unoccupied orbital naturally interacts with a reactant as an acid. In the case of Si_2, the LUMO mainly comprises atomic orbitals of silicon and should not be exposed on surface, so that this orbital hardly interacts with a reactant.

Both the rate and the stereochemistry of dehydrobromination of 2-bromobutane and 2,3-dibromobutane over metal ion-exchanged silica gel reported previously (*10*) apparently reflect the trend in the acid–base properties expected from the present calculation. These properties have also been confirmed by experiments. Bivalent cation-exchanged silica (Mg, Ca, Ni, etc.) were acidic and catalyzed the reaction via an alkyl cation intermediate. On the other hand, for alkali-treated silicas basic sites seem to control the rate and the stereochemistry.

Silica–Alumina

In the models of silica–alumina, Al atoms (one or two) were substituted for Si atom(s) in the corresponding oligomer of silicic acid. To make the model neutral, the appropriate number of hydrogen atom(s) or alkali atom(s) were added. The most stable structure was the one in which hydrogen atom(s) or alkali atom(s) are located just below the bridging oxygen (O_b), as shown in Fig. 2. The charge distributions for the silica–alumina models are also given there and in Table 2. The positive charge carried by the hydrogen atom (H_b) is large and is comparable with that in a hydronium ion (H_3O^+: +0.32 by CNDO/2), showing strong protonic acidity. Similar results have been reported by Mikheikin *et al.* (*4b*). This charge is almost independent of the shape of the model (linear or triangular in the trimer) and of the Si/Al ratio (2/1 or 1/2). Moreover, it was noted that the acidity of this proton was very sensitive to the perturbation imposed on the model. For example, when F replaces OH, the positive charge on this proton increases ("inductive effect"), while the other protons are almost un-

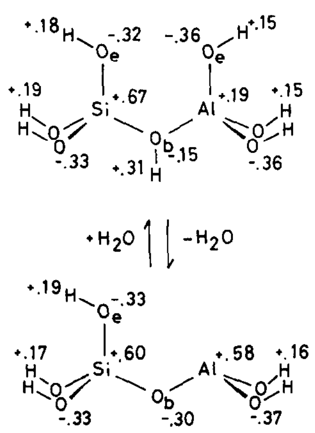


FIG. 2. Charge densities calculated for models of silica–alumina (SiAl) and its dehydrated form.

changed. This effect may explain the fact that in our laboratory the selective poisoning of either the Lewis sites of silica–alumina or the Brönsted sites was found to diminish completely the catalytic activity (*17*). Pyridine (a poison) adsorbed on Lewis site adjacent to a protonic site weakens the protonic acid-strength by the "inductive effect" (*17*) so as to make the protonic site catalytically inactive. This phenomenon was also confirmed by MO calculation (*18*).

The intertetrahedron bonds, Si–O_b and Al–O_b, are also affected by the composition of the model: the incorporation of any foreign atom into the frame of silica acts as the destabilizing factor. For example, a great destabilization of the silicon–oxygen bond, as judged from the two-center energies, was observed when aluminum replaced silicon. Li addition to bridging oxygen (O_b) partially restabilized this bond. However, regardless of the presence of alkali, the Si–O_b bond was always more stable than the Al–O_b bond, suggesting that the fission of the Al–O_b bond is easier. In fact, dealumination of aluminosilicate often occurs, accompanied or unaccompanied by the collapse of the structure. The introduction of alkali into the silica–alumina frame possibly makes the system more resistant to the breakdown of the Al–O_b bond.

pK_a and Charge Density

The charge density on a hydrogen atom is often well correlated with the pK_a value. Figure 3 shows the relationship between the charge of a hydrogen atom calculated by CNDO/2 and the pK_a value, for several compounds. Although the relevancy was found for only a limited number of compounds and the pK_a values were measured in aqueous solutions, the models discussed above fall within a reasonable range of the pK_a and the tendency seems to be meaningful. According to the correlation in Fig. 3, protons in silica–alumina could be considered strong acids (pK_a ~ −15), while the silica and alkali ion-exchanged silicas were very weak or moderately weak acids (pK_a ~ 10). The bond strength of the O–H bond (two-center energy) also follows the order expected from the charge (see Table 2). The greater the positive charge on the hydrogen, the weaker the O–H bond and the stronger the acid strength.

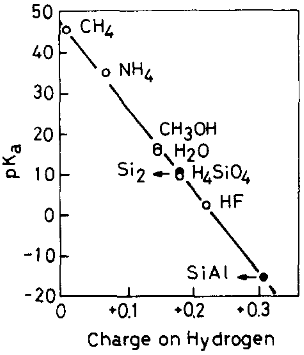


FIG. 3. Correlation between pK_a and calculated charge density on a hydrogen atom. Charge densities of models calculated are shown by solid circles on the linear plot.

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