

# Electronic and structural properties of montmorillonite—a quantum chemical study

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## Abstract

The importance of geometry and its relation with property in montmorillonite have been studied in terms of octahedral aluminum and tetrahedral silicon present in the framework. Quantum chemical (QC) calculations were performed using MNDO (modified neglect of differential overlap) and DFT (density functional theory) is reported. Cluster calculations were performed on two octahedral aluminum sites present in the unit cell of montmorillonite to show the distinguishability between the two octahedral aluminums. The energy difference between two aluminum octahedral cluster was 1.12 eV. This was further justified by the calculation of magnesium substitution energy for two different positions of aluminum. This difference in two octahedral aluminum sites was mainly due to the typical orientation of the bridging hydroxyl groups attached with the octahedral aluminums. Calculations were also performed on tetrahedral silica hexagons with and without aluminum substitution to predict the Brønsted acid strength of the surface both by MNDO and DMOL QC methods; which shows that aluminum substitution is an unfavorable process in this type of clay. The above structure property relationship in case of montmorillonite will further help in explaining the catalytic activity of the material. © 1998 Elsevier Science B.V. All rights reserved.

*Keywords:* Framework aluminum and silicon; Montmorillonite; Quantum chemical calculations

## 1. Introduction

The valuable catalytic and adsorptive properties of clays provide ample reason for establishing a firm theoretical understanding of their structure and behavior. Computer simulation studies can contribute significantly in achieving the goal of structure property relationship by the synthesis of current understanding and data, and by their perspicacity in revealing critical con-

ceptual issues whose resolution demands additional experimentation. Monte Carlo simulation is the most studied simulation techniques in case of clays to determine the water content in the interlayer as a function of interlamellar distance [1,2]. There are classical mechanical simulations of adsorption of hydrocarbons on the surfaces of clay minerals [3]. There are very few quantum chemical calculations to correlate the structure and property in case of clay materials [4,5]. Arnowitz et al. [5] used extended Huckel theory to model the isomorphic substitution of  $Al^{3+}$  by other cations in the octahedral layer of

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a dioctahedral smectite. Octahedral aluminum plays a very important role in the catalytic activity of dioctahedral or trioctahedral clay materials. In our earlier studies [6] we compared the DFT results with infrared spectra for isomorphous substitution in Montmorillonite, we have also compared XPS results with density of states as calculated by DFT method [7]. Bailey [8] has shown that monoclinic dioctahedral micas have two independent types of octahedra; one lies on a center of symmetry on the mirror plane for space group  $C_{2/m}$  or on a center of symmetry for  $C_{2/c}$ ; and a pair of equivalent octahedra related to each other by these symmetry elements. The two OH groups of each octahedra lie on the symmetry plane of each layer, for the first octahedra it lies in the *trans* orientation and in the second case it lies at the *cis* position. This leads to an interest in working out a structure property relationship in case of montmorillonite clays which are a member of dioctahedral smectite family.

In the present study we are considering montmorillonite with a formula  $(Na_{0.66}^+, nH_2O)(Al_{3.34}Mg_{0.66})Si_8O_{20}(OH)_4$ , whose crystal structure refinement is not yet established. To clarify the structural characteristics of the clay, we have performed both computer graphics and quantum chemical calculations on localized cluster models of montmorillonite generated from the crystal structure data of pyrophyllite. As a result, the existence of two distinguishable aluminum sites are found like in case of mica [8]. We have also calculated the magnesium substitution energy to verify the distinguishability between the two octahedral aluminums present in montmorillonite unit cell. Our aim was to correlate geometry with energetics to propose a structure property relationship in case of montmorillonite. To correlate Brønsted acidity with catalytic activity of clay resulting from surface substitution, we have also calculated the substitution energy for aluminum substitution in place of tetrahedral silicon. This further helps in explaining the catalytic activity of montmorillonite clay materials.

## 2. Model and methods

The ideal formula of clay montmorillonite used in this study is  $(Na_{0.66}^+, nH_2O)(Al_{3.34}Mg_{0.66})Si_8O_{20}(OH)_4$ . As there is no crystallographic data for this structure, we have created the initial model of montmorillonite from the crystal structure of well-defined dioctahedral clay pyrophyllite having formula  $Si_8Al_4O_{20}(OH)_4$  [9] using INSIGHTII code of BIOSYM version 2.3.5. Montmorillonites are swelling clays made up of a layer of octahedral aluminum oxides between two layers of tetrahedral silicon oxides [10]. It is already known that in natural montmorillonite some Al(III) atoms of the octahedral sites can be replaced by Fe(III), Fe(II) or Mg(II) ions [10] leading to a residual negative charge on the clay compensated by interlayer countercations ( $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ , etc.). Fig. 1 displays a top view of one tetrahedral and one octahedral sheet showing the hexagonal cavities at the oxygen surface of the silicon layers. The two different aluminums and the oxygens attached with them were labeled. The dangling bonds were saturated by hydrogen atoms (not drawn in Fig. 1). In Fig. 1, the dotted silicons were bonded with black aluminums through blank oxygen bridges. The black hydroxyl hydrogens were connected with blank oxygens, only one of them is visible the second one which is just below O2 oxygen is labeled as H1. The hydroxyl at the center of the hexagonal cavity is parallel to the clay surface and pointing in the direction of the vacancy of the octahedral network. The black hydrogen replacing Si attached to O8 oxygen is labeled as H2. The localized cluster model approach to study the crystal lattice properties proposed elsewhere [11] was used. Geometrical parameters have been calculated from the cluster having formula  $Al_2Si_6O_{24}H_{18}$ , composed of six tetrahedral silicons and two octahedral aluminums. Accurate quantum chemical calculations were performed on  $Al(OH)_6$  clusters for two different crystallographic positions of aluminum in the unit cell in coherence with pyro-

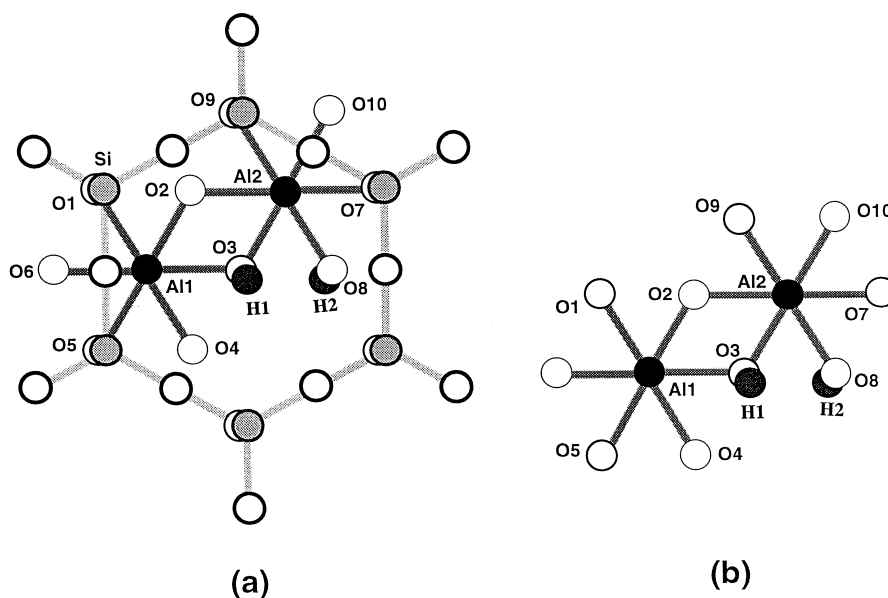


Fig. 1. (a) The cluster model of montmorillonite with six tetrahedral silicons and two octahedral aluminums and (b) the two octahedral aluminums connected to each other by bridging oxygens.

phyllite. The monomer clusters were generated by terminating the bridging oxygen bond between two different aluminum sites as labeled in Fig. 1b and the adjacent silicon or aluminum sites were approximated by hydrogen atoms only. The overall charge on  $\text{Al}(\text{OH})_6$  cluster was  $-3$  and charge on  $\text{Mg}(\text{OH})_6$  cluster was  $-4$ . Aluminum substitution energy has been calculated by substituting the  $\text{Si}(\text{IV})$  by  $\text{Al}(\text{III})$  in the hexagonal cavity of silicates, i.e., with a cluster having formula  $\text{Si}_6\text{O}_{18}\text{H}_{12}$  and also calculated for a suitable dimer cluster generated from the hexagonal cavity having a formula  $\text{Si}_2\text{O}_7\text{H}_6$ , in both cases the atomic positions are according to the crystallographic structure. The dangling bonds were saturated by hydrogen atoms.

Quantum chemical calculations based on density functional theory (DFT) was performed using the DMOL [12] package of BIOSYM Technologies version 2.3.5. The geometry optimization calculations were carried out using a minimal numerical basis set [13]. The total energy for the final optimized geometry was then evaluated using a double numerical polarization basis set [14]. A VWN local type functional [15]

was used for the exchange-correlation energy terms in the total energy expression. The calculations for aluminum substitution were also performed using MNDO approximation, included in the MOPAC program of Quantum Chemistry Program Exchange (QCPE no. 506) and calculation procedure is described by Dewar and Thiel [16]. The static visualization of molecular configurations and the optimized molecular geometries from QC-DFT calculations were made with the INSIGHTII code of BIOSYM Technologies, on a Silicon Graphics IRIS INDIGO2 workstation.

### 3. Results and discussion

#### 3.1. Geometrical parameters

The geometrical parameters obtained from the localized cluster model were given in Table 1. The result shows that although both the aluminums present in the chosen cluster were octahedral in nature but the aluminum located at the center of the cluster [Al(1)] has a longer Al–O bond length in comparison to the aluminum

Table 1  
Geometric parameters

Aluminum(1)		Aluminum(2)		Silicon	
Al–O and Si–O bond lengths in Å					
Al1–O6	1.96	Al2–O2	2.01	Si1–O11	1.60
Al1–O3	1.96	Al2–O7	2.01	Si1–O12	1.59
Al1–O1	2.00	Al2–O3	1.94	Si1–O13	1.59
Al1–O2	2.00	Al2–O8	1.94	Si1–O14	1.44
Al1–O4	2.00	Al2–O10	1.98		
Al1–O5	2.00	Al2–O9	1.98		
Average	1.986		1.976		1.555
O–Al–O and O–Si–O bond angle in degree					
O1–Al1–O2	82.81	O2–Al2–O9	83.45	O14–Si1–O11	107.5
O2–Al1–O3	82.79	O15–Al2–O10	83.89	O11–Si1–O12	111.2
O3–Al1–O4	82.79	O16–Al2–O7	83.45	O12–Si1–O13	110.2
O4–Al1–O5	82.81	O22–Al2–O8	83.00	O13–Si1–O14	108.0
O5–Al1–O6	82.79	O17–Al2–O3	81.30		
O6–Al1–O1	82.79	O3–Al2–O2	83.00		
Average	82.796		83.015		109.22

present diagonal to that [Al(2)], as shown in Fig. 1a. It is also observed from Table 1 that the O–Al–O bond-angle is smaller in case of Al(1) than in Al(2). This shows that Al(1) is more strained than Al(2) in comparison with ideal octahedron. Other geometrical parameters like Si–O bond-length or O–Si–O bond angle are the same in both cases. The Si–O bond with an unusually short bond distance of 1.44 Å is the only one that is attached with the octahedral aluminum through oxygen bridges; the other Si–O bonds with longer bond distances are not attached with octahedral aluminums. The silicons in the hexagonal cavity are all equivalent with same Si–O and Si–O–Si angle. The geometrical parameters show that the distortions from ideal octahedral geometry for both the aluminums were due to the Al–O–Al bridges, Al–O–Si bridges and Al–O–H bridges. This results therefore show that there must be a relation between the energy and geometry of these clusters.

### 3.2. Proof of two different aluminum sites

To confirm the presence of two different types of octahedral aluminums, we have per-

formed DFT calculations using the DMOL package of BIOSYM on both the Al(OH)<sub>6</sub> clusters. Two different –O–H connections are present in these clusters: (i) is the respective silicon replaced by hydrogen (H2) and (ii) is the hydroxyl hydrogen attached with the oxygens of the cluster (H1), which is easily visualized from the cluster shown in Fig. 1a and b. It is also observed that in terms of bond distances the hydroxyl hydrogen (H1) has a bond length of 1.01 Å, whereas the hydrogen replacing Si (H2) has a bond length of 1.44 Å (where H is replacing the Si to keep the crystallographic positions unchanged). Octahedral aluminums are connected with four silicons through bridging oxygens and the rest of the six, i.e., two oxygens are attached with hydroxyl hydrogens (H1). We therefore, put a geometric constrain over the cluster by keeping the positions of the H1 type hydrogens constant and then optimize the full cluster. The results are shown in Table 2. In this case, it is observed that the Al(2) cluster is energetically more stable than Al(1) cluster by 0.04 Ha equivalent to 1.12 eV. When we repeated the calculation by keeping the H2 hydrogen positions fixed (i.e at the initial conformation) the energies of the clusters were the same.

Table 2

DMOL energy values for clusters to show the existence of distinguishable octahedral Al

Property	Aluminum(1)	Aluminum(2)
Total energy (Ha)	-693.2671998	-693.308454
Mg(II) substitution energy (Ha)	-42.8151478	-42.6484189

This proves that the hydroxyl groups attached with octahedral aluminum were playing the crucial role in the variation of energy. This is due to the different conformation of the hydroxyl groups attached with Al(1) and Al(2). This results in the difference in energy between two octahedral sites. Now, to justify the enhanced stability of Al(2) we have substituted both the aluminums in the cluster by magnesium and then calculated the substitution energy for each of the clusters by optimizing the full cluster. The substitution energy values are also incorporated in Table 2. It is observed that the magnesium(II) substituted Al(1) cluster is 0.166 Ha (4.53 eV) more stable than the substituted Al(2) cluster. This difference in energy clearly shows that the magnesium(II) substitution is easier in case of Al(1) rather than Al(2).

The Mulliken population analysis shows a very interesting correlation between charge density on oxygens of the cluster and their geometric properties. The results are shown in Table 3.

Table 3  
Mulliken population analysis results

Al(1)		Mg(1)		Al(2)		Mg(2)	
Atom	Charge	Atom	Charge	Atom	Charge	Atom	Charge
Al1	0.612	Mg1	1.215	Al2	0.431	Mg2	1.015
O1	-0.746	O1	-0.955	O2	-0.892	O2	-1.015
O2	-0.747	O2	-0.967	O3	-0.880	O3	-0.966
O3	-0.749	O3	-0.944	O7	-0.874	O7	-0.951
O4	-0.747	O4	-0.895	O8	-0.880	O8	-0.942
O5	-0.746	O5	-0.949	O9	-0.842	O9	-1.022
O6	-0.749	O6	-0.968	O10	-0.858	O10	-1.024
H1	0.130	H1	0.098	H2	0.286	H2	0.138
H2	0.128	H2	0.110	H3	0.299	H3	0.125
H3	0.153	H3	0.049	H7	0.209	H7	0.149
H4	0.153	H4	0.033	H8	0.354	H8	0.123
H5	0.154	H5	0.038	H9	0.431	H9	0.194
H6	0.152	H6	0.135	H10	0.314	H10	0.210

It is observed that aluminum in Al(1) cluster is having a more positive charge of 0.181 than the aluminum of Al(2) cluster. Similar trend is observed in case of magnesium. The difference in charge density on aluminum results from the difference in geometry of the two clusters, as we have emphasized earlier the basic difference between the two clusters is the difference of Al–O bond length, O–Al–O bond angle and the difference in the orientation of hydroxyl groups attached with the octahedral aluminums. The hydroxyl hydrogen nearer to the cluster, i.e. H2 type affects the charge density of oxygen to a more extent than the H1 type of hydrogen present in hydroxyl group. This is because the H2 type hydrogen comes closer to the bridging oxygen, and an electronic interaction is predicted which is observed from the charge density values given in Table 3. The variations of charge density on oxygens in the Al(OH)<sub>6</sub> cluster with respect to Al–O bond length and O–Al–O bond angle have been shown in Fig. 2. It is observed that charge density on oxygen is directly proportional to the O–Al–O bond angle and inversely proportional to the Al–O bond length. For magnesium substituted cluster models also, the same correlation is valid with all the oxygen atoms attached to magnesium having uniformly more negative charge. The energy

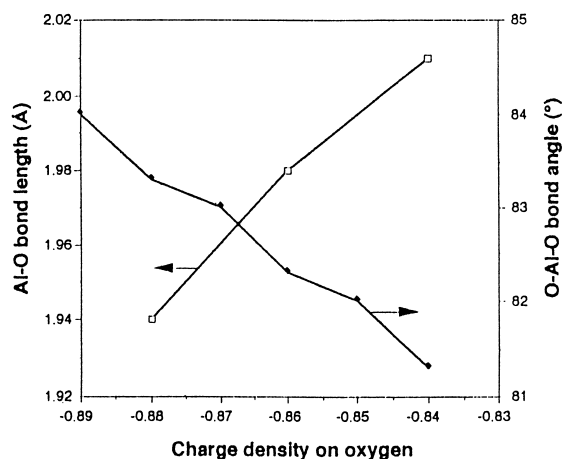


Fig. 2. The variations of charge density on oxygens in Al(OH)<sub>6</sub> cluster with respect to Al–O bond length and O–Al–O bond angle.

variations were due to the combined factors of Al–O and O–Al–O parameters but their contributions were not equal.

To explain the observations of charge density calculations it is better to see the occupancies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Isomorphous substitution of an  $\text{Al}^{3+}$  ion at an octahedral site by  $\text{Mg}^{2+}$  was treated as was the case in which both octahedral sites initially were empty (each possessed a formal excess charge of  $-3$ ) followed by subsequent substitution by the above metal ion at one vacant site. It is noted that the nature of the highest filled orbitals do not change drastically regardless of the specific cation in the octahedral site. These HOMOs are basically centered on oxygens composing the octahedral layer framework. The filled orbitals are pushed up with respect to the valence band for magnesium substitution. Similarly, the LUMOs are interspersed in a conduction band. The highest filled orbitals are essentially localized in regions of specific octahedral sites, and the conduction band molecular orbitals are diffuse. Hence, promotion of an electron from a localized site to the conduction band affects the entire system.

### 3.3. Significance of cluster geometry

The importance of the geometry in controlling the electronic properties is studied. A typical aluminum octahedra was chosen from our clusters. The dangling bonds are saturated with hydrogen. The cluster model has an overall charge of  $-3$ . The geometric parameters given in Table 1 show that the system has a distorted structure, now to include the distortion in the model the clusters were optimized by keeping the terminal hydrogens fixed. The variation of relative energy of the  $\text{Al}(\text{OH})_6$  cluster with respect to Al–O bond length and O–Al–O bond angle (bridging) has been shown in Fig. 3. When all Al–O distances are  $1.98 \text{ \AA}$  and O–Al–O angles (bridging) are  $82^\circ$ , the total energy of the cluster model is minimum with the value

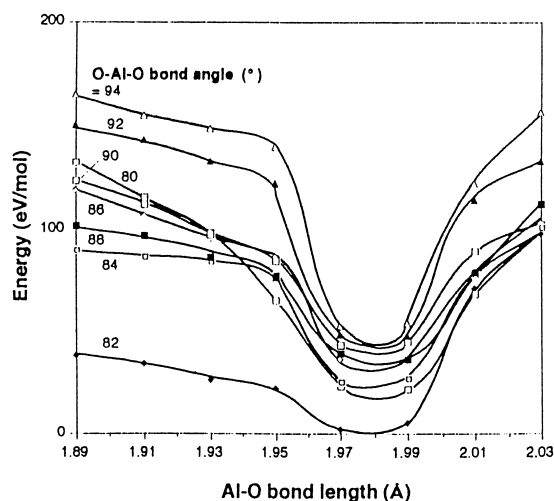


Fig. 3. The variation of relative energy of  $\text{Al}(\text{OH})_6$  cluster with respect to Al–O bond length and O–Al–O bond angle (bridging).

$-18912.7$ . This is a situation of maximum distortion resulting in a greater stability. This was treated as a cluster with zero energy and the energy values of other clusters are calculated relative to this cluster. O–Al–O bond angles (bridging) were varied from  $80^\circ$  to  $95^\circ$  while the Al–O bond lengths were varied from  $1.7$  to  $2.0 \text{ \AA}$ . These variations were carried out systematically in steps. The energetically favorable Al–O and O–Al–O values were  $1.98 \text{ \AA}$  and  $82.0^\circ$ , respectively. It was observed that the preferred ranges for Al–O bond length was  $1.97$  to  $1.99 \text{ \AA}$  in a regular octahedral arrangement. The energy values are sensitive to minor deviations in the O–Al–O (bridging) bond angle, whereas respectively more flexibility is allowed in the Al–O bond length. In other words the contribution of the O–Al–O variation from equilibrium causes a lot more strain in the lattice than when Al–O varies from equilibrium value. So it can be predicted that Mg substitution will be favorable with a shorter Al–O bond distance and longer O–Al–O bond angle. From this model, it is observed that all these parameters contribute to a different extent in minimizing the strain in the lattice. This shows that the geometry has a marked effect on the electronic properties of the system.

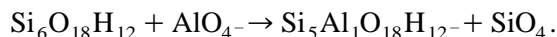
Table 4

Calculation of Al substitution energy at tetrahedral Si using both MNDO and DMOL

Property	Si <sub>6</sub> O <sub>18</sub> H <sub>12</sub>	Si <sub>5</sub> AlO <sub>18</sub> H <sub>13</sub>	Si <sub>3</sub> Al <sub>3</sub> O <sub>18</sub> H <sub>15</sub>
(a) MNDO results			
Total energy (eV)	−6531.3808	−6505.0972	6452.6129
Substitution (eV)	−	8.5623	21.2398
(b) DMOL results			
Property	Si <sub>2</sub> O <sub>7</sub> H <sub>6</sub>	Si <sub>1</sub> Al <sub>1</sub> O <sub>7</sub> H <sub>7</sub>	
Total energy (Ha)	−1103.8353	−1057.4562	
Substitution energy (Ha)	−	0.1203	

### 3.4. Calculation of aluminum substitution energy

We have chosen the tetrahedral silica hexagon for this study. The geometrical parameters given in Table 1 show that all the silicons are equivalent in nature, with a smaller bond length for the silicon attached to the octahedral aluminum through oxygen bridge. We have performed MNDO calculations for all silica cluster with formula Si<sub>6</sub>O<sub>18</sub>H<sub>12</sub>, one aluminum and five silicons with an additional proton on the oxygen bridge to balance the charge having formula Si<sub>5</sub>AlO<sub>18</sub>H<sub>13</sub>, and a cluster with three silicons and three aluminums with three additional protons on the respective bridging oxygens to balance the charge of the cluster having a formula Si<sub>3</sub>Al<sub>3</sub>O<sub>18</sub>H<sub>15</sub>. The results are given in Table 4a. The total energy values show that the aluminum substitution in place of tetrahedral silicon is not a favorable process. It is observed that with incorporation of aluminum the system gets more destabilised to show that the additional protons on the system undergoes interaction with bridging oxygens. The substitution energy values for the substitution of SiO<sub>4</sub> unit by AlO<sub>4</sub> unit have been calculated by the following equation:



The substitution energy values given in Table 4a shows that the substitution of aluminum is an unfavorable process. To verify the results of a semiempirical calculation we have generated a

dimer cluster from the hexagonal silicon cavity with a formula Si<sub>2</sub>O<sub>7</sub>H<sub>6</sub>, which is two tetrahedral SiO<sub>4</sub> units connected through oxygen bridges. We have substituted one silicon by one aluminum to generate a cluster with formula SiAlO<sub>7</sub>H<sub>7</sub>, with an additional proton on the bridging oxygen to balance the charge on the cluster. We have performed DMOL calculations on both all silicon and one silicon and one aluminum cluster. The results are shown in Table 4b. The total energy confirms the earlier result. The substitution energy has been calculated by using the above equation. It is observed that the aluminum substitution in a dimer cluster is also energetically unfavorable. The Mulliken

Table 5  
Mulliken population analysis results

Si <sub>2</sub> O <sub>7</sub> H <sub>6</sub>		Si <sub>1</sub> Al <sub>1</sub> O <sub>7</sub> H <sub>7</sub>	
Atom	Charge	Atom	Charge
Si	0.947	Al	0.861
Si	0.942	Si	1.016
O	−0.552	O	−0.864
O	−0.755	O	−0.771
O	−0.757	O	−0.860
O	−0.763	O	−0.882
O	−0.763	O	−0.776
O	−0.834	O	−0.961
H	0.583	H	0.606
O	−0.736	O	−0.706
H	0.448	H	0.434
H	0.589	H	0.589
H	0.533	H	0.569
H	0.548	H	0.548
H	0.569	H	0.544
		H	0.651

population analysis results are shown in Table 5. It is observed that the charge density on oxygen increases in a considerable amount in case of aluminum substituted cluster. As observed from the results that Al substitution in clay surface is an unfavorable process; this will further predict the infeasibility of surface acidity resulting from the deprotonation of the bridging hydrogen which will be shown in our future studies.

#### 4. Conclusions

We have performed a quantum chemical calculation over a critical structure of montmorillonite whose crystal structure refinement is not yet established. We have shown by our studies that there are two distinguishable aluminum octahedral sites present in the unit cell of montmorillonite. Our finding is based on the geometrical parameters which are different for two distinguishable aluminums. It is also observed from the DFT results that the difference in two aluminums were due to the different conformation of hydroxyl groups attached with octahedral aluminums. The molecular orbital picture clarifies the weak catalytic activity of montmorillonite as observed from the DFT calculation. From the charge density calculation it can be concluded that the charge density on oxygen is inversely proportional to the Al–O bond length and directly proportional to O–Al–O bond angle. Charge density on oxygen has been shown to be indicative of the strength of Brønsted acidity of the sites in case of zeolites [11]. Same correlation may be observed in case of clays.

These findings justify our novel approach to propose the identification of two different kinds of aluminum present in montmorillonite unit cell. It is observed that all the silicons present in the tetrahedral position are geometrically equivalent. The MNDO and DFT calculation results show that the substitution of tetrahedral silicons by aluminum is an unfavorable process, which justifies the low acidity of this variety of montmorillonite. The above finding is a step forward toward explaining the low catalytic activity of montmorillonites.

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