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Quantum Chemical Study on Acidity of Silica–Alumina Catalysts

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Acidities of silica–alumina systems are studied by the CNDO/2-FA method. A hypothetical atom is suggested for saturating the covalence of the outermost oxygen atoms of the models. It turns out that the hydrogen charge Q_H can serve as a rough measure of Brønsted acidity of silica–alumina systems, whereas the LUMO energy as a measure of Lewis acidity can only be used for comparing the generally accepted Lewis sites of the same kind of atom in the same valence state and with the same coordinate number. Using the Q_H data, the strong Brønsted site is assigned to the structure Al–OH–Si, and the moderate one is assigned to the Si–OH in connection with a four-coordinate aluminum. The Q_H data do not support the view that Si–OH in connection with a three-coordinate aluminum or Al–OH is the strong Brønsted site.

INTRODUCTION

Research on the acidity of catalysts is important to the development of the theory of catalysis. Although surface acidity has long been studied through various experimental methods, the development of theoretical research still lags behind. Since solid catalysts are macromolecules, the application of quantum chemical calculations is severely restricted. Use of the *ab initio* method is usually considered to be too expensive, thus the semiempirical SCF-MO method such as CNDO/2 is applied preferably (*1–4*).

It is important to choose suitable cluster models for quantum chemical calculations in order to obtain meaningful data for illustrating the behavior and structure of acid sites. This problem, which seems to be seldom discussed in the literature, has been taken care of in this work and will be discussed in the next section.

Furthermore, discussions of the structure of acid sites appear to be controversial (*1, 5–8*). Further study based on experiment and on quantum chemical calculations is necessary.

The quantum chemical method used in this work is the first approximation of CNDO/2 (CNDO/2-FA) (*9*). The *sp* basis set for the second row elements (*10*) is used instead of the *spd* one owing to the existence of the convergence problem in using the latter (*2*). Calculations were carried out using a program written by one of the authors (C.Z.).

MODELS AND CHARGE DISTRIBUTION OF SILICA–ALUMINA FRAMEWORK

Since charge distribution plays an important part in explaining the strength of Brønsted acidity, the models should be chosen to give reasonable results of the charge distribution.

The framework of the models consists of tetrahedrons of SiO_4 and AlO_4 with Si–O bond length of 1.60 Å and the Al–O one of 1.75 Å. The Si–O–Si and Al–O–Si angles are chosen to be 141.06°, thus making one bond parallel to another (bonds 2–1 and 6–7 in Fig. 1). In most real systems, two such bonds are not parallel but separated by a small angle, hence the Si–O–Si angle is greater than 141.06°. However, calculation shows that the charge distributions are affected only in the third decimal place even though the angle is increased to 150°; thus the difference is not a matter of importance.

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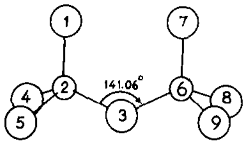

FIG. 1. Choice of the Si–O–Si angle.

In order to saturate the covalence of the outermost oxygen atoms, a customary approach (*1–4*) is to link a hydrogen atom to each of them. However, such an approach cannot give reasonable results, as shown below. If the catalyst consists purely of SiO_4 tetrahedrons, the positive charge of a silicon atom ought to be equal to the negative charge of two oxygen atoms in order to keep the system neutral. However, the charges calculated on the model of Fig. 2 (Table 1) show that the absolute value of the charge of two oxygen atoms is $0.59 + 0.57 = 1.16$, far from that of a silicon atom of 1.69. The results provided by different authors also show a similar discrepancy, as shown in Table 1. This discrepancy is due to the effect of the hydrogen atoms. In real systems, most of the atoms linked to the oxygen atoms are silicon, rather than hydrogen as in the model.

In order to avoid the direct influence of the hydrogen atoms, the four hydrogen atoms of the $Si(OH)_4$ model are replaced by $Si(OH)_3$. A comparison between the data after the replacement and those before is shown on the left half of Table 2. The central silicon atom has a charge of 1.63, while two oxygen atoms linked to it have a charge of $-0.75 + (-0.74) = -1.49$. A great improvement is achieved, but the discrepancy still exists. Furthermore, the outer oxygen atoms have a charge far different from that of the inner ones. Apparently, such an approach does not provide reasonable charge distributions for simulating those of the real systems.

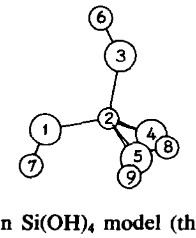

FIG. 2. Chosen $Si(OH)_4$ model (the plane 7–1–2–3–6 is perpendicular to the plane 9–5–2–4–8).

TABLE 1

Charge Distribution of Models of SiO_4 Tetrahedron Connected with Hydrogen

	This work	Ref. (*4*)	Ref. (*2*)	Ref. (*1*)
Si	1.69	2.77	1.59	0.63
O	−0.59, −0.57	−0.99, −1.04	−0.76, −0.56	−0.35, −0.33
H	0.15, 0.16	0.31	0.13, 0.14	0.17, 0.18

We hereby present a method to reduce the discrepancy. The SiO_4 and AlO_4 tetrahedrons are saturated by hypothetical atoms, symbolized by L, whose CNDO/2 parameters are the same as those of hydrogen except for the electronegativity. The Si–O–L and Al–O–L angles are chosen to be 141.06° as if they are the Si–O–Si and Al–O–Si ones. The O–L bond length, 1.03 Å, is chosen to minimize the energy. The electronegativity of L, 0.096, is chosen to make the algebraic sum of the charge of two oxygen atoms and that of the silicon atom in $Si(OL)_4$ vanish, as shown in Table 3.

In order to verify the rationality of such an approach, the charge distribution is calculated after replacing two L of $Si(OL)_4$ by $Si(OL)_3$ and the results are compared with those of $Si(OL)_4$, as shown on the right of Table 2. We can see that the charges of silicon and oxygen remain practically constant. we can thus accept a value of 1.58 for the charge of a silicon atom in silica systems, and a value of −0.79 for that of oxygen. On the other hand, we can see from the left half of Table 2 that either from $Si(OH)_4$ to $Si[OSi(OH)_3]_4$ or from the outer part to the inner part in $Si[OSi(OH)_3]_4$ the charges of silicon and oxygen are likely to tend toward their limits of 1.58 and −0.79, respectively. Therefore, we believe that the model with the hypothetical atoms can well simulate the systems of a great number of silicon–oxygen tetrahedrons. In other

TABLE 2

Charge Distribution of Models of Silicon–Oxygen Framework

	Groups attached to silicon–oxygen tetrahedron			
	H	$Si(OH)_3$	L	Two L, two $Si(OL)_3$
Central Si	1.69	1.63	1.58	1.58
Central O	−0.59, −0.57	−0.75, −0.74	−0.80, −0.78	−0.79, −0.76
External Si	—	1.66, 1.67	—	1.57, 1.58
External O	—	−0.59, −0.58	—	−0.80, −0.79
H or L	0.15, 0.16	0.15	0.39, 0.40	0.39, 0.40

words, the hypothetical atom L can be used fairly well in place of the silicon atom and the outer part of the silica framework.

When the hypothetical atom L is used in the systems with AlO_4 as well as SiO_4 tetrahedrons, some discrepancy is inevitably present because L is nevertheless not exactly the same as the silicon atom and the outer part. We must examine how serious the discrepancy will be. The results of some typical examples are listed in Table 4. We can see that the charge of the oxygen atom between Al and L is obviously more negative than that between Al and Si. This fact tells us that certain errors will be caused by L. We can also see that such errors will quickly fade away as the distance from L increases. Thus, the charge of the oxygen atom between Al and Si in $Al[OSi(OL)_3]_4^-$ is −0.63, while those between Al and L are $-0.80 \sim -0.83$; the difference between them is as great as $0.17 \sim 0.20$, but the charge of Al in $Al(OL)_4^-$ is less than that in $Al[OSi(OL)_3]_4^-$ by only 0.08. In the structure Al–O–L, the aluminum atom is much less affected by L than the oxygen atom. Consequently, the charge distribution is believed to be reasonable, except on the atoms near the hypothetical ones.

TABLE 3

Choice of Electronegativity of the Hypothetical Atom L

Electronegativity	Charge of SiO_2
2	0.1313
0	−0.00677
0.09269	−0.000239
Interpolated 0.096	0

The effect of L on charge distribution can be understood in another way. If the charge of the atoms were equal to their oxidation number, the aluminum–oxygen tetrahedron would have a net charge of −1 (half the charge of the four oxygen plus that of the aluminum). However, the charge of the AlO_4 tetrahedron in $Al[OSi(OL)_3]_4^-$ is only $1.13 - 0.63 \times 2 = -0.13$. In other words, the tetrahedron keeps only 13% of the negative charge, while 87% has been spread out. In $Al(OL)_4^-$, L is used to replace the Si and its outer part. It results in much less capacity for the negative charge, so that the Al and O in $Al(OL)_4^-$ will abnormally have a more negative charge than in the greater model.

On the other hand, the silicon–oxygen tetrahedron deficient in an oxygen atom has an apparent charge of +1, which will also be spread out. A few results are listed in Table 5, in which Si* stands for a three-coordinate silicon atom. The net charge of a deficient silicon–oxygen tetrahedron calculated from the data of $Si^*[OSi(OL)_3]_3^+$ is $1.47 + (-0.70) \times 3/2 = 0.42$, which shows that the positive charge is spread out to a lesser extent than the negative one of the aluminum–oxygen tetrahedron. As a result, the charge of the oxygen between Si* and L is different from that between Si* and Si by only 0.08, which is much less than that of

TABLE 4

Effect of Aluminum–Oxygen Tetrahedron on Charge Distribution

	$Al(OL)_4^-$	$Al(OL)_3Si(OL)_3^-$	$Al[OSi(OL)_3]_4^-$
Al	1.05	1.06	1.13
O, between Al and L	−0.81, −0.83	−0.80, −0.82	—
O, between Al and Si	—	−0.66	−0.63
O, between Si and L	—	−0.81, −0.83	−0.80, −0.83
Si	—	1.47	1.47
L, attached to AlO	0.31	0.31	—
L, attached to SiO	—	0.36, 0.37	0.36

0.17 ~ 0.20 in the case of Al–O–L. Nevertheless, for a model containing an apparently charged part such as aluminum–oxygen tetrahedron or deficient silicon–oxygen one, the charge of the atom near L is more or less abnormal. This fact should be borne in mind in applying such a method.

The central part of $Al[OSi(OL)_3]_4^-$ and $Si^*[OSi(OL)_3]_3^+$ is believed to be practically unaffected by the hypothetical atom L. The data of charges from them are summarized in Table 6 together with those mentioned previously.

THE QUANTUM CHEMICAL MEASURE OF ACIDITY

The surface acidity of silica–alumina catalysts is usually divided into two kinds, the Brønsted (B) one and the Lewis (L) one.

TABLE 5

Effect of Three-Coordinate Silicon (Si*) on Charge Distribution

	$Si^*(OL)_2OSi(OL)_3^+$	$Si^*[OSi(OL)_3]_3^+$
Si*	1.44	1.47
Si	1.59	1.59, 1.60
O, between Si* and Si	−0.74	−0.70
O, between Si* and L	−0.62	—
O, between Si and L	−0.72, −0.79	−0.74, −0.80
L, attached to SiO	0.41, 0.42	0.41
L, attached to Si*O	0.47	—

The B-Acidity

The charge of the acidic hydrogen atom (Q_H) has been adopted as a quantum chemical measure of B-acidity by a number of chemists. For example, Grabowski *et al.* (*1*) plotted the p*K* of some molecules against Q_H calculated by the CNDO/2 method and showed very good linearity. Lygin and Seregina (*4*) provided data of some oxy-acids to show the monotonic change of p*K* with respect to CNDO/2 Q_H, but the relation was found to be far apart from linearity. They also reported that the monatomic energy contribution (E_H) of the acidic hydrogen was a monotonical function of p*K*, and the diatomic one of the hydroxyl group (E_{OH}) was roughly so. Therefore, E_H and E_{OH} as well as Q_H can be considered to be quantum chemical measures of B-acidity.

In our opinion, however, either precise linearity or strict monotonicity of the relation between p*K* and Q_H is fortuitous only for the few data cited by those authors. We have arbitrarily chosen several molecules to perform the CNDO/2-FA calculations.

TABLE 6

Charge Distribution of Silica–Alumina Systems

Si, not adjacent to Al	1.58	O(Si–O–Si)	−0.79
Si, adjacent to Al	1.47	O(Al–O–Si)	−0.63
Si* (three-coordinate)	1.47	O(Si*–O–Si)	−0.70
Al	1.13		

TABLE 7

Results of Geometry Optimization by CNDO/2-FA

	Q_H	E_{AH}[a]
C_2H_6	-0.005	-0.740
C_2H_4	0.008	-0.748
CH_4	0.012	-0.764
NH_3	0.071	-0.753
H_2O	0.136	-0.758
HCl	0.141	-0.486
CH_3OH	0.157	-0.732
HNO_2	0.212	-0.713
HCOOH	0.230	-0.739
HF	0.245	-0.756
HNO_3	0.263	-0.731

[a] A is the atom in connection with the acidic hydrogen.

The geometry of these molecules has been fully optimized to the minimum of the total energy in order to avoid the influence of the arbitrariness of the geometry. The results are listed in Table 7. The p*K* (*11*, *12*) of those molecules is plotted against Q_H (Fig. 3). We can see the correlation, as expected, is not very good.

Nevertheless, we still believe that the Q_H can serve as a measure of B-acidity with some restrictions. The reasons are as follows:

First, the trend of the data in Fig. 3 except that for HCl is roughly linear. The correlation coefficient is 0.989.

Second, as shown later, the experimental observations of surface acidity of silica–alumina systems can be explained fairly well by the Q_H as a measure of B-acidity.

Of course, the Q_H is not the whole story of Brønsted acidity. The problem can be understood as follows.

The strength of B-acidity inherently relates to the deprotonation energy, which depends obviously on E_H of the acidic hydrogen atom. The higher the E_H, the less the deprotonation energy, and the stronger the acid. It is well known that there is a simple relation between E_H and Q_H in CNDO/2:

$$E_H = (1 - Q_H)(-X_H - \tfrac{1}{2}\gamma_{HH}) + \tfrac{1}{4}(1 - Q_H)^2\gamma_{HH},$$

where $X_H = 7.1761$ eV = 0.26373 a.u. is the electronegativity of hydrogen; $\gamma_{HH} = 0.75$ a.u. is the electron repulsion in the 1*s* orbital of hydrogen. Therefore, using Q_H as a measure of Brønsted acidity is just the same as using E_H. However, the deprotonation energy depends not only on E_H, but also on the diatomic energy contribution E_{AH}, where A is the atom in connection with the acidic hydrogen. The less the magnitude of E_{AH}, the weaker the A–H bond, and the stronger the acid. Obviously, using Q_H as a measure of B-acidity means neglecting the effect of E_{AH}. If so, discrepancy is inevitable when E_{AH} is not a constant. HCl, which is too low in Fig. 3, is too low in $-E_{AH}$ (Table 7). The E_{AH} of the remaining molecules in Fig. 3 are almost the same, so that the Q_H or E_H serves as a rough measure for their acidity.

It is not accidental that $-E_{AH}$ of HCl is extraordinarily low. This fact can be attributed to the large size and the great polarizability of the chlorine atom. The acidity of hydrogen halide, decreasing in the order HI > HBr > HCl > HF, depends mainly on the size and the polarizability. On the other hand, the electronegativity of the halogen, which leads to the reverse order of Q_H, is not important to the acidity.

In silica–alumina catalysts, the atom A in connection with the acidic hydrogen is ex-

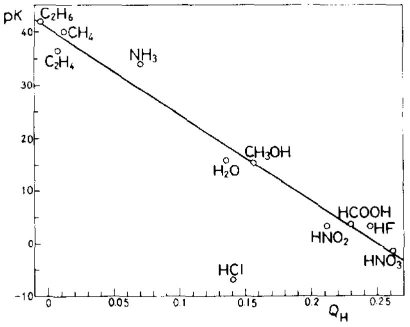

FIG. 3. p*K* correlated with Q_H.

TABLE 8

Results for Models with Four-Coordinate Silicon and Aluminum

Symbol	Remarks	Site	Q_H	E_{OH}
Si	$HOSi(OL)_3$, Fig. 4		0.111	−0.773
Si_2	Condensed from two Si model, Fig. 4		0.110	−0.772
SiLi	Li substituting for an L of Si		0.107	−0.770
SiNa	Na substituting for an L of Si		0.086	−0.761
Si_2Mg	Mg substituting for two Ls of Si_2		0.115	−0.773
SiF	F substituting for an OL of Si		0.127	−0.777
SiF_2	F substituting for an OL of SiF		0.139	−0.775
SiF_3	F substituting for an OL of SiF_2		0.158	−0.776
SiCl	Cl substituting for an OL of Si		0.121	−0.774
SiP	$PO(OL)_2$ substituting for an L of Si		0.115	−0.773
Al	$HO_eAl(OL)_2O_bHL$, Fig. 4	O_e	0.065	−0.762
		O_b	0.237	−0.770
SiAl	Si condensed with Al, Fig. 4	SiO_e	0.139	−0.776
		AlO_e	0.063	−0.763
		O_b	0.251	−0.769
AlF	F substituting for an OL of Al	O_e	0.098	−0.769
		O_b	0.253	−0.772
AlCl	Cl substituting for an OL of Al	O_e	0.072	−0.764
		O_b	0.246	−0.770

clusively oxygen, so the differences in size and in polarizability of atom A are absent. We can see that the E_{AH} (i.e., E_{OH}) of various models in Table 8 stays nearly constant. Consequently, it will be good enough to choose Q_H as a quantum chemical measure of the B-acidity for silica–alumina catalysts.

Furthermore, we cannot say that the B-acidity depends only on E_H and E_{AH}. Solvent and entropy factors will affect the pK value to a substantial extent. Another important factor is the so-called reorganizational energy. When the proton is split off, the charge and the bonds will be reorganized to attain the lowest energy, and such a lowering of energy (i.e., the reorganizational energy) will make a contribution to the acidity. The catalyst is a macromolecule, in which there is greater room for reorganization than in a small molecule. As a result, its acidity will be stronger than expected. For example, the Q_H of H_4SiO_4 (Table 1) is 0.16, corresponding to pK = 15 at the line in Fig. 3, while the experimental pK is 9.66 (*12*), which is under the line by about 5 ~ 6 pK units.

We can see in Fig. 3 that a variation of Q_H of 0.01 corresponds to a variation of pK of ca. 1.6. The results of calculation without geometry optimization show deviation of charges in the second decimal place and give a much more random plot in Fig. 3. Therefore, geometry optimization is important. In our calculation on the models of silica–alumina systems, the geometrical parameters related directly to the Q_H data are optimized.

The L-Acidity

The strength of L-acid cannot be measured by a single experimental value. The concept that the lower the lowest unoccupied molecular orbital (LUMO), the stronger the L-acid, has appeared in research on silica–alumina catalysts (*1*). For example, according to their CNDO/2 LUMO data, Grabowski *et al.* (*1*) suggested that the L-acidity of silica with metal ions decreases in the order $Mg^{2+} > Na^+ >$

$Li^+ > H^+$. Our results are in agreement with them, i.e., the LUMO energies are −0.0067 a.u. for the model Si_2Mg (Table 8), 0.0219 for the model SiNa, 0.0495 for the model SiLi, and 0.185 for the model Si; the LUMO coefficient concentrates on the metal atom for the former three models. However, such a measure of L-acidity will encounter severe contradictions. For example, the LUMO energies of the models of silica with metal ions are much lower than those of the models containing three-coordinate aluminum (models SiAl* and Al*, Table 9). It can hardly be accepted that the alkali metal ions are more acidic than the three-coordinate aluminum, for the latter is a generally accepted strong L-acid, whereas the former are not. Furthermore, Na^+ has been found to be a catalyst poison of the L-acid as well as the B-acid of silica–alumina. Thus, Bremer *et al.* (*13*) carried out an extensive study of the poisoning effect of sodium and pointed out that as sodium is added to silica–alumina in increasing amounts, the strongest B-acids are poisoned first, then the L- and remaining B-acids, and finally the weakly acidic OH groups. In our opinion, the LUMO can serve as a suitable measure of L-acidity only at the generally accepted Lewis sites of the same kind of atom in the same valence state and with the same coordination number.

RESULTS FOR VARIOUS MODELS AND DISCUSSION

As mentioned above, neglecting geometry optimization will produce considerable influence on the results. Accordingly, the geometrical parameters directly related to acidity are locally optimized by using simple models and the optimized parameters are used in various models in order to make a comparison of the results of silica–alumina systems with the data in Fig. 3, which are obtained by geometry optimization. The optimized parameters are 1.03 Å for O–H bond length, 131° for the Si–O–H angle, and 135° for the Al–O–H angle. Other bond lengths and angles are chosen by referring to experimental data or geometry optimization.

TABLE 9

Results for Models with Three-Coordinate Aluminum

Symbol	Remarks	LUMO energy	Q_H	E_{OH}
SiAl*	$HOSi(OL)_2OAl(OL)_2$	0.083	0.046	−0.745
Al*	$HOAl(OL)_2$	0.094	0.084	−0.764
Al*F	F substituting for an OL of Al*	−0.020	0.128	−0.771
Al*Cl	Cl substituting for an OL of Al*	0.011	0.101	−0.765

The results for various models of silica–alumina catalyst are listed in Tables 8 and 9. As in the cases of AlO_4 tetrahedron and three-coordinate silicon mentioned previously, charged models will lead to discrepancy because of the difficulty of spreading out the charge. The models are thus limited to neutral ones.

The aluminum–oxygen tetrahedron has an apparent charge of −1. If there is no metal ion, a proton should be added to maintain neutrality. Two models have been calculated to find the suitable position of the proton: (i) a proton is placed on the external bisector of the angle $Al–O_b–L$ of $Al(OH)(OL)_3$, where O_b denotes the bridged oxygen, and the bond length of $O_b–H$ is optimized to the minimum of the total energy; (ii) a proton is placed on the line with identical distances to the three oxygens of OL of $Al(OH)(OL)_3$, and the distance between Al and the proton is optimized. The total energies for the two models are −77.33 and −76.98 a.u., respectively, showing that the former is much more stable than the latter. As a result, the extra proton is believed to be attached to one bridged oxygen but not to three. The optimized $O_b–H$ length is 1.037 Å, which has been adopted for the models in Table 8.

The charge distributions of a few models are shown in Fig. 4. We can see that the charge distribution of the model Si is similar to that of Si_2. The smaller models can thus be used instead of the larger ones for

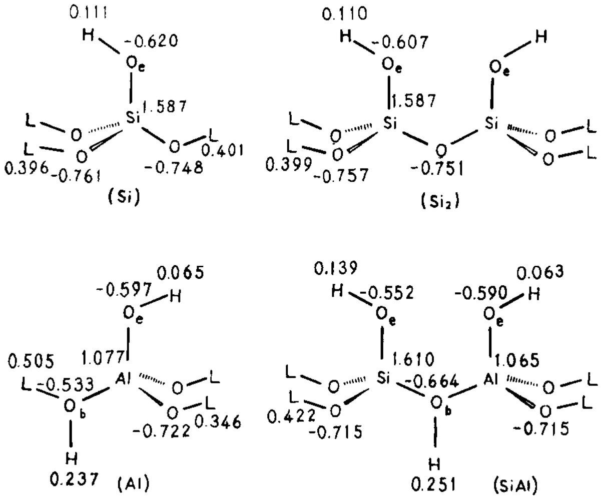

FIG. 4. Charge distributions of some models.

describing the catalysts. The charge of O_b in the model Al is obviously different from that in SiAl, as mentioned previously, whereas the charges of H attached to O_b have little difference. Therefore, the models of a single aluminum–oxygen tetrahedron can be used for some comparisons.

A few aspects are discussed in the following paragraphs.

Silica and Silica–Alumina

The structure of the acid sites of various strength has not yet been assigned reliably by using experimental data. Quantum chemical methods may provide some information for reference.

The hydrogen charge on O_bH, ca. 0.25, being by far the greatest in Fig. 4 and in Table 8, can be assigned to the above-mentioned "strongest B-acids" suggested by Bremer *et al.* (*13*). If we assume the pK of silica–alumina to be the value under the line of Fig. 3 by 5 ~ 6 pK units, the charge 0.25 will correspond to a pK of about $-5 \sim -6$. According to Rouxhet and Sempels (*14*), the pK of the strong acid sites on silica–alumina is $-4 \sim -8$, which is in agreement with that corresponding to the O_bH. However, Take *et al.* (*15*) employed indicators with p$K = -10.5$ and -12.8 to measure the surface acidity and found that the acid sites on silica–alumina had an acid strength corresponding to an H_0 between -10.5 and -12.8 or even stronger. The structure of such extraordinary strong acid sites remains to be studied further.

Pure silica gel is inactive for the reactions demanding acid catalysis, but can be activated by a small amount of aluminum. Thus, West *et al.* (*16*) found that addition of 0.01% Al to silica gel resulted in a 10,000-fold increase in the rate of hexene-1 isomerization at 100°C over pure silica gel. The models Si and Si_2 in Fig. 4 for simulating silica gel show their Q_H value to be 0.11, corresponding to an acidity less than H_4SiO_4 and to the acid catalytically inactive SiOH sites. The SiOH groups of the model Si and Si_2 also correspond to the SiOH sites on silica–alumina far apart from the aluminum atoms and can be assigned to the weakly acidic OH groups suggested by Bremer *et al.* The Q_H value of the AlOH group of the model SiAl, being 0.063 ~ 0.068, corresponds to an even lower acidity. The SiOH near a four-coordinate Al has a Q_H of 0.139, which is substantially stronger than 0.11 of the SiOH of the models Si and Si_2, and may correspond to a moderate acidity in agreement with the "remaining B-acid" suggested by Bremer *et al.*

Védrine *et al.* (*5, 6*) studied HZSM-5 zeolite with ir spectroscopy. They found two bands at 3605 and 3720 cm^{-1} and a band of low intensity at 3665 cm^{-1}. The 3605 cm^{-1} band, which corresponds to strong acid sites and whose intensity decreases with the increase of Si/Al ratio, was assigned to Al–OH–Si, which is in agreement with Grabowski *et al.* (*1*). Our assignment for the strongest B-acids is also in agreement with them. Guo *et al.* (*7*) also found a strong acidic band at 3608 cm^{-1} assigned to Al–OH, and two bands at 3668 and 3720 cm^{-1} assigned to Al–OH–Si and Si–OH, respectively. The Q_H of Al–OH in Table 8 is very small and in disagreement with the strong acidity assigned by Guo *et al.* As pointed out in a previous section, the negative charge of an AlO_4 tetrahedron will spread out. As a result, the charge of the hydrogen atom linking directly to it will certainly decrease, and such a hydrogen atom cannot be a strong acid site.

Hirschler (*8*) suggested that the Si–OH attached to a three-coordinate aluminum was the strong acid. However, the Q_H in our SiAl* model is only 0.046, so that Hirschler's suggestion cannot be accepted.

The Effect of Other Elements

Experiments show that the acidity can be elevated by addition of nonmetallic elements such as F, Cl, B, and P (*17*).

The data in Table 8 show that addition of F, Cl, or P increases the Q_H of Si–OH and O_bH, especially in the case of fluorine. Such data tell us that F, Cl, and P will elevate the acidity of silica–alumina systems, and fluorine will have the strongest effect. However, the cracking activity and the amount of acids with $pK < -5.6$ of halided silica gel decrease in the order Cl > Br > I > F, as reported by Taniguchi *et al.* (*18*). This fact does not support the prediction that F is more efficient than Cl in elevating B-acidity. On the other hand, fluorine is a stronger promoter of cracking activity of alumina (*17*). Tanaka and Ogasawara (*19*) pointed out that the chlorided alumina had a ratio of Brønsted and Lewis acid site concentrations of about 0.3, so the fluoride may have a stronger effect on the L-acid than the chloride. The LUMO energies listed in Table 9 show that F and Cl do elevate the L-acidity and F is more efficient than Cl. Nevertheless, the effect of halide on both Brønsted and Lewis acidity remains to be studied further by experiment as well as by quantum chemical calculation.

As for metallic atoms, a few models are far from sufficient for illustrating all the complicated effects on the acidity of silica–alumina systems. In this work, calculations were done on only three models, i.e., SiNa, SiLi, and Si_2Mg, for preliminary examination. The poisoning effect of Na^+ is shown by the much lower Q_H in SiNa than in the model Si (Table 8).

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