

Electronic and structural properties of aluminum in the ZSM-5 framework

A. Chatterjee, R. Vetrivel*

Catalysis Division, National Chemical Laboratory, Pune 411 008, India

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Abstract

The relative importance of the geometry and size of clusters involved in the calculation of the electronic structure of ZSM-5 using MNDO (modified neglect of differential overlap) quantum chemical cluster calculations is reported. Calculations were carried out on Al-containing pentamer cluster models with a tetrahedral symmetry, and their geometrical parameters were systematically varied. Calculations were also performed for cluster models of varying size whose geometry was derived from the crystal structure reports of ZSM-5. The electronic properties such as density of states, energy of frontier molecular orbitals and contribution from different atomic orbitals could be derived from the results of even small cluster models, while pentamer clusters were needed to study the energetically favorable substitution sites of aluminum.

Keywords: Framework aluminum; ZSM-5 zeolite; Quantum chemical calculations; Frontier molecular orbitals; Density of states

1. Introduction

The location of aluminum in the framework of ZSM-5 remains a question without a conclusive and definite answer. The low concentration of aluminum in ZSM-5 poses a problem to experimental structure analysis techniques, and the same holds for other isomorphously substituted elements such as Ti in TS-1, V in VS-1, etc. Computational techniques such as quantum chemical calculations [1–5] and classical energy minimization studies [6] have been reported.

In this paper, we report the use of semi-empirical quantum chemical calculations using the MNDO method to advance a further understanding of this problem. The influence of the local geometry and

the cluster size on the location of Al and the electronic properties of ZSM-5 are analyzed.

In 1983, Fripiat *et al.* [1] found that the T12 and T2 sites in the ZSM-5 structure reported by Olson *et al.* [7] were the likely sites for the substitution of aluminum. They used *ab initio* calculations with STO-3G basis for dimer (two corner-shared TO₄ tetrahedra) cluster models. The most recent study by White and Hess [2] used the periodic Hartree–Fock (PHF) method with STO-3G basis for the whole unit cell with 288 atoms. This calculation is computationally demanding, and only the results of an all-silicon structure (silicalite), which provides a baseline for the study of the aluminated form, have been reported. Redondo and co-workers [3,4] reported aluminum substitution studies in ZSM-5 using *ab initio* calculations with different basis sets and MNDO calculations

* Corresponding author.

on clusters of various size. Their earlier study [3] using *ab initio* calculations with extended valence double zeta (VDZ) basis set calculations for monomer cluster models (one TO_4 tetrahedron linked to four hydrogen atoms) indicated the T6, T12 and T9 sites as the favorable sites for Al substitution. Their recent study [4], using the MNDO method for clusters with nearly 100 atoms, reports T9 as the most favorable site for Al substitution. The results of our earlier MNDO study [5] on monomer cluster models with all-silicon atoms coincided with those of Fripiat *et al.* [1].

On the other hand, the classical simulation of Al substitution in ZSM-5 by Schroder *et al.* [6] for the low-temperature monoclinic structure showed a random distribution of Al, since the substitution energies for Al at various sites lie within the range of 0.35 eV. In this background, we have calculated the electronic structure of cluster models by systematically varying their geometry and size to derive fundamental correlations for determining the location of Al in ZSM-5 and other zeolites.

2. Cluster models and calculation methods

The localized cluster model approach to study the crystal lattice properties proposed by Fripiat *et al.* [1] has been used. Calculations have been performed on monomer $[\text{T}(\text{OH})_4]$, dimer $[(\text{OH})_3\text{-T-O-T}(\text{OH})_3]$ and pentamer $\{\text{T-O}_4[\text{T}(\text{OH})_3]_4\}$ cluster models. The pentamer cluster model represents a TO_4 group which shares a corner with four adjacent TO_4 groups through the bridging oxygen atoms; a typical cluster model representing the crystallographic site 1 in ZSM-5 is shown in Fig. 1a. In the monomer cluster models the adjacent T sites are approximated by hydrogen atoms only. The dimer cluster model consists of two TO_4 groups bridged by a commonly shared oxygen. The boundary oxygens are saturated by hydrogen atoms, with hydrogen atoms occupying the position of nearest T site. We carried out calculations for the cluster models whose geometry is derived from the crystal structure of ZSM-5 reported by Van Koningsveld *et al.* [8]. Regular pentamer cluster models with tetrahedral symmetry, in which T-O, O-H, O-T-O, T-O-T and

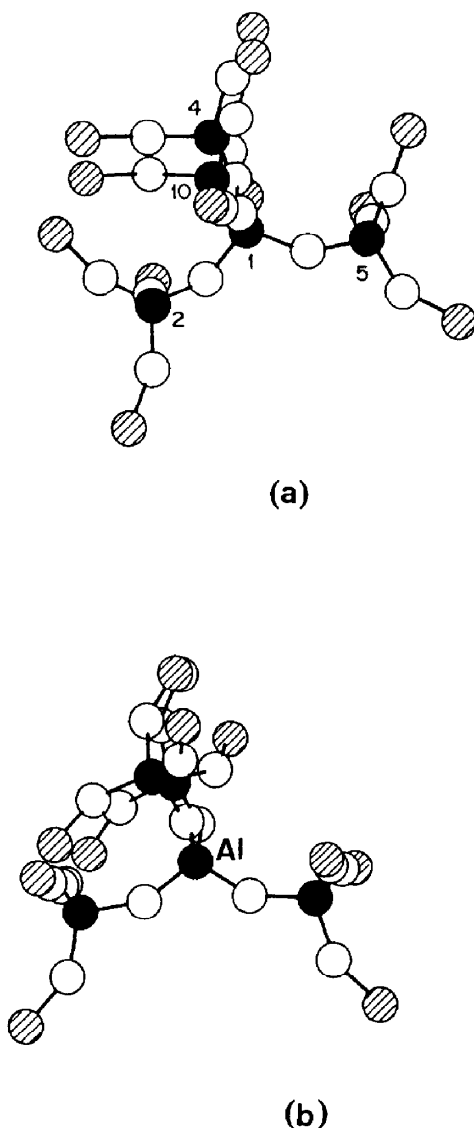


Fig. 1. Typical pentamer cluster models (a) representing the crystallographic site T1 of the ZSM-5 crystal structure surrounded by T2, T4, T5 and T10 sites, as reported by Van Koningsveld *et al.* [8], and (b) representing a regular geometry model with tetrahedral symmetry, where the central Al is surrounded by four silicons; the exact values of various geometrical parameters are explained in the text. Black circles are T (where T=Si or Al), white circles are oxygens and hatched circles are hydrogens.

T-O-T-O parameters had uniform values, were also considered; a typical cluster model is shown in Fig. 1b.

Although non-empirical calculations would be desired, the MNDO technique was adopted as this semi-empirical hamiltonian has been shown to be well parametrized and its predictability matches *ab initio* calculations as described in detail by Redondo and Hay [4]. Further, our interest was to perform a multitude of calculations on different cluster models and derive some unified concepts for which the MNDO method is well suited. The calculations were carried out using the standard MNDO code [9] which is part of the AMPAC (QCPE Program No. 506) in the Silicon-Graphics IRIS work station.

3. Results and discussion

In our earlier study [5] on all-silicon pentamer cluster models, MNDO calculations showed that the favorable Si–O and Si–O–Si parameters were 1.6 Å and 150°. These results correlate well with the average equilibrium geometries of highly siliceous zeolites as derived from experimental structure studies. Before proceeding to the calculations for cluster models with the structure of ZSM-5, we studied Al-containing pentamer clusters with uniform geometry. Then we considered cluster models of different size to represent the twelve distinct crystallographic sites of ZSM-5. The results of these calculations are discussed in the following sections.

3.1. Significance of the cluster geometry

Calculations were carried out for a cluster containing an AlO_4 group attached to four SiO_4 groups in a regular tetrahedral symmetry. All Si–O and O–H distances were 1.60 Å. The O–H distance was purposely kept at 1.6 Å, as the hydrogen atoms are added to represent the adjacent T sites. Previously, calculations were performed [3] with hydrogen in both “water-like” positions at a distance of 0.95 Å from oxygen and “lattice-like” positions at a distance of 1.60 Å. The lattice-like position for hydrogen was reported to create realistic net charges on the boundary oxygens and, hence, we used lattice-like hydrogens to fix the

boundary conditions. A typical pentamer cluster model with Si–O, O–H, O–Si–O, O–Al–O, Al–O–Si, Al–O–Si–O and Al–O values of 1.6 Å, 1.6 Å, 109.47°, 109.47°, 140°, 120° and 1.6 Å, respectively, is shown in Fig. 1b. This cluster model had an overall charge of -1 . Al–O–Si angles were varied from 140 to 170° while the Al–O distances were varied from 1.5 to 1.9 Å. These variations were carried out systematically in steps, and the relative energies calculated for nearly twenty cluster models are shown in Fig. 2. One can see that the energetically favorable Al–O and Al–O–Si values are 1.8 Å and 140°, respectively. It can be noted that, while the preferred Al–O distance is longer than that of Si–O, the preferred Al–O–Si angle is smaller than that of Si–O–Si. Thus, it can be generalized that the T sites with longer T–O and smaller T–O–T values will be preferred for Al substitution.

While more flexibility is allowed in the Al–O bond length, the energy variations are sensitive to Al–O–Si bond angles, and the reverse was found for the silicon pentamer clusters [5]. Although aluminum prefers a smaller Al–O–Si angle, larger Al–O distances are needed to avoid Al—Si non-bonded repulsive interactions. Hence the limiting higher value of 1.8 Å for the Al–O distance controls the Al–O–Si angle. In addition to T–O and T–O–T, the T–O–T–O dihedral angle will also play an important role in the energetics. T–O–T–O determines the orientation of the adjacent TO_4 groups relative to the central TO_4 group. In our calculations, these dihedral angles are uniformly 120°. However, in the ZSM-5 structure, these dihedral angles had quite a variation. The values of the T–O–T–O parameters for a few typical sites in ZSM-5 are shown in Table 1. The correlation between the extent of deviation in the T–O–T–O dihedral angles from the tetrahedral symmetry and the energy of the cluster models are discussed in the following section.

3.2. Significance of the cluster size

Calculations were carried out for cluster models of different size, *viz.* monomer, dimer and pentamer. The geometry of these cluster models was derived from the reported crystal structure [8].

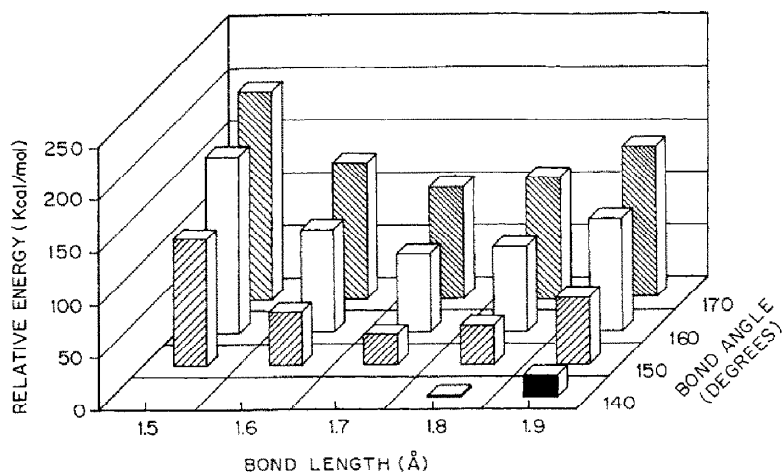


Fig. 2. Variation of the relative energy of the pentamer cluster model $\text{AlO}_4\text{--}[\text{Si}(\text{OH})_3]_4$ shown in Fig. 1b with respect to Al–O bond length and Si–O–Al bond angle. O–Al–O and O–Si–O are uniformly 109.5° , Al–O–Si–O dihedral angles are uniformly 120° and Si–O and O–H distances are uniformly 1.60 \AA . When all the four Al–O distances are 1.8 \AA and Al–O–Si angles are 140° , the total energy of the cluster is minimum with a value of -5690.06 eV . This was treated as the cluster with zero energy, and the energy values of other clusters are calculated relative to this cluster.

The density-of-state curves for typical monomer, dimer and pentamer silicon clusters representing site 1 are shown in Fig. 3. It can be seen that the overall energy band pattern is the same for all clusters, while the number of energy levels for a given energy value (density of states) is increasing with the size of the cluster. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy values for the all-silicon monomer, dimer and pentamer clusters representing site 1 are given in Table 2. The percentage contribution of different atomic orbitals to these molecular orbitals are also included in Table 2. It can be seen that the HOMO and LUMO values and the contribution of atomic orbitals are qualitatively the same for all these clusters. Mainly the 2p orbitals of the oxygens contribute to HOMO values, while the LUMO values get their major share from the 1s orbital of hydrogen. In reality, LUMO will get its contribution from the 3s orbital of Si, since hydrogen atoms are used as proxy to Si in our cluster models to fix the boundary conditions. This trend of an increased contribution from the Si 3s orbital to LUMO can be observed when the cluster size increases from monomer to pentamer. Thus, the cluster models with different sizes are adequately representing the gross

electronic characteristics such as energy of frontier molecular levels and contributions from different atomic orbitals to molecular orbitals.

Further, we analyzed the energetics of the cluster models of varying size which represent different sites in ZSM-5 structure. The energy of the all-silicon clusters and aluminum-containing clusters, in relation to the cluster having the minimum energy, are shown in Table 3 for the monomer, dimer and pentamer cluster models. One can see that the rank ordering of energies of clusters representing various crystallographic sites are the same for all-silicon and Al-containing clusters as long as the size of the cluster is same. However, the predictions by monomer, dimer and pentamer cluster models are not coinciding with each other and, hence, the preferred sites of Al substitutions are also different for clusters with different sizes. Previously [5] we compared the results of the calculations carried out on pentamer clusters representing the structures reported by Olson *et al.* [7] and Van Koningsveld *et al.* [8]. It was found that a pentamer cluster model was needed to satisfactorily predict the rank ordering of aluminum substitution energy at the twelve sites.

In the pentamer cluster models the substitution energy was calculated by considering the following

Table 1
T–O–T–O parameters for few typical crystallographic sites in the ZSM-5 structure [8]

Site No.	Atoms considered	Actual dihedral angles (°)	Difference between two angles (°)	Deviation from 120°
4	Si ₄ –O ₁₇ –Si ₇ –O ₁₃	162.93	120.77	0.77
	–O ₇	42.16	118.51	1.49
	–O ₂₂	–76.35	120.72	0.72
	Si ₄ –O ₃ –Si ₃ –O ₂₀	25.48	118.70	1.30
	–O ₂	–93.22	120.15	0.15
	–O ₁₉	146.63	121.15	1.15
	Si ₄ –O ₄ –Si ₅ –O ₂₁	114.60	115.80	4.20
	–O ₅	–129.60	121.31	1.31
	–O ₁₄	–8.29	122.89	2.89
	Si ₄ –O ₁₆ –Si ₁ –O ₁₅	–113.14	121.94	1.94
	–O ₁	8.80	119.07	0.93
	–O ₂₁	127.87	118.99	1.01
	Average deviation			
8	Si ₈ –O ₁₃ –Si ₂ –O ₁	18.33	118.95	1.05
	–O ₂	–100.62	120.26	0.26
	–O ₆	139.12	120.79	0.79
	Si ₈ –O ₇ –Si ₇ –O ₂₂	140.65	120.77	0.77
	–O ₁₇	19.88	119.28	0.72
	–O ₂₃	–99.40	119.95	0.05
	Si ₈ –O ₈ –Si ₉ –O ₁₈	–123.18	116.29	3.71
	–O ₂₅	120.53	123.54	3.54
	–O ₉	–3.01	120.17	0.17
	Si ₈ –O ₁₂ –Si ₁₂ –O ₁₁	–114.69	119.90	0.10
	–O ₂₄	125.41	118.22	1.68
	–O ₂₀	7.19	121.88	1.88
	Average deviation			
11	Si ₁₁ –O ₁₄ –Si ₅ –O ₅	–90.24	117.62	2.38
	–O ₂₁	27.38	122.09	2.09
	–O ₄	149.47	120.29	0.29
	Si ₁₁ –O ₁₀ –Si ₁₀ –O ₁₅	68.23	117.98	2.02
	–O ₂₆	–173.79	121.39	1.39
	–O ₉	–52.40	120.63	0.63
	Si ₁₁ –O ₁₁ –Si ₁₂ –O ₂₀	–115.87	123.41	3.41
	–O ₁₂	7.54	120.73	0.73
	–O ₂₄	128.27	115.86	4.14
	Si ₁₁ –O ₂₂ –Si ₇ –O ₁₇	33.79	120.84	0.84
	–O ₇	154.63	119.94	0.06
	–O ₂₃	–85.43	119.22	0.78
	Average deviation			
12	Si ₁₂ –O ₂₀ –Si ₃ –O ₁₉	–50.64	118.41	1.59
	–O ₂	–169.05	120.67	0.67
	–O ₃	70.28	120.92	0.92
	Si ₁₂ –O ₁₂ –Si ₈ –O ₁₃	44.27	121.70	1.70
	–O ₇	–77.43	118.62	1.38
	–O ₈	163.95	119.68	0.32
	Si ₁₂ –O ₂₄ –Si ₁₂ –O ₂₀	–176.90	121.65	1.65
	–O ₁₂	–55.25	120.54	0.54
	–O ₁₁	65.29	117.81	2.19
	Si ₁₂ –O ₁₁ –Si ₁₁ –O ₁₀	–51.60	120.55	0.55
	–O ₁₄	68.95	120.52	0.52
	–O ₂₂	–170.53	118.93	1.07
	Average deviation			

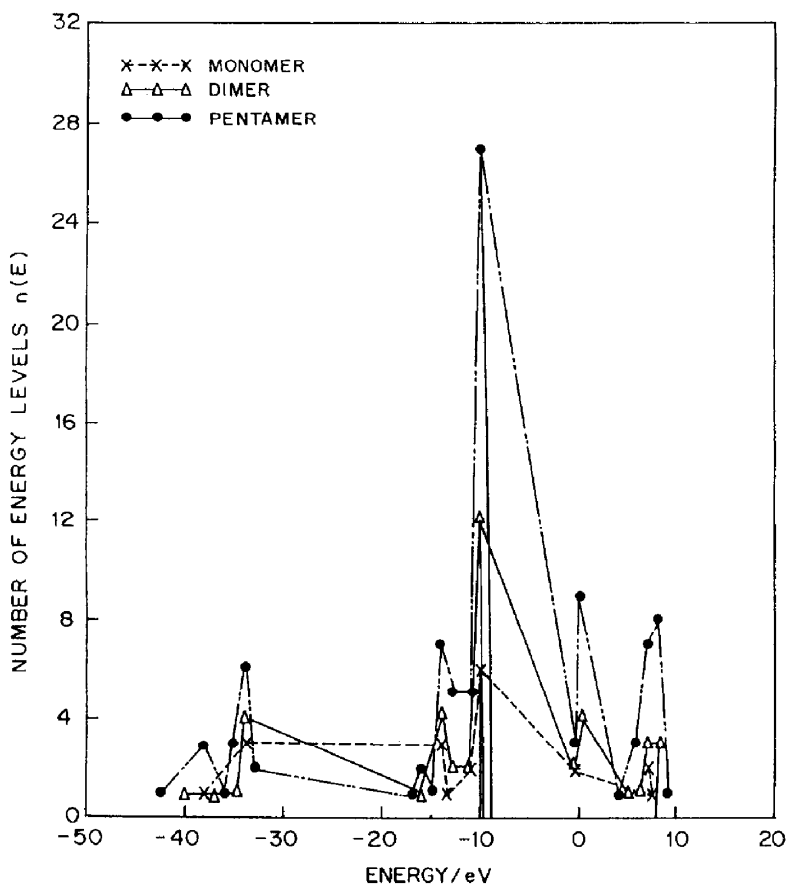
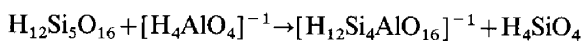


Fig. 3. Density-of-state curves for typical monomer, dimer and pentamer clusters centred at site T1 (all-silicon). The description of the clusters are as given in Table 2. The HOMO levels are shown to indicate the level of occupancy.

process for the substitution:



The substitution energy was lowest for the T4, T8 and T11 sites and highest for the T7 and T12 sites in agreement with their relative total energy values given in Table 3. These results could be correlated to the deviation observed in the T–O–T–O angle as given in Table 1. It was found that the cluster models that have the maximum deviation of the T–O–T–O angle from 120°, such as clusters representing sites T4, T8 and T11, have minimum energy, while that with least distortion, such as clusters representing site T12, has the maximum energy. In fact, it can be seen from Fig. 1b that in a regular tetrahedral structure where the dihedral angles are 120°, the peripheral atoms come too

close within their Van der Waals radii. Thus our results indicate that the sites where the T–O–T–O angle has the largest deviation from 120° are favorable for Al substitution.

4. Conclusions

The quantum chemical calculations performed for pentamer clusters with tetrahedral symmetry and their geometrical variations show the importance of various geometric parameters such as T–O bond length and T–O–T bond angles in determining the energetics. It was found that for the substitution of aluminum by silicon, the sites with higher T–O and lower T–O–T are the preferred ones. Additionally, the effects of the

Table 2

Percentage contribution of different atomic orbitals to the HOMO and LUMO levels and their eigenvalues for clusters with different sizes representing site 1

Atomic orbital	Monomer Si ₁ H ₄ SiO ₄		Dimer Si ₁ -Si ₂ H ₆ Si ₂ O ₇		Pentamer Si ₁ -(Si ₂ ,Si ₄ ,Si ₅ ,Si ₁₀) H ₁₂ Si ₅ O ₁₆		
	HOMO	LUMO	HOMO	LUMO	HOMO	LUMO	
Si	3s	0.09	5.20	0.10	6.14	1.16	8.76
	3p _x	0.01	1.50	0.01	1.35	0.01	0.57
	3p _y	0.02	3.80	0.22	2.02	0.23	2.15
	3p _z	0.18	0.01	0.03	0.15	0.03	0.18
O	2s	0.48	5.65	0.53	5.79	0.60	7.98
	2p _x	24.56	6.74	36.84	1.84	37.97	5.19
	2p _y	47.59	5.33	20.99	16.95	20.23	5.30
	2p _z	25.05	2.28	38.59	0.94	37.95	4.37
H	1s	1.98	69.34	2.66	64.78	2.90	66.52
Eigenvalues (eV)		-9.91	-0.56	-9.63	-0.30	-9.45	-0.55

Table 3

Total energy of monomer, dimer and pentamer models of silicon- and aluminum-substituted clusters in relation with the lowest-energy clusters

Site No.	Relative total energy (kcal/mol)						Relative substitution energy for pentamer (kcal/mol)
	Monomer		Dimer		Pentamer		
	H ₄ AlO ₄	H ₄ SiO ₄	H ₆ SiAlO ₇	H ₆ Si ₂ O ₇	H ₁₂ Si ₄ AlO ₁₆	H ₁₂ Si ₅ O ₁₆	
1	3.37	2.47	6.52	8.32	34.22	22.51	14.50
2	9.25	6.57	8.76	10.31	23.47	15.77	8.72
3	15.80	12.27	13.14	12.71	28.75	18.42	10.49
4	10.19	6.66	7.59	10.03	10.38	9.73	0.81
5	2.67	1.80	6.41	5.42	35.00	20.36	17.46
6	0.00	0.00	3.97	7.54	34.61	23.04	15.27
7	4.77	2.37	9.85	8.23	45.13	26.59	19.83
8	8.99	5.30	4.24	5.14	0.00	0.00	0.00
9	0.39	0.78	0.00	0.00	27.39	15.31	16.17
10	4.20	3.60	2.49	8.83	30.28	21.56	11.81
11	9.78	6.69	4.82	10.08	11.41	5.33	6.69
12	3.27	3.02	10.86	12.54	44.39	29.63	18.19

T-O-T-O dihedral angle have been explored in this work for the first time. The deviation of T-O-T-O from 120° causes the distortion of tetrahedral symmetry and the sites with maximum distortion are the favorable sites for Al substitution.

By comparing the results of the calculations on cluster models representing the ZSM-5 structure of varying size it appears that a pentamer cluster

is needed to locate the siting of heteroatoms in the zeolite framework, since this incorporates the effects of variations in the T-O-T-O angle. In a recent study by Brand *et al.* [10], it is shown that the properties such as proton affinity, hydroxyl stretching frequency and ammonia interaction energy do not show a linear variation as a function of cluster size. Hence, more elaborate calculations and critical analysis of the results are needed in

this direction. The monomer and dimer cluster models which are widely reported in literature predict the gross electronic structure such as the molecular orbital diagram and the individual contributions of atomic orbitals to frontier molecular orbitals. However, the substitution energy could not be reliably predicted since the electronic effects owing to T–O–T and T–O–T–O interactions are absent in the monomer and dimer cluster models, respectively. The ultimate goal of these studies is to work out the contribution of each of the geometrical factors in the stabilization of the zeolite structure, so that the prediction of electronic properties and isomorphous substitution sites could be made possible, once the crystal structure of a zeolite is known.

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