

A MOLECULAR ORBITAL APPROACH TOWARD SOFT-MECHANOCHEMICAL SYNTHESIS FROM THE VIEW POINT OF HETERO-METALLOXANE BONDING UNDER MECHANICAL STRESSING

Y. Fujiwara¹, T. Isobe¹, M. Senna¹, J. Tanaka²

¹Faculty of Science and Technology, Keio University, Yokohama 223-8522, Japan

²National Institute for Research in Inorganic Materials, Tsukuba 305-0044, Japan

Key words: mechanochemistry, coordination number, calcium silicate, molecular orbital calculation, chemical shift

Abstract: Criteria of formation of amorphous complex oxide via a mechanochemical route were explored via a molecular orbital calculation. A discrete variational (DV-) $X\alpha$ method was applied to calculate the magnitude of bond order (BO) between metal and oxygen on the basis of the Mulliken population analysis, which was the criterion of the stabilization of Me(I) - O - Me(II) bonds. A model reaction systems comprising $\text{Ca}(\text{OH})_2$ and SiO_2 was chosen. A water molecule is found to form preferentially from a hydroxyl group of $\text{Ca}(\text{OH})_2$ and proton from surface silanol, when a calcium hydroxide comes close enough to SiO_2 with surface silanol groups. Decrease in the coordination number (CN) for Ca in $\text{Ca}(\text{OH})_2$ increases the BO between Ca and O. These changes in BO favor the formation and stabilization of Ca-O-Si bridging bonds. Calculated results are in good agreement with the experimental observation toward calcium silicate during milling a mixture of $\text{Ca}(\text{OH})_2$ and SiO_2 . An apparent chemical shift of Si 2p is observed by x-ray photoelectron spectroscopy on the milled mixture of $\text{Ca}(\text{OH})_2$ and SiO_2 . The shift is attributed to the formation of a tricalcium silicate, Ca_3SiO_5 , as confirmed calculating the transition state of Si 2p.

1. INTRODUCTION

Mechanical stress makes dissimilar particles attach with each other. Simultaneously, local plastic deformation derived from shear stress at contact points of two particles results in structural disorder or partial amorphization, and increase in amount of low coordinated atoms [1]. Dislocations or vacancies around low coordination number (CN) atoms cause atomic transport called mechanical diffusion, ending up with chemical reaction [2]. This process leads raw materials to a highly reactive precursor toward a final product. For example, a milled mixture comprising $\text{Ca}(\text{OH})_2$ and SiO_2 serves as a precursor of a calcium mono-silicate [3].

A soft-machanochemical process, in which metal hydrates or hydroxides are used as the raw materials, precursors of complex oxides are obtained for the systems $\text{Ca}(\text{OH})_2$ - SiO_2 mentioned above, $\text{Mg}(\text{OH})_2$ - TiO_2 [4], and in many other systems, which are often difficult to obtain via a conventional ceramic route [5,6].

As a result of milling a mixture of $\text{Ca}(\text{OH})_2$ and SiO_2 , Ca-O-Si hetero-metalloxane bridging bonds (HMB) were formed together with dehydration [7], followed by the formation of a precursor of a calcium mono-silicate. Furthermore, we examined Si_{2p} electrons by x-ray photoelectron spectroscopy (XPS) for a milled mixture of $\text{Ca}(\text{OH})_2$ and SiO_2 [3], and found that only near surface Si atoms exhibit lower binding energy. However, we did not observe any significant chemical shift in separately milled SiO_2 sample. Therefore we attribute the chemical shift results to a mechanochemical reaction, to form hetero-metalloxane bonds [8].

In this study, we try to confirm suggestions mentioned above by a Discrete variational X alpha molecular orbital method (DV- $X\alpha$), and to find a clew to dissolve a mechanism of soft- mechanochemical reaction.

2. METHODS OF CALCULATION

2.1 Focus of this study

In the present study, we aim to examine the following items;

(1) Whether, how and to what extent does mechanochemical dehydration take place between a hydroxyl group of $\text{Ca}(\text{OH})_2$ and surface silanol group of SiO_2 ?

(2) What are the effects of decreasing the coordination number for Ca, i.e., the number of oxygen atoms around a Ca atom, on the probability of the bridging hetero metalloxane bonds, Ca-O-Si?

(3) Why does a Si_{2p} binding energy change after milling the $\text{Ca}(\text{OH})_2$ and SiO_2 mixture?

The last item may also confirm the validity of the entire calculation. We here carry out a DV- $X\alpha$ in order to examine the three headings mentioned above.

2.2 DV- $X\alpha$ method

$X\alpha$ method is based on the assumption that exchange correlation potential, μ_{XC} , is proportional to the third root of an electron density, i.e., $\mu_{XC}(\rho) = -(3\alpha/2)(3\rho/\pi)^{1/3}$, where, α is the parameter to reproduce experimental valence orbital energy (eigenvalues) of each atom. ρ is the electron density [9], and π is the ratio of the circumference (of a circle) to its diameter. The constant α is often fixed at 0.7 [10].

DV - $X\alpha$ method is widely used from light to heavy atoms for its convenience [9]. Hamiltonian potential was made by a self-consistent charge (SCC) method [9] on the basis of spherical electrostatic potential and Mulliken's population analysis [11].

Necessary parameters were rationally determined by restricting the potential area in an attempt to better conversion of the calculation. The depths of the well potential were chosen to be -4.0 Hartree for Ca and -2.0 Hartree for other atoms, and their widths of well potential were chose to be 2.0 ± 0.2 atomic units. Molecular orbitals were numerically calculated by linear combination of atomic orbitals (LCAO). Basis sets were adopted from available orbitals, i.e., Ca:1s~4s,3d,4p, O:1s~2p, Si:1s~3s,3p,3d and H:1s. Details of these conditions are given elsewhere [12].

2.3 Practical aims for calculations

According to these two features of $X\alpha$ approximation mentioned above, we can calculate an electron population density of chemical bonds in a model containing a limited number of atoms, i.e., a cluster, cut out of a solid crystal, to represent properties of the bulk. The cluster can be cut out of an interface of

two crystals, e.g., $\text{Ca}(\text{OH})_2$ - SiO_2 interface. Actually, we evaluated an electron population density by a bond order between two atoms, which is based on the Mulliken's population analysis. Furthermore, we can calculate electron transition energy during ionization of one Si_{2p} electron, by means of calculation of Si_{2p} orbital energy with a half of Si_{2p} electron removed.

First, we calculated the bond order between an oxygen atom of Ca-OH and a hydrogen atom of Si-OH. For this calculation, we examined whether the mechanochemical dehydration occurs due to the two types of OH groups, leading to the decrease in the coordination number of OH groups for the calcium atom of this Ca-OH bond. Next, we calculated the bond order between a calcium atom of Ca-OH and an oxygen atom of Si-O. The coordination number of OH groups for this Ca atom is varied from 6-fold, which is the number of full-coordinated Ca atom, to 3-fold, which corresponds a bare Ca atom on $\text{Ca}(\text{OH})_2$ surface. We here study effects of decreasing the coordination number for Ca atom on the stability of the Ca-O-Si HMB. Finally, we calculated a transition energy [13] during ionization of Si_{2p} electron in some clusters of Si compounds which exist during milling a mixture of $\text{Ca}(\text{OH})_2$ and SiO_2 . In this calculation, we pursued the origin of a chemical shift of Si_{2p} binding energy observed by XPS for a milled $\text{Ca}(\text{OH})_2$ - SiO_2 mixture.

2.4 Procedures of calculations

2.4.1 Mechanochemical dehydration reaction between $\text{Ca}(\text{OH})_2$ and surface silanol

We made a model structure of mechanochemical interfacial reaction, shown in Fig. 1. This model consists of $\text{Ca}_1(\text{OH})_6^{4-}$ cluster, a group of atoms cut out of $\text{Ca}(\text{OH})_2$ crystal surface, and $\text{Si}_1\text{O}_4\text{H}_2^{2-}$ cluster with one SiOH group on the surface. This is cut out of β -cristobalite surface, which is the simplest model of SiO_2 because of 180 degrees of all the Si-O-Si angles. Bond orders between atoms on each cluster are evaluated as a function of a distance between $\text{Ca}(\text{OH})_2$ and SiO_2 .

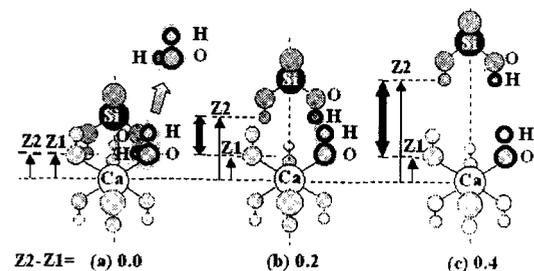


Fig. 1 ($\text{Ca}(\text{OH})_6^{4-}$ - $\text{SiO}_4\text{H}_2^{2-}$) cluster calculated for $\text{Ca}(\text{OH})_2$ - SiO_2 interface.

(a): difference in the Z coordinate, Z_2-Z_1 is 0.0nm.
(b): $Z_2-Z_1=0.2\text{nm}$, (c): $Z_2-Z_1=0.4\text{nm}$.

The inter-cluster distance, Z_2-Z_1 is defined in Fig. 1, as the difference between the Z coordinate of the oxygen atoms of surface OH groups in $\text{Ca}_1(\text{OH})_6^{4-}$ and a hydrogen atom of surface Si-O₁ bond in $\text{Si}_1\text{O}_4\text{H}_2^{2-}$. Since the X and Y coordinates of these atoms are different, diatomic distance between these atoms becomes 0.1 nm at $Z_2-Z_1=0.0$.

Madelung potential for $\text{Ca}(\text{OH})_2$ was built in order to rationalize the $\text{Ca}_1(\text{OH})_6^{4-}$ cluster as similar to the surface state of $\text{Ca}(\text{OH})_2$ as possible. At first, a spherical or a hemispherical symmetry of the electrostatic potential around the cluster is postulated to set the same electrostatic potential around equivalent sites of atoms. Since we cannot take the infinite atomic layers of Madelung potential into account, we have to cut off crystals for Madelung potential within a finite

radius from the center of the cluster. Then, we try to neutralize the total charge of all the laid atoms for Madelung potential in order to create appropriate Madelung potential. Accordingly, the total number of atoms in a cluster and around the cluster is set to be 154 of Ca atoms, 309 of oxygen atoms and 309 of H atoms including one Ca atom, 6 oxygen atoms and 6 hydrogen atoms of the $\text{Ca}_1(\text{OH})_6^{4-}$ cluster. The surrounding atoms are laid within a sphere of the radius 1.47nm. Total charge of the surrounding atoms is -1 valence unit. For a $\text{Si}_1\text{O}_4\text{H}_2^{2-}$ cluster, Madelung potential is less important because of the lower ionicity of Si-O bonds. We nevertheless put atoms for Madelung potential in order to keep potential balance with that of $\text{Ca}(\text{OH})_2$. In total, numbers of atoms are 85 Si atoms and 174 oxygen atoms, including one Si atom and 4 oxygen atoms of the $\text{Si}_1\text{O}_4\text{H}_2^{2-}$ cluster. The surrounding atoms were laid within the radius of 1.19nm, and total charge of the surrounding atoms is -4 valence units.

2.4.2 Reaction at $\text{Ca}(\text{OH})_2$ - SiO_2 interface

As shown in Fig. 2, we here use clusters of $\text{Ca}_7(\text{OH})_{12-n}^{(2+n)+}$ and $\text{Si}_4\text{O}_{13}^{10-}$, the latter representing the (111) surface of β -cristoballite after deprotonation. We vary the value n , i.e., the coordination number of oxygen atoms from OH for Ca from 6 to 3. We calculated a bond order for HMB, Ca-O₁-Si, from a Ca atom of the $\text{Ca}_7(\text{OH})_{12-n}^{(2+n)+}$ cluster and an Si-O₁ dangling bond of the $\text{Si}_4\text{O}_{13}^{10-}$ cluster.

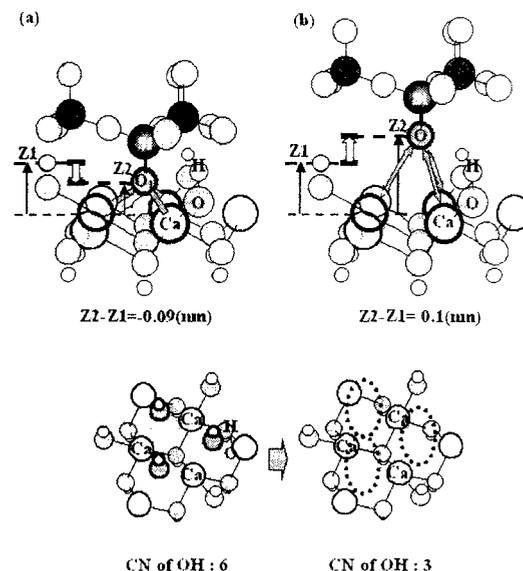


Fig. 2 ($\text{Ca}_7(\text{OH})_{12-3}^{(2+3)+}$ - $\text{Si}_4\text{O}_{13}^{10-}$ - H^9) cluster model.

Madelung potential for $\text{Ca}(\text{OH})_2$ was laid around the cluster. Total number of atoms in and around the cluster was 243 for Ca, 487 for O, and 487 for H within the radius of 1.73nm. We also put atoms for Madelung potential for SiO_2 . Numbers of atoms in and around a cluster are 162 Si atoms and 323 oxygen atoms within the radius of 1.44nm. As the function of the inter-cluster distance, Z_2-Z_1 , shown in Fig. 2, is defined as the difference between the Z coordinate of the oxygen atoms of surface OH groups in $\text{Ca}_7(\text{OH})_{12-n}^{(2+n)+}$ and hydrogen atom of surface Si-O₁ bond in $\text{Si}_4\text{O}_{13}^{10-}$.

In order to form a bond between calcium and oxygen atoms in these clusters, the distance between a surface calcium atom in $\text{Ca}_7(\text{OH})_{12-n}^{(2+n)+}$ and an oxygen atom of Si-O₁ bond in $\text{Si}_4\text{O}_{13}^{10-}$ needs to be close to 0.24nm which correspond to a average Ca-O bond length in $\text{Ca}(\text{OH})_2$ crystal at 293K [14]. The condition is realized by $Z_2-Z_1=$

-0.09, therefore, Z2-Z1 was varied between -0.09 and 0.1nm.

2.4.3 Change in Si_{2p} transition energy

Model clusters for Si_{2p} transition energies are the follows.

- A model cluster of Ca_3SiO_5 , $Ca_{12}Si_1O_{14}^0$ is prepared. This complex oxide is created at the interface between $Ca(OH)_2$ and SiO_2 as a first product of the present reaction [3]. Furthermore,
- the cluster at $Ca(OH)_2$ - SiO_2 interface, $Ca_7(OH)_{12-n}^{(2+n)+}$ and $Si_4O_{13}^{10-}$,
- a cluster of β -crystalalite (111) surface with surface silanol terminating, $Si_4O_{13}H_1^{9-}$, and
- bulk clusters of β -crystalalite are adopted for the calculation of transition energy of Si_{2p} .

In order to delineate the transition state of Si_{2p} in the course of electron detachment, half electrons of Si_{2p} is reduced. Madelung potential was built for each cluster. For the Ca_3SiO_5 cluster, 207 Ca atoms, 69 Si atoms, and 345 oxygen atoms are laid with a spherical symmetry within the radius of 1.26nm. Meanwhile, surrounding atoms for $Ca(OH)_2$ - SiO_2 interface are the same as the previous section. For the β -crystalalite (111) surface clusters, 162 Si atoms and 323 oxygen atoms are laid with a hemispherical symmetry within the radius of 1.44nm. For the bulk cluster of β -crystalalite, 239 Si atoms and 476 oxygen atoms are laid with a spherical symmetry within the radius of 1.40nm.

3. RESULTS AND DISCUSSION

3.1 Reaction at $Ca(OH)_2$ - SiO_2 interface (i) Dehydration

As the distance Z2-Z1, defined in Fig. 1, decreases, the bond order between an O(Ca), i.e., the oxygen atom from $Ca_1(OH)_6^{4-}$ and a H(sil), the hydrogen atom from the surface silanol in $Si_1O_4H_2^{2-}$, increases, as shown in Fig. 3. At the same time, a bond order between Ca and O within $Ca_1(OH)_6^{4-}$, and between O and H of the surface silanol unit in $Si_1O_4H_2^{2-}$ decrease. These synchronized changes clearly favor the formation of a new bond between the oxygen atom of $Ca(OH)_2$ and the hydrogen atom from silanol, with a simultaneous weakening of the two bonds in a reactant mixture, i.e., Ca-O and Si-O-H. This favors our postulation that a water molecule is formed from the OH group in $Ca(OH)_2$ and the surface silanol group, leading to dehydration which was actually observed during mechanochemical processes [3].

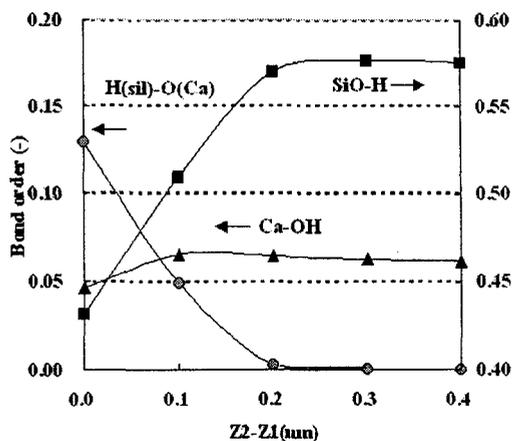


Fig. 3 Bond order between H of SiOH and O of CaOH in $(Ca(OH)_6^4-SiO_4H_2^2-)$ cluster.

3.2 Reaction at $Ca(OH)_2$ - SiO_2 interface (ii) HMB formation

A distance between Ca atom and the oxygen atom,

Ca-O₁, becomes 0.2405nm at Z2-Z1= -0.09, which is near to the literature value from a lattice constant of $Ca(OH)_2$ crystal, 0.24nm [14]. Therefore, we compared the bond orders between atoms in $Ca_7(OH)_{12-n}^{(2+n)+}$ cluster and in $Si_4O_{13}^{10-}$ cluster at Z2-Z1= -0.09 as the change in the CN of oxygen atoms from OH for Ca from 6 to 3. We here found two significant trends in changes of the bond orders. One is the change of a bond order between the Ca atom and the O₁ atom, which are, respectively, the calcium atom of Ca-OH bond in $Ca_7(OH)_{12-n}^{(2+n)+}$ cluster and the oxygen atom of Si-O₁ bond in $Si_4O_{13}^{10-}$ cluster. The other is a change of bond orders between the O₁ atom and the other O atoms, which are an oxygen atom of Si-O₁ bond mentioned above and its neighboring oxygen atoms of Ca-OH bonds in $Ca_7(OH)_{12-n}^{(2+n)+}$ cluster. At first, a bond order between the Ca atom and the O₁ atom increases with decreasing the CN for Ca in $Ca(OH)_2$. This behavior is consistent with the previous report [12].

Furthermore, an absolute value of a bond order of O₁-O was reduced with decreasing the CN for Ca in $Ca(OH)_2$. A negative bond order represents that the anti-bonding orbitals are occupied dominantly over the bonding orbitals between an O₁ atom and the other O atoms. Accordingly, severe exchange repulsion occurs due to a repulsive electrostatic interaction between electron clouds of two atoms. Therefore, the decrease in the OH groups in $Ca_7(OH)_{12-n}^{(2+n)+}$ cluster leads to be free from significant large repulsion between the silanoic oxygen atom of $(Si_4O_{13})^{10-}$ and the other oxygen atoms of OH groups in $Ca_7(OH)_{12-n}^{(2+n)+}$. Thus, the decrease in OH groups in $Ca(OH)_2$ surface results in the formation of Ca-O₁ bond toward Ca-O₁-Si HMB because of the possibility of $Ca(OH)_2$ to come close enough to SiO_2 during milling.

3.3 The effects of decreasing the coordination number for Ca on the stability of the Ca-O-Si

In this section, we discuss the reason for the increase of the bond order between Ca atom and O₁ atom with decreasing the CN for the Ca atom in $Ca(OH)_2$. We notice an electronic structure of $Ca(OH)_2$ and their variation with the CN of OH groups for a centered calcium atom of each cluster.

An electronic structure of a calcium atom with full-coordination remains unchanged regardless of the atomic position, either in bulk or on the surface. However, when the calcium atom is under-coordinated from 5-fold to 3-fold, a hybrid orbital is created, which consists of Ca_{4s} and Ca_{4p} and is distributed against the surface atoms toward the vacuum or atomic vacancies. Furthermore, the eigenvalue of hybrid orbital has lower energies as decreasing the CN of OH groups.

When the surface Ca atom with lower CN combines with an oxygen atom from a Si-O₁ bond in SiO_2 surface, a lowered orbital energy of the Ca atom with smaller energy difference against the O_{2p} of Si-O₁ bond, triggers a further hybridization between the orbitals of the calcium atom and those of the oxygen atom, resulting in the formation of a chemical bond with higher covalency [15].

3.4 Change in Si_{2p} transition energy

We showed transition energies during removing one Si_{2p} electron in the clusters in Fig. 4 (a) - (d). As shown in Fig. 4 (c), Si_{2p} transition energy of the silica with a surface silanol group is eventually the same as that of bulk silica, and is never lower than that of bulk, as shown in Fig. 4 (d). This agrees with the invariance of the Si_{2p} binding energy when silica is milled alone [3]. However, as shown in Fig. 4 (a), the transition energy of Si_{2p} in Ca_3SiO_5 is known to be lower by 2eV than that of bulk silica. This is caused by the difference of the Madelung potential and bonding characters [16,17] between SiO_2 and Ca_3SiO_5 . This tendency favors with

the experimental fact, that the Si_{2p} binding energy of the $\text{Ca}(\text{OH})_2$ - SiO_2 mixture decreased by 2eV after milling for 3h [3]. We therefore suggest that the reduction of Si_{2p} results not only from the increased SiO_2 surface area but much more importantly, from incipient formation of complex oxide, Ca_3SiO_5 , i.e., as the nuclei of calcium silicates at the surface of a milling mixture.

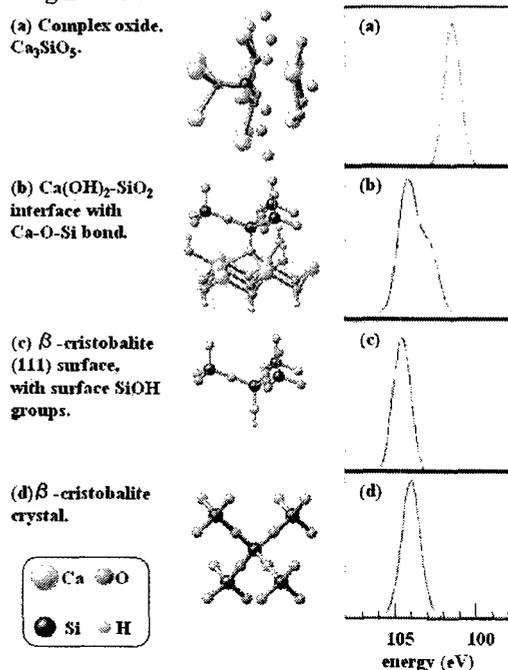


Fig. 4 Calculated Si_{2p} transition energy.

Meanwhile, Si_{2p} transition energy of the cluster with $\text{Ca-O}_1\text{-Si}$ HMB is split into two as shown in Fig. 4 (b), and the lower one is by 1eV smaller than that of bulk silica. The separation to bimodal peak might be attributed to the asymmetric electrostatic potential created in the different surfaces. However, no experimental results correspond to the result in Fig. 4 (b) are observed. This might be attributed to the neglect of atomic displacements at the $\text{Ca}(\text{OH})_2$ -

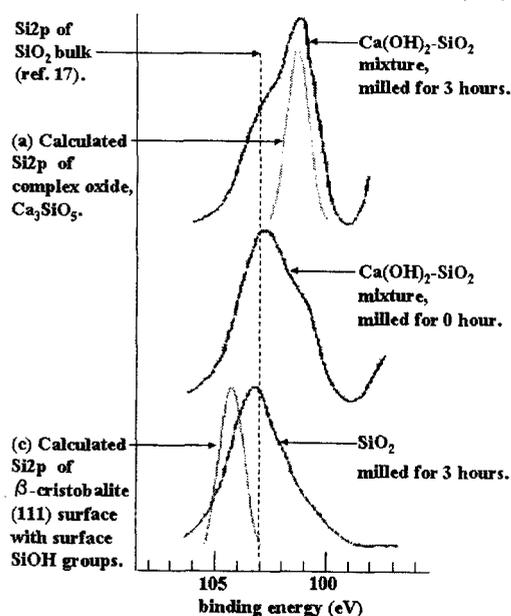


Fig. 5 X-ray photoelectron spectra of Si_{2p} .

SiO_2 interface. Further discussion is needed for detailed elucidation.

Comparing present calculations with the experimental XPS results, as shown in Fig. 5, they show qualitatively good accordance. Therefore, we can suggest that the former calculation with respect to bond orders is also valid because of using the same cluster and same parameters.

4. CONCLUSION

At the interface between $\text{Ca}(\text{OH})_2$ and SiO_2 , surface dehydration process occurs when the coordination number of OH groups for Ca atoms at the $\text{Ca}(\text{OH})_2$ surface decreases, though the reduction of the repulsion with surface oxygen.

For a hetero-metalloxane bond $\text{Ca-O}_1\text{-Si}$ to form, the decrease in the number of OH groups coordinated to Ca atom is a prerequisite to decrease the degree of bond order. This, in turn, favors the increase in the degree of bond order for Ca-O_1 . These simultaneous changes favor stabilization of $\text{Ca-O}_1\text{-Si}$ HMB as well.

Si atoms with lower binding energy than those of bulk Si are found as a result of transition energy calculation. They are in accordance with our previous experimental results. All these calculation results confirm the hypothetical mechanism of soft mechanochemical reaction between SiO_2 and $\text{Ca}(\text{OH})_2$ toward a precursor of calcium silicates. This can well be extended for other complex oxide systems because of its generality.

ACKNOWLEDGEMENT

This study was partly supported by Special Coordination Funds for Promoting Science and Technology from the Japanese Science and Technology Agency, to whom we are deeply indebted.

REFERENCES

- [1] M. Senna, *Trans. Inst. Chem. Eng.* **76**, 67(1998).
- [2] G. Heinicke, *Tribochemistry*; Akademie-Verlag: Berlin, 354(1984).
- [3] T. Watanabe, T. Isobe, M. Senna, *J. Solid State Chem.* **122**, 74 (1996).
- [4] J. -F. Liao, and M. Senna, *Solid State Ionics* **66**, 313(1993).
- [5] J. -G. Baek, K. Gomi, T. Watanabe, T. Isobe, and M. Senna, *Mater. Sci. Forum* **235/238**, 115(1997).
- [6] J. -G. Baek, T. Isobe, and M. Senna, *J. Am. Ceram. Soc.* **80**, 973(1997).
- [7] M. Senna, *Solid State Ionics* **63/65**(3) (1993).
- [8] T. Watanabe, T. Isobe, and M. Senna, *Chem. Sustainable Dev.* **6**, 165(1998).
- [9] A. Rosén, D. E. Ellis, H. Adachi, F. W. Averill, *J. Chem. Phys.* **65**, 3629 (1976).
- [10] H. Adachi, M. Tsukada, C. Satoko, *J. Phys. Soc. Jpn* **45**, 875 (1978).
- [11] R. S. Mulliken, *J. Chem. Phys.* **23**, 1833 (1955); **23**, 1841 (1955).
- [12] Y. Fujiwara, T. Isobe, M. Senna, *J. Phys. Chem. A* **103**(48), 9842-9846(1999).
- [13] J. C. Slater and K. H. Johnson, *Phys. Rev B* **5**(3), 844 (1972).
- [14] O. Chaix-Pluchery, J. Pannetier, J. Bouillot, *J. Solid State Chem.* **67**, 225 (1987).
- [15] C. Satoko, M. Tsukada, and H. Adachi, *J. Phys. Soc. Japan* **45** (4), 1333(1978).
- [16] P. A. Cox, *Electronic Structure and Chemistry of Solids*; Oxford University Press: Oxford, 1987; Chapter 3, 7.
- [17] T. L. Barr, *J. Vac. Sci. Technol. A* **9**, 1793 (1991).