Short communication

MODEL CLUSTER STUDY OF THE ACID—BASE PROPERTIES OF ZEOLITE CATALYSTS

R. VETRIVEL and B. VISWANATHAN

Department of Chemistry, Indian Institute of Technology, Madras 600 036 (India)

(Received 14 April 1982)

The remarkable catalytic properties of aluminosilicates are usually associated with their surface acid—base properties [1]. These properties depend on various factors such as the nature of the metal ion which neutralises the negative charge created by $[AlO_4]^-$ units, the extent of metal ions exchange, the electrostatic field produced by such ions and the number of oxygen vacancies present at the surface. Several attempts have been made to evaluate the acid—base properties of these systems by a number of experimental procedures using probe molecules [2—4] and also to correlate them with the observed specific catalytic activity [5]. Recently, the activity as oxidation catalysts of a number of mixed oxides has also been ascribed [6] to their acid—base properties. In view of this sustained interest in evaluating the acid—base properties of solid catalysts, it has become necessary to devise theoretical procedures for their estimation [7] and to rationalise the observed catalytic properties on the basis of these estimated acid—base properties.

METHOD OF COMPUTATION AND MODELS USED

The CNDO/2 calculations have been performed on typical cluster species representing the silica and alumina—silica framework. The details of the calculation procedure are available in the literature [8]. The bond parameters used in the model calculations are given in Table 1. Typical cluster models chosen for this computation are shown in Figs. 1—4. The calculations have been performed on clusters containing one, two and three silicon atoms in a silicic acid framework. Among the two geometries for Si_2 clusters given in Fig. 2a (proposed in ref. 7a) and Fig. 2b (used in these calculations) the geometry ($Si_2(b)$) given in Fig. 2b is found to be the more stable (judging from the calculated total and binding energies given in Table 2).

The charges on the exposed atoms are almost the same in both $Si_2(b)$ and Si_3 clusters, so the cluster model shown in Fig. 2b has been used to study the properties of silica—alumina systems formed by replacing one of the silicon atoms in a silicic acid unit by an aluminium atom (Fig. 4a). The additional negative charge introduced by replacement of a $[SiO_4]$ unit by $[AlO_4]^-$ has been compensated by the addition of cation "C" (where C = H^+, Li^+, Na^+ or $Mg(OH)^+$) to the bridging oxygen atom as shown in Fig. 4(a—d).

TABLE 1

The parameter values used for the model calculations (distances in A, angles in deg.)

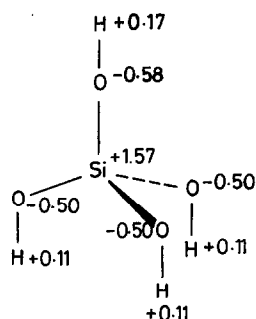| Parameter	Value	Parameter	Value
$d(Si-O)$	1.65	$\angle O-Si-O$	109
$d(Al-O)$	1.65	$\angle O-Al-O$	109
$d(O-H)$	0.98	$\angle Si-O-Si$	109
$d(O-Li)$	1.95	$\angle Al-O-Al$	109
$d(O-Na)$	2.50	$\angle Si-O-H$	109
$d(O-Mg)$	2.05	$\angle Al-O-H$	109

Fig. 1. Cluster model containing one silicon atom and the calculated charge densities on each atom.
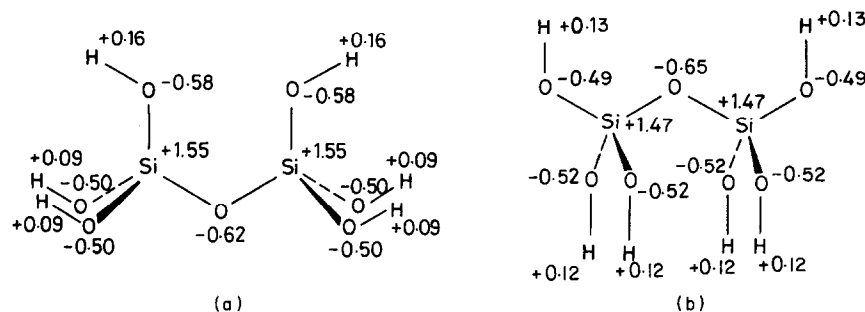

(a)

(b)

Fig. 2. (a) Cluster model (angular) containing two silicon atoms and the calculated charge densities on each atom. (b) Cluster model (linear) containing two silicon atoms and the calculated charge densities on each atom.

RESULTS AND DISCUSSION

Studies on silica clusters

The charge density distributions obtained for various silica clusters are given in Figs. 1—3 and the corresponding data are collected in Table 3. It has
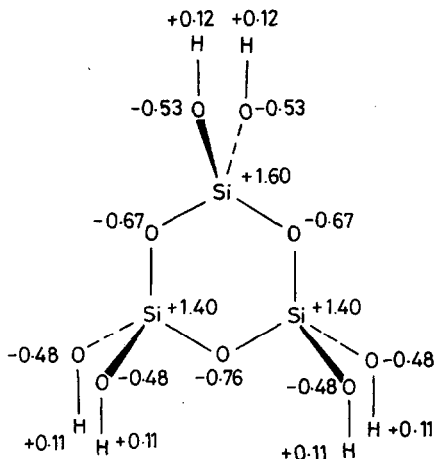
Fig. 3. Cluster model (hexagonal) containing three silicon atoms and the calculated charge densities on each atom.

been observed that the charge distributions are almost the same despite attempted geometry variation in the silicic acid entity. The charge densities also remain unaffected by variation in the Si—O—H angle from 109° to 180°. The results that emerge from charge density calculations on the hydrogen atom (this density is rather low for all the three clusters considered) is that, these systems should behave as weak protonic acids, which is in general agreement with the experimental observations on pure silica catalysts.

Aluminosilicates and ion-exchanged aluminosilicates

The charge distributions observed for aluminosilicates are shown in Fig. 4a. The effect of cation exchange on this cluster has also been studied by the substitution of Li^+, Na^+ or $[Mg(OH)]^+$ (this last species was necessary to keep the cluster model neutral) for the most positive hydrogen and representative charge distributions obtained are shown in Fig. 4(b—d). The data derived from these calculations are given in Table 3. In these clusters the "most positive" hydrogen appears to be the one located just above the bridging oxygen as shown in Fig. 4a. As a result of ion exchange, the negative charge on the oxygen atom linked to the metal atom increases (for example from —0.52 for HSiAl to —0.72 for MgSiAl) while the corresponding change in the charge of the out-of-plane oxygen is only marginal. Since the frontier MO levels consist mainly of oxygen orbitals, the increase in negative charge on bridged oxygen is the reason for the increase in basicity of these catalysts. This result is in general agreement with the experimental observations that the ion-exchanged aluminosilicates promote basicity-controlled reactions [5, 9]. It has been reported [10] that these metal-exchanged zeolites also enhance acid-catalysed reactions like ethanol dehydration. The cations in
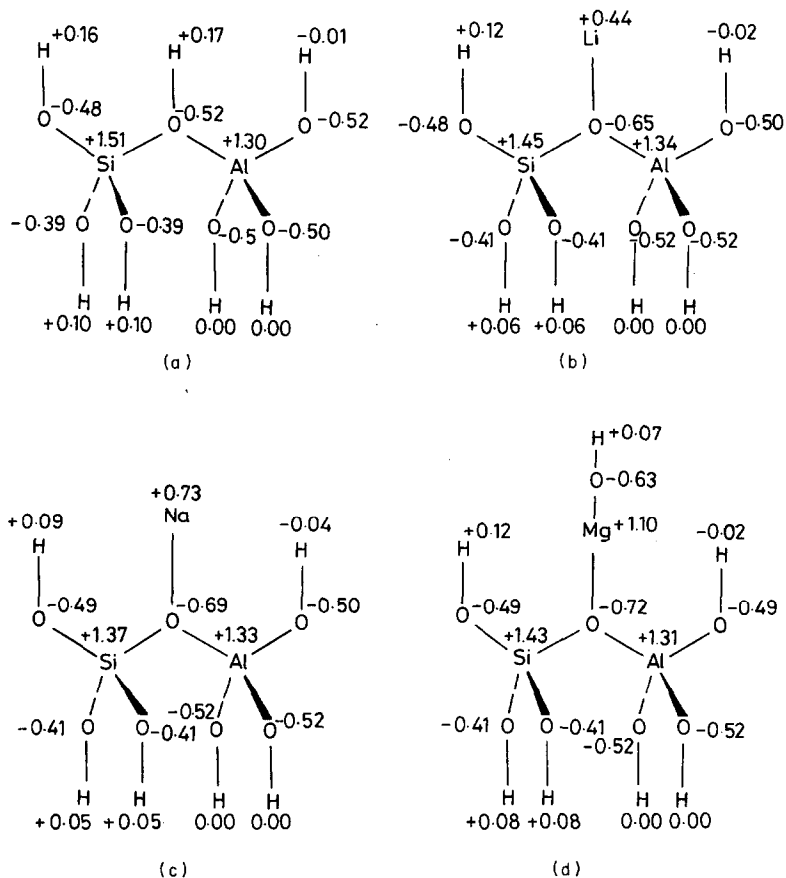
Fig. 4. (a) Charge densities calculated for the silica—alumina cluster. (b) Charge densities calculated for the lithium ion-exchanged silica—alumina cluster. (c) Charge densities calculated for the sodium ion-exchanged silica—alumina cluster. (d) Charge densities calculated for the magnesium ion-exchanged silica—alumina cluster.

TABLE 2

Values of calculated parameters for silica clusters

Cluster	Configuration	Total energy (a.u.)	Binding energy (a.u.)
Si	Tetrahedral	−79.14	−0.36
$Si_2(a)$	$\angle O{-}Si{-}O = 120°$		
	$\angle Si{-}O{-}Si = 120°$	−137.99	+0.21
$Si_2(a)$	$\angle O{-}Si{-}O = 109°$		
	$\angle Si{-}O{-}Si = 109°$	−137.88	+0.32
$Si_2(b)$	$\angle O{-}Si{-}O = 109°$		
	$\angle Si{-}O{-}Si = 109°$	−138.31	−0.11
Si_3	Hexagonal ring	−177.15	+0.11

TABLE 3

Charges on various atoms of the metal clusters

Cluster model	Geometry	Charge densities on		
		Most positive hydrogen	Metal	Most negative oxygen
H_4SiO_4—Si_1	Tetrahedral	+0.17	—	—0.58
$H_6Si_2O_7$—Si_2(a)	$\angle$O—Si—O = 120°			
	$\angle$Si—O—Si = 120°	+0.16	—	—0.62
$H_6Si_2O_7$—Si_2(a)	$\angle$O—Si—O = 109°			
	$\angle$Si—O—Si = 109°	+0.13	—	—0.62
$H_6Si_2O_7$—Si_2(b)	$\angle$O—Si—O = 109°			
	$\angle$Si—O—Si = 109°	+0.14	—	—0.64
$H_6Si_3O_9$—Si_3	Hexagonal ring	+0.13	—	—0.67
H_7SiAlO_7—HSiAl	$\left.\begin{array}{l}\angle\text{O—Si—O}\\\angle\text{O—Al—O}\end{array}\right\}$ = 109° $\left.\begin{array}{l}\angle\text{Si—O—Si}\\\angle\text{Al—O—Al}\end{array}\right\}$ = 109°	+0.17	—	—0.52
LiH_6SiAlO_7—LiSiAl	a	+0.12	+0.44	—0.65
NaH_6SiAlO_7—NaSiAl	a	+0.09	+0.73	—0.69
$(OH)MgH_6SiAlO_7$—MgSiAl	a	+0.12	+1.10	—0.72

[a] Geometry as for H_7SiAlO_7—HSiAl.

such catalysts may be acting as Lewis acid sites. The activity of metal-exchanged mordenite is in the order Mg > Na > Li which is in the same order as the positive charge on these metals (Mg = 1.10, Na = 0.73, Li = 0.44).

It is known that the positions of the HOMO and LUMO are generally indices of donor ability or basicity, as well as Lewis acidity. The HOMO levels of these clusters are in the order

MgSiAl(—0.417) < LiSiAl(—0.395) < HSiAl(—0.388) < NaSiAl(—0.369)

The LUMO levels of these clusters are in the order

NaSiAl(—0.0303) > LiSiAl(—0.0479) > MgSiAl(—0.0685) > HSiAl(—0.0885)

Active sites on the surfaces

Silica—alumina systems behave as Brönsted acids at elevated temperatures. To explain this behaviour calculations have been carried out on the cluster illustrated in Fig. 5 in which the bridging oxygen—aluminium distance is much higher (3.6 Å) so that overlap between them is negligible. At reaction conditions, there is interaction between the aluminium atom and oxygen on adjacent [SiO$_4$] units, leading to the structure (Fig. 4a) which has an acidic proton, thus implying the acidity of these catalysts. In the "in situ" IR studies of Ward [11], carried out on zeolites during cumene cracking, it was observed that there is a decrease in the frequency of the O—H band, showing
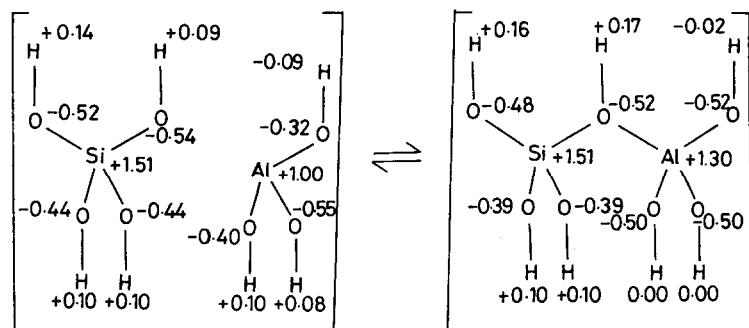
Fig. 5. Charge densities calculated for the silica—alumina cluster where overlap between the orbitals of aluminium and the oxygens of a $[SiO_4]$ unit is negligible.

that a more polar H-atom is formed during the reaction, thus providing support for this view.

CONCLUSIONS

The points that emerge from these computations are:

(i) silica—alumina catalysts can be expected to show higher protonic acidity because the magnitude of the positive charge on the hydrogen atom is higher than in silica and alumina clusters.

(ii) The incorporation of alkali and alkaline earth metals reduces the net protonic acidity of the aluminosilicate moiety.

(iii) The Lewis basicity of the catalysts increases as a result of ion-exchange by alkali metals.

(iv) The net charge densities observed on silica and alumino-silicate clusters do not vary much with changes in the geometry assumed for the cluster.

REFERENCES

1 M. L. Poutsma, Zeolite Chemistry and Catalysis, ACS Monograph, No. 171, 1976, pp. 437 and 529.
2 B. C. Gates, J. R. Katzer and G. C. A. Schuit, Chemistry of Catalytic Processes, McGraw—Hill, New York, 1979.
3 H. Sugihara, L. Y. Chen and I. Yasumori, Bull. Chem. Soc. Jpn., 47 (1974) 2089.
4 S. H. C. Liang and I. D. Gay, J. Catal., 66 (1980) 294.
5 M. A. Schobert and Y. H. Ma, J. Catal., 70 (1981) 111.
6 M. Ai and T. Ikawa, J. Catal., 40 (1975) 203.
7 (a) W. Grabowski, M. Misono and Y. Yoneda, J. Catal., 61 (1980) 103.
   (b) W. J. Mortier and P. Geerlings, J. Phys. Chem., 84 (1980) 1982.
   (c) S. Beran, J. Phys. Chem., 85 (1981) 1951, 1956.
   (d) V. B. Kazanskii, Proceedings of IV National Symposium on Catalysis, Bombay, 1978, p. 14.
8 (a) J. A. Pople, D. P. Santry and G. A. Segal, J. Chem. Phys., 43 (1965) S129.
   (b) J. A. Pople and G. A. Segal, J. Chem. Phys., 43 (1965) S136.
9 S. Malinowski and S. Basinski, J. Catal., 2 (1963) 203.
10 D. E. Bryant and W. L. Kranich, J. Catal., 8 (1967) 8.
11 J. W. Ward, J. Catal., 11 (1968) 259.