# NATURE AND PROPERTIES OF ACIDIC SITES IN ZEOLITES REVEALED BY QUANTUM CHEMICAL AB INITIO CALCULATIONS

J. SAUER
Central Institute of Physical Chemistry, Academy of Sciences,
DDR-1199 Berlin, German Democratic Republic

## ABSTRACT

Molecular models for Brönsted and Lewis sites are proposed. For bond lengths and angles empirically corrected theoretical values are used. To reveal differences between various sites, binding energies of the $H_2O$ molecule on the respective models are considered.

## INTRODUCTION

There has been continuous interest in the nature and properties of acidic sites, both Brönsted and Lewis, of zeolites. Recent stimulation of research in this field came from the development of highly efficient catalytic materials such as ZSM-5 zeolites. Nonempirical quantum chemical methods proved to be a valuable tool for making predictions of local structures and properties of minerals provided that suitable molecular models were used [1]. This is also true for active sites in zeolites [2-5]. While in a previous paper [3] local structures, vibrational properties and deprotonation energies of bridging and terminal hydroxyls were compared, in this work we construct molecular models that are appropriate for Brönsted and Lewis sites. These models are to be used to obtain reliable energies for the interaction of adsorbed molecules with active sites. Here, we report first results for the $H_2O$ molecule. Some of them can be compared with the outcome of a related study by Geerlings et al. [4].

## SPECIFICATION OF MODELS AND LOCAL STRUCTURES OF ACTIVE SITES

While there is no doubt that bridging hydroxyls are the source of Brönsted acidity [3], the existence and nature of Lewis sites in zeolites is debatable. We investigate in this study the threefold coordinated framework aluminium site and the $Al^{3+}$ cation as possible candidates for Lewis sites. However, the $AlO^{+}$ species or the $Al^{3+}(H_2O)_n$ and $AlO^{+}(H_2O)_n$ complexes may be more realistic models than

the free $Al^{3+}$ cation and will be considered in forthcoming studies. Figure 1 shows molecular models that we propose for bridging hydroxyls (B-O) and threefold coordinated aluminium atoms (L-O). There are two possibilities for choosing the geometry parameters: (i) theoretical results which are obtained by optimization for the particular molecule serving as model, and (ii) realistic values which are inferred from all that is known from theory and experiment for the active sites and related molecules. While Geerlings et al. [4] adopt the first possibility, we strive for realistic models which reflect as closely as possible the local structure of the sites considered. To this end, use is made of empirically corrected theoretical geometries for bridging and terminal hydroxyls as well as for nonprotonated $\gtrless Si\text{-}O\text{-}Al^{\ominus} \lesssim$ framework sites (Table 1), which were taken from previous studies [3,7,8]. The results of the quantum chemical calculations were corrected for (empirically) known systematic errors and limitations of models. The justification of the procedure is outlined in Ref.3. Table 1 shows all the values used in this work. The models T-O for terminal hydroxyls and L-O for Lewis sites (Figure 1) retain the values of the B-O model for the geometry parameters.

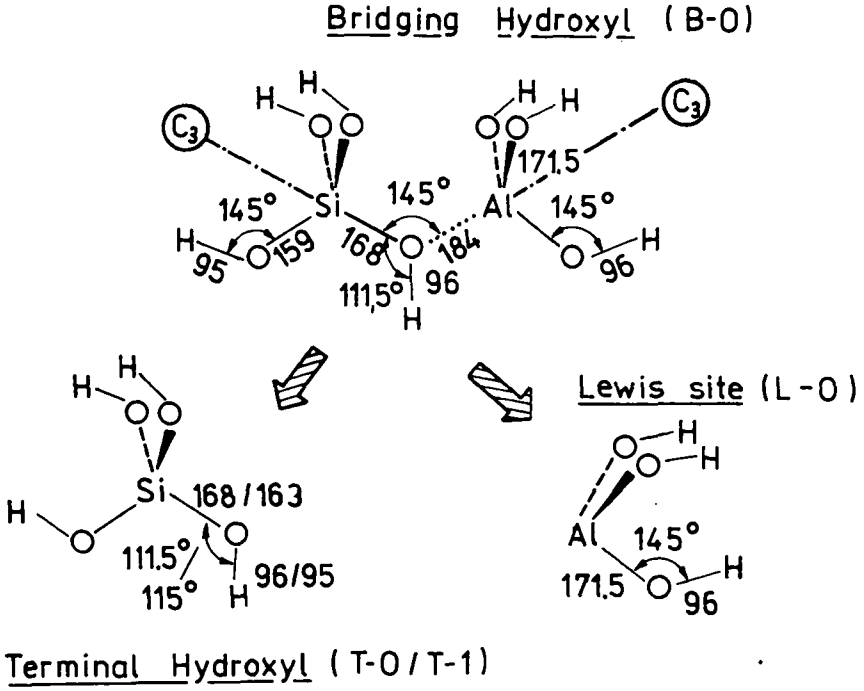


Fig. 1. Molecular models of active sites and values of bond lengths (in pm) and angles (in degree).

Table 1

Values of bond lengths and angles for molecular models of active sites in zeolites (cf. Figure 1)

| Parameter | Value [a] | Source |
|---|---|---|
| | (i) models B-O, T-O, and L-O | |
| Si-O(H) | 168 | Values recommended for bridging hydroxyls [3] |
| (Si)O-Al | 184 | |
| (Si)O-H | 96 | |
| ∢ Si-O-H | 111.5 | |
| Si-O | 159 | Values recommended for nonprotonated ≥Si-O-Al⊖≤ bridges [3,7] |
| Al-O | 171.5 | |
| ∢ Si-O-Al | 145 | Typical value from X-ray results, may be subjected to variations |
| ∢ Si-O-H | 145 | These are models of Si-O-Si and Al-O-Si bridges and, therefore, the same value as above is adopted |
| ∢ Al-O-H | 145 | |
| (Si)O-H | 95 | STO-3G results for Si(OH)4 and [Al(OH)4]⊖ [7], empirically corrected by -3pm (see Tab. IV of Ref. 3) |
| (Al)O-H | 96 | |
| | (ii) model T-1 | |
| Si-O(H) | 163 | Values recommended for terminal hydroxyls [3,8] |
| (Si)O-H | 95 | |
| ∢ Si-O-H | 115 | |

[a] Distances in pm, angles in degree

CALCULATIONS

Interaction energies are obtained within the "supermolecule" approach by means of ab initio calculations of SCF energies for the models M, the $H_2O$ molecule and the complexes M-$H_2O$:

$$\Delta E^{SCF}_{M\text{-}H_2O} = E_{M\text{-}H_2O} - ( E^{SCF}_{M} + E^{SCF}_{H_2O} ).$$

Corrections are made for the basis set superposition error. The MINI-1 basis set is used which proved to be particularly suitable for calculating complexes, both of hydrogen-bonded and ionic type [6]. It yields more reliable absolute values of interaction energies than the 3-21 G basis set employed in Ref.4. Details of the computational procedure can be found in Ref. 6.

RESULTS AND DISCUSSION

Figure 2 shows the approach of the $H_2O$ molecule towards the models of active sites. It was found by step-by-step optimization of the six intermolecular degrees of freedom. The hydrogen bonds are virtually linear, and the $H_2O$ molecule is within the plane of the $\geq$SiOH group. Table 2 shows the optimum distances and binding energies (defined as the negative interaction energy at the optimum structure) for the complexes of $H_2O$ with different sites. For comparison, the results of the hydrogen-bonded $H_2O$ dimer [6] are included. Note, that contributions due to dispersion interaction are not yet considered

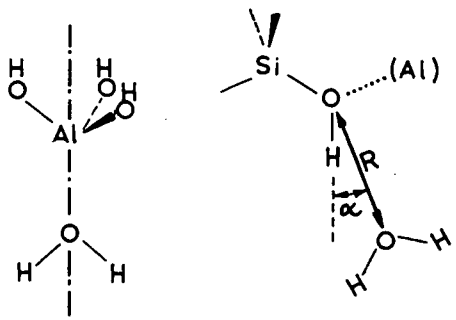


Fig. 2. Structure of complexes of different models with $H_2O$

Table 2

Optimum distances [a] and binding energies [b], $-\Delta E$, for complexes of $H_2O$ with different models for active sites in zeolites

| Site (Model) | R(pm) [a] | $-\Delta E$(kJ/mol) |
|---|---|---|
| Bridging hydroxyl (B-O) | 259[c] | 58.4 |
| Terminal hydroxyl (T-O) | 288[c] | 16.4 |
| Siloxan bridge ( $(HO)_3SiOSi(OH)_3$ )[d] | 325[c,d] | 10.1±0.3[d] |
| $H_2O$ [e] | 288[c,e] | 20.1 |
| Threefold coordinated Al (L-O) | 191[f] | 194 |
| $Al^{3+}$ [e] | 176[f,e] | 791[e] |

[a] Cf. Fig. 2. [b] SCF energies corrected for the basis set superposition error. [c] Linear hydrogen bond ($\alpha$ =0), R=R(O,O). [d] Ref. 10. [e] Ref. 6. [f] R=R(Al,O).

and that, therefore, the final values of the binding energy may be larger by 5-10 kJ/mol. This, however, will not affect the conclusions reached below.

For bridging hydroxyls a binding energy is obtained which is 2.9 times the value of the $H_2O$ dimer, while the previous estimate was 2.0 times this value [4]. In order to understand the substantial difference between the binding energies of bridging hydroxyls (about 60 kJ/mol, this work) and terminal hydroxyls (about 25 kJ/mol, [9]) the T-O model has been investigated. In this model the ≥SiOH group has exactly the same geometry as in bridging hydroxyls (B-O model). The binding energy for the B-O model is 3.5 times that of the T-O model (Table 2). Two effects may contribute to this result: (i) the additional direct interaction of the $H_2O$ molecule with the $Al(OH)_3$ part of the B-O model and (ii) the enhanced acidity of the ≥SiOH group due to its polarization by the neighboring $Al(O-)_3$ group. This polarization is reflected (Figure 3) by changes of net charges when passing from the T-O (values in parenthesis , Figure 3) to the B-O model. Ref. 4 provides a detailed discussion. While we observe the same increase of the negative charge on the oxygen atom as the authors of Ref. 4, the increase of the positive charges on the acidic hydrogen atom and, in particular, on the silicium atom that we obtain is larger.

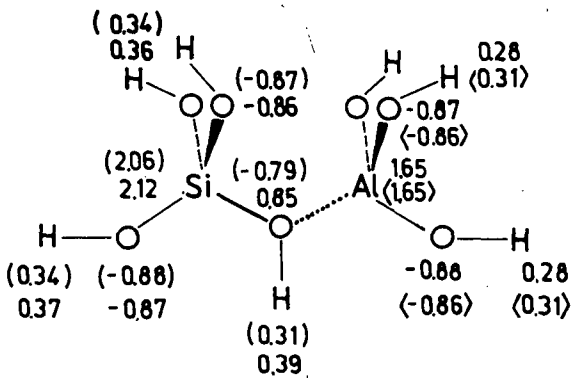


Fig. 3. Atomic net charges for the B-O model (bridging hydroxyls) compared to those of the T-O (in parenthesis) and L-O models in brakets .

Siloxan bridges, ≥Si-O-Si≤, are the constituents of microporous silica. The energies of binding for $H_2O$ on these groups amount to only a fraction of that of bridging hydroxyls. This finding supports the view (see, e.g., [11]) that in siliciumrich molecular sieves bridging

hydroxyls act as hydrophilic sites within an environment of hydrophobic siloxan bridges.

Finally we comment on tentative models of Lewis sites. The huge stabilization energy of the $H_2O$-$Al^{3+}$ complex makes it very unlikely that the $Al^{3+}$ cation exists in noncoordinated form in zeolites. Even threefold coordinated framework aluminium sites bind $H_2O$ with a three times larger energy than bridging hydroxyls do. We conclude that this type of sites may act as defect sites which are strongly preferred by $H_2O$ molecules on adsorption in zeolites.

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