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Simulation of topography and acid properties of silicon substituted AlPO_4 -11 framework¹

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Abstract

We report MNDO calculations of the energies of substitution of either a single silicon atom in place of phosphorus or two silicon atoms in place of a pair of aluminium and phosphorus atoms in an AlPO_4 -11 framework, leading to SAPO-11. The preferred sites for silicon substitution and its consequences on acidic properties are also reported.

Key words: acid properties; aluminium; MNDO energetics; silicon substituted AlPO_4 -11 framework; topography simulation

Introduction

The AlPO_4 -11 molecular sieve has an electrically neutral framework, but it has been shown [1] that there are acidic centres in AlPO_4 -11 which are responsible for its mild catalytic activity. It is possible to generate active catalysts by incorporating different elements into the framework [2]. Recently Mertens et al. [3] have discussed possible mechanisms for the substitution of silicon in AIPO molecular sieves to obtain silicoaluminophosphate (SAPO) molecular sieves. SAPOs are known to be acidic and their activity allows them to catalyse industrially important reactions [4-6]. The incorporation of silicon in the AIPO framework has been reported to occur via the following two mechanisms: (i) a silicon atom replaces a phosphorus atom in the framework; and (ii) two silicon atoms replace a pair of aluminium and phosphorus atoms in adjacent sites.

The possibility of a silicon atom replacing an aluminium atom has not yet been reported. Substitution with silicon does not alter the nature of the micropores of this molecular sieve [3], but it does impart an acidic character, which

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is an indication of isomorphous substitution of phosphorus and aluminium in the framework.

Actually, very little information is available on the preferred site occupied by silicon in SAPOs. Recently Carson et al. [7] and Derouane et al. [8] have performed ab initio quantum chemical calculations on cluster models to study the local electronic structure of AlPOs and SAPOs. Their studies consider ideal cluster models where all the T-O bond lengths, and O-T-O and T-O-T bond angles have same values. Some valuable information has been derived in respect of the chemical bonding and the preferred geometries of TO_4 for silicon substitution.

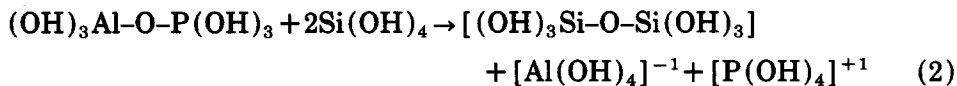
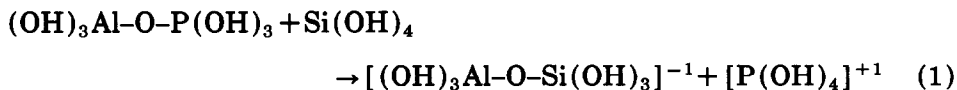
In the present study we have carried out calculations on cluster models derived from the crystal structure of AlPO_4 -11 using the semi-empirical MNDO (modified neglect of diatomic overlap) method [9]. We report the preferred sites for the substitution of silicon, their topology in AlPO_4 -11, and the acidic properties of the resulting SAPO-11 framework.

Model and computational method

The geometry of cluster models representing different sites in AlPO_4 -11 is derived from the reported crystallographic study [10]. A cluster containing one tetrahedral group, namely $\text{T}(\text{OH})_4$ (denoted as a monomer), and two tetrahedral groups sharing a corner oxygen atom, namely $(\text{OH})_3\text{-T-O-T}(\text{OH})_3$ (denoted as a dimer) are considered for the calculation of the electronic properties. In the monomer cluster, T represents either Al or P. The T and oxygen atoms are positioned as in the AlPO_4 -11 framework reported by the XRD study [10]. In the dimer clusters the Ts are either Al or P and the cluster model represents two adjacent TO_4 groups which share a corner. The terminal oxygen atoms are bonded to hydrogen atoms to maintain the electrical neutrality of the cluster. The positions of the hydrogen atoms were located at the nearest neighbour T-site locations. Whenever silicon is substituted in place of Al or P in the framework the geometry of TO_4 remain unchanged. The cluster charge is 0 when the T atoms are Al^{3+} and P^{5+} or two Si^{4+} , and it is -1 when the T atoms are Al^{3+} and Si^{4+} . Considering that the electronic effects are short range forces and that the substitution of a 'T' atom will be a localised phenomenon, these cluster models have proved to be adequate for the study of the substitution process [11-12]. Although, ideally, a larger cluster consisting of second nearest neighbour atoms will provide accurate results, the dimeric cluster model has been adopted for reasons of computational feasibility. However, the electronic properties such as substitution energy and proton binding energy are calculated for every site as an average value of four dimer cluster models. This procedure, which takes care of the effect of all of the four neighbouring TO_4 units, is explained in detail in the following section.

Earlier, we reported the electronic structure and adsorption properties of

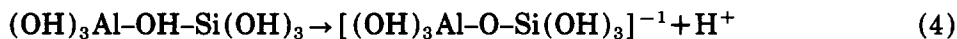
AlPO₄-11 calculated by the MNDO method [13,14]. In the present study we calculate the substitution energy (SE) from the total energy (TE) of cluster models and predict the preferred sites of substitution. The method has been found to predict the substitution energy for different sites in the same order as predicted by ab initio calculations [12]. The substitution process of silicon in AlPO₄-11 lattice is considered as follows:



The substitution energy of silicon for phosphorus and aluminium in the above processes are calculated according to the equation:

$$\text{SE} = \text{TE of products} - \text{TE of reactants} \quad (3)$$

The negative charge in the $[(\text{OH})_3\text{Al-O-Si}(\text{OH})_3]^{-1}$ cluster is compensated by adding a hydrogen at the bridging oxygen (O_b) to form $(\text{OH})_3\text{Al-OH-Si}(\text{OH})_3$. The hydrogen (H_b) is attached to the bridging hydroxyl group on the obtuse side of the Al-O-Si angle. The hydrogen is placed in such way that the angle Al-O- H_b is equal to the angle Si-O- H_b and the O_b - H_b distance is 1.0 Å. The binding energy of the proton (BE_H) is calculated by considering the following process:



and the following relation:

$$\text{BE}_\text{H} = \text{TE of } [(\text{OH})_3\text{Al-OH-Si}(\text{OH})_3] - \text{TE of } [(\text{OH})_3\text{Al-O-Si}(\text{OH})_3]^{-1} \quad (5)$$

Results and discussion

Substitution of silicon in the framework

Altogether there are eleven crystallographically distinct bridging oxygen atoms in the ordered AlPO₄-11 structure [10]. All these eleven unique oxygen sites are simulated by suitable dimer cluster models. The geometry and the abbreviated notations for the clusters have been explained in detail elsewhere [13]. The cluster models and the total energy of $\text{T}_1\text{-O-T}_2$ clusters, where T_1 and T_2 are either one of P, Al or Si atoms, are given in Table 1. The total energy values of tetrahedral monomer clusters representing various crystallographic sites have been reported earlier [14]. The substitution energy (SE_1) of single silicon in the place of phosphorus and the substitution energy (SE_2) of two

TABLE 1

Calculated electronic properties of dimer clusters

(av.): Average of four values. (X₂): This connectivity occurs twice

Cluster No.	Model ^a of dimer cluster	Total energy of P-O-Al cluster (eV)	Total energy of Si-O-Al cluster (eV) [Si in place of P]	Substitution energy for single silicon [SE ₁] (eV)	Total energy of Si-O-Si cluster (eV) [Si in place of P and Al]	Substitution energy for a pair of silicons [SE ₂] (eV)
1	P ₁ -O ₁ -Al ₁	-2519.21	-2454.22	-3.12	-2493.61	-2.84
2	P ₁ -O ₄ -Al ₁	-2519.86	-2454.24	-3.75	-2493.80	-3.30
3	P ₁ -O ₅ -Al ₂	-2519.85	-2454.51	-3.47	-2494.34	-2.98
4	P ₁ -O ₆ -Al ₂	-2517.75	-2452.65	-3.23	-2491.89	-3.33
				-3.39 (av.)		-3.11 (av.)
5	P ₂ -O ₂ -Al ₂	-2521.07	-2455.32	-3.16	-2495.21	-2.61
6	P ₂ -O ₇ -Al ₃	-2524.15	-2458.30	-3.26	-2497.68	-2.77
7	P ₂ -O ₈ '-Al ₁	-2519.14	-2453.48	-3.07	-2492.85	-2.81
8	P ₂ -O ₈ '-Al ₁	-2519.59	-2453.51	-3.49	-2493.43	-2.68
				-3.25 (av.)		-2.72 (av.)
9	P ₃ -O ₃ -Al ₃	-2518.78	-2451.82	-3.13	-2491.21	-2.63
10	P ₃ -O ₇ -Al ₂	-2517.29	-2450.18	-3.28 (X ₂)	-2490.18	-2.62
11	P ₃ -O ₈ -Al ₃	-2518.38	-2451.34	-3.21	-2490.55	-2.89
				-3.23 (av.)		-2.69 (av.)

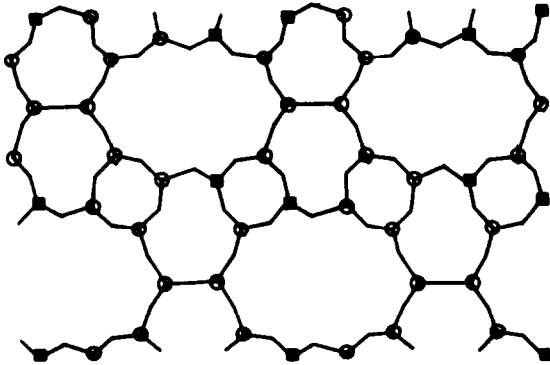
^aCrystallographic site numbers for the 'T' sites of two TO₄ units and the bridging oxygen in the dimer cluster models are given.

silicons in the place of a pair of phosphorus and aluminium atoms are evaluated according to eqn. (3) for the processes (1) and (2), respectively. These substitution energy values are also listed in Table 1. Whenever a phosphorus is substituted by silicon, silicon will be bonded to four adjacent AlO₄ groups. Hence, four dimer cluster models are studied wherein the geometry of the SiO₄ group is the same, but the geometries of adjacent AlO₄ are those of the four possible neighbours. The substitution energy of silicon at a given phosphorus site is calculated as the average of the four cluster models. For example, site P₁ is bonded to two Al₁ and two Al₂ sites through O₁, O₄, O₅ and O₆, respectively. Hence the energy for substitution of silicon at site P₁ is calculated as an average of four dimer clusters involving Si₁-O₁-Al₁, Si₁-O₄-Al₁, Si₁-O₅-Al₂, Si₁-O₆-Al₂ linkages.

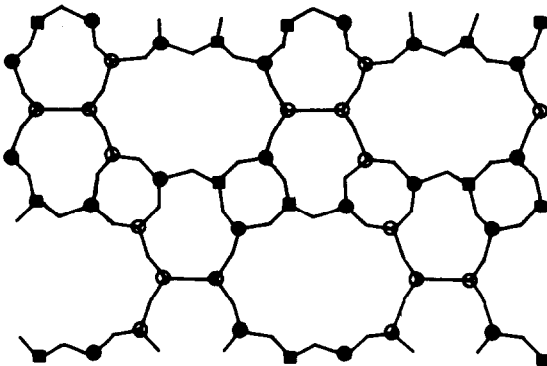
The values of the substitution energy given in Table 1 indicate the ease of substitution of silicon at various sites. For a given site it can be seen that the substitution of a single silicon in the place of phosphorus (eqn. 1) is energetically more favourable than the substitution of a silicon pair for phosphorus

and aluminium atoms (eqn. 2). Unlike $\text{AlPO}_4\text{-5}$, where there is only one P site and where 90% silicon substitution has been reported [15], $\text{AlPO}_4\text{-11}$ has three crystallographically distinct P sites. The substitution energy for site P_1 is the most favourable and hence preferential substitution at site P_1 is expected. Site P_1 is connected through O_4 and O_6 to the Al_1 and Al_2 sites, respectively. The results presented in Table 1 also show that silicon pair substitution is specifically favourable at $\text{P}_1\text{-O}_4\text{-Al}_1$ and $\text{P}_1\text{-O}_6\text{-Al}_2$ sites.

The above results predict that the P_1 site alone is substituted by silicon



(a)



(b)

Fig. 1. The silicon substitution sites in place of P_1 (a) are shown by filled squares and the silicon substitution sites in place of Al_1 and Al_2 (b) are shown by filled circles in the [001] plane of the $\text{AlPO}_4\text{-11}$ lattice.

when small amounts of silicon are available, and that the P_1 - Al_1 pair as well as the P_1 - Al_2 pair are substituted by silicons when greater amounts of silicon are available. The P_1 site alone represents 20% of the T sites in $AlPO_4$ -11, while the P_1 , Al_1 and Al_2 sites together represent 60% of the T sites. These predictions are in accordance with the experimental findings [15] that, when monomeric sources of silicon, such as tetraethyl orthosilicate, are used, lower levels of Si incorporation (less than 20%) occur on the T sites. This indicates that the process occurs according to eqn. 1, with silicon replacing the P_1 sites. The use of polymeric sources of silicon, such as Ludox, leads to higher levels of incorporation (46%), indicating that silicon is replacing the P_1 - Al_1 pair and the P_1 - Al_2 pair. The topography of silicon substituted in the place of P_1 as well as in the place of P_1 - Al_1 and P_1 - Al_2 pairs in the $AlPO_4$ -11 framework are shown in Figs. 1a and 1b, respectively. Since each P_1 site is linked to both Al_1 and Al_2 sites, silicon substitution leads to the formation of islands. When all P_1 , Al_1 and Al_2 sites are substituted by silicon atoms, the alternate four-member rings of the [001] plane are fully substituted by silicon atoms (Fig. 1b).

Acidity due to silicon substitution

When a silicon atom is substituted in the place of phosphorus, the framework becomes anionic. The anionic framework leads to exchangeable cations, typically protons, imparting Brønsted acidity to the system. The binding strength of protons to the oxygen atoms bridging silicon and aluminium is an indication of Brønsted acid strength. We have evaluated the acidity of protons bound to different oxygen sites by calculating the proton binding energy according to eqn. (5). The strength of adsorption of a proton to an oxygen bridging two T sites could depend on two parameters, namely the T-O-T angle and the T-O bond distances. In Fig. 2 the variation of proton binding energy with respect to T-O-T angle and T-O distances (calculated as an average of T_1 -O and T_2 -O, where T_1 and T_2 are the tetrahedral atoms connected by the oxygen) are represented for various oxygen sites.

It was found that the proton binding energy is inversely proportional to the charge on the hydrogen atom. The partial charge, in turn, is controlled by a complex factor involving both bond lengths and bond angles. In general, the proton binding energy is found to increase with increasing values of the T-O and decreasing values of the T-O-T parameters for a given T site. In regard to the T-O-T angle, a linear relation was found for the lower angles and the higher angles, while there is a break in between, which indicates that in addition to T-O and T-O-T, some other factors, such as O-T-O and long range effects, also control the proton binding energy. Since our calculations predict silicon substitution at P_1 , Al_1 and Al_2 sites (Table 1), the protons will be attached to oxygen atoms 1, 4, 5 and 6. Among these oxygen atoms, with the exception of O_6 , all other oxygen atoms are in the ten-membered channel and hence the protons attached to them are available as acidic protons to molecules entering the ten-membered channel of $AlPO_4$ -11. Hence, the Brønsted acid

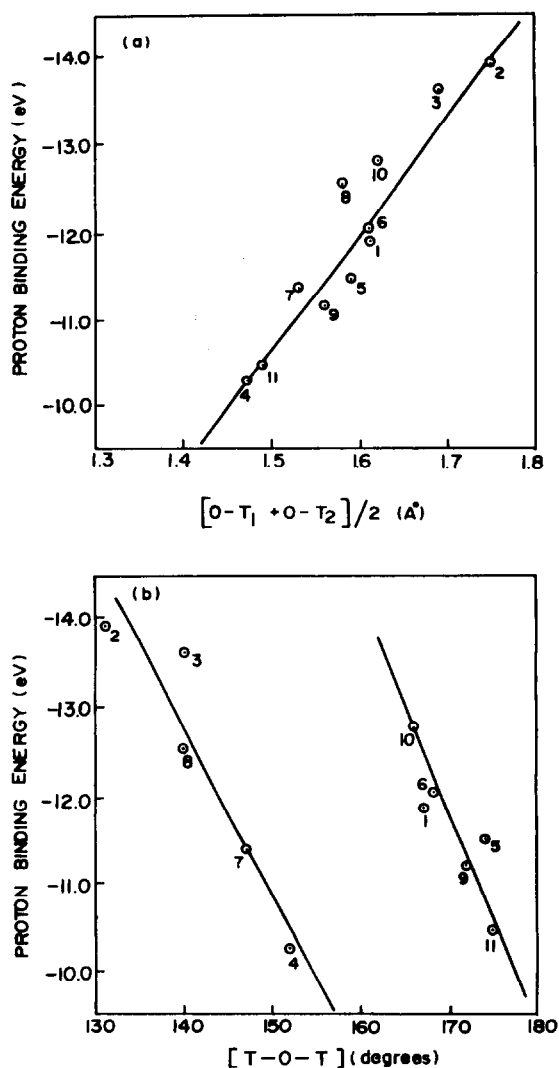


Fig. 2. The variation of proton binding energy with T-O distance (a) and T-O-T angle (b) for the eleven crystallographically distinct oxygen sites. Each point is labelled with the corresponding cluster number in Table 1.

centres are expected to be present in the ten-membered channel and the strength of the Brønsted acidity can be seen from the proton binding energy values shown in Fig. 2; the proton binding energy at oxygen atoms 1, 4 and 5 are shown by the cluster numbers 1, 2 and 3, respectively.

Conclusions

The energetically favourable sites for silicon substitution in the $AlPO_4$ -11 molecular sieve have been evaluated. There is a clear priority for silicon sub-

stitution to specific T sites in $\text{AlPO}_4\text{-11}$. The results of the calculation predict that, with monomer sources of silicon in the gel, silicon substitution occurs at site P_1 and, with polymeric sources of silicon in the gel, sites P_1 , Al_1 and Al_2 could be substituted with silicon. Although the binding energy is dependent on T-O-T angles and T-O bond lengths, there is no well defined correlation. The specific conclusions emerging from the above results may be summarized as follows:

(1) P_1 is the site where silicon preferentially becomes substituted and further substitution occurs at sites Al_1 and Al_2 .

(2) These silicon substitution sites form siliceous islands of four-membered channels: alternate four-membered channels have all the T sites substituted by silicon atoms.

(3) The silicon substitution in $\text{AlPO}_4\text{-11}$ will impart Brønsted acidity, as indicated by proton binding energy calculations.

Acknowledgement

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