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## Change in Surface Acidity of Nano-Ball Allophane upon Zinc Adsorption and its Mechanisms

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**Abstract:** Effect of zinc adsorption on the change in surface acidity of two nano-ball allophane samples with varying Si/Al ratio was studied. Zinc adsorption caused the enhancement in the surface acidity of nano-ball allophane samples. The enhancement in the surface acidity after zinc species adsorption is attributed to the inductive effect on the Si–OH groups near the adsorption sites. Molecular orbital calculations indicated that Zn<sup>2+</sup> ion has the possibility to accelerate deprotonation of the Si–OH functional groups near the adsorption site. The result showed that the surface acidity of the allophane sample with a higher Si/Al ratio (KnP) was stronger than the KyP sample with lower Si/Al ratio. This tendency was observed under RH between 0 and 76%; then, the acid strength for the two nano-ball samples was the same at RH of 100%. The stronger acidity of the KnP sample is attributed to its a higher number of accessory polymeric silanol groups attached to the main frame structure, which cause the enhancement of the Brønsted acidity. The higher increase in the acid strength of the KnP could be also attributed to its higher adsorptive capacity for zinc species.

**Key words:** Zinc adsorption, surface acidity, allophane, molecular orbital method, acid strength, zinc species

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## INTRODUCTION

Allophane formed in weathered volcanic ash and pumice has morphology of aggregates composed of fine hollow spherules with diameters of 3.5 to 5.0 nm. The chemical composition of the wall of hollow spherules varies in Si/Al atomic ratio from 1:2 to 2:2. There is a regular tendency in physicochemical characteristics such as structural stability against grinding, heating, change in CEC, AEC and surface acidity depending on Si/Al ratio of allophane samples (Henmi *et al.*, 1997). Nano-ball allophane has surface acidity that is weaker than kaolinite and montmorillonite clay minerals, but stronger than for imogolite. The functional groups (Si–OH and Al–OH) in the nano-ball allophane structure are able to behave as the Brønsted acidity sites. The surface acidity of a lower Si/Al ratio (KyP) sample was found to be increase upon sulfate (Padilla, 2003), phosphate adsorption (Johan, 1999) on the nano-ball allophane samples. In these previous studies, the increase in the acidity was attributed to the enhancement of the Brønsted acidity of the silanol (Si–OH) functional groups on the allophane structure. Elhadi *et al.* (2001) using molecular orbital calculations indicated that Brønsted acidity of Si–OH groups of allophane near the adsorption sites increased with molybdate adsorption. In our previous study (Ghoneim *et al.*, 2001; Ghoneim, 2002) we found that zinc was

strongly adsorbed on nano-ball allophane at different pH. The adsorption brought about a change in CEC and AEC. It is expected that the adsorption would also affect the surface acidity of allophane. Therefore the aim of this study was to know the influence of zinc adsorption on the surface acidity of nano-ball allophane and the mechanism by means of molecular orbital analysis.

## MATERIALS AND METHODS

### Allophane Samples Preparation

The study was initiated at the Faculty of Agriculture, Environmental Soil Science Laboratory, Ehime University, Matsuyama, Japan during 2002 to 2005. Two nano-ball allophane samples used in this study were separated from weathered pumice grains taken from two different volcanic ash locations in Japan. The KyP sample was collected from Kurayoshi, Tottori prefecture and KnP sample from Kakino, Kumamoto prefecture. Fine clay fraction ( $<0.2 \mu\text{m}$ ) was separated from the inner part of pumice grains after removing the outer part to eliminate any possible contamination of allophane samples. The separation was carried out by ultrasonification at 28 kHz and then, dispersion at pH 4 for KyP sample or pH 10 for KnP sample according to Henmi and Wada (1976). The obtained samples were flocculated by NaCl solution, washed with water to remove excess salts and then freeze-dried. The samples were analyzed by electron microscopy, IR, DTA and chemical analysis (data not shown) to ascertain the purity of the sample. Atomic arrangement near the defect (pore) of hollow spherical nano-ball allophane with low Si/Al ratio is shown in Fig. 1C, while the allophane with high Si/Al ratio is shown in Fig. 1B, in which some accessory silicon is attached and dimeric or polymeric  $\text{SiO}_4$  tetrahedra are formed.

### Surface Acidity Measurement

Zinc adsorption experiment was carried out by equilibrating 150.0 mg of the freeze-dried KyP and KnP allophane samples with 100 mL of  $\text{ZnCl}_2$  solutions with different concentrations. The initial zinc concentration varied from 0 to 0.18 mM with the initial pH between 4 and 7 using either HCl or NaOH solution. The total  $\text{Na}^+$  concentration was kept at 10.0 mM by adjusting the amount of NaCl added. The suspensions were then shaken for 24 h, centrifuged after which the supernatant was decanted. The levels of Zn concentration in the supernatant was determined by an atomic absorption spectrophotometer (Hitachi Z-5000) and the amounts of zinc adsorbed by nano-ball allophane samples was calculated from the difference in concentrations before and after adsorption. The separated clay samples (precipitates) was then washed with distilled water and dried in oven at  $105^\circ\text{C}$  for 6 h. The collected samples were then brought to different Relative Humidity (RH) sets of 0.0% (after heating up to  $105^\circ\text{C}$ ), 31.0% (saturated  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  solution), 76.0% (saturated  $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$  solution) and 100% (water). The most wanted RH levels were obtained by equilibrating the samples in desiccators with the suitable medium given in parenthesis for 24 h.

The acid strength was determined according to the method of Benesi (1956) and Walling (1950). The principle of this method is to observe and determine the change in the color of the samples upon the donation of  $\text{H}^+$  to the neutral base with known  $\text{pK}_a$  values (Hammett, 1940), where suitable indicators are used as bases for measurement of the change in strength of the surface acidity. The indicators used are shown in Table 1. The concentration of each indicator was 1.0% dissolved in benzene. The acidity ( $\text{H}_0$ ) was expressed with ordinary numbers rank form I to VI as shown in Table 1. After equilibrating the allophane sample under different RH levels, about two drops of indicators were added to the samples and the change in color was observed by the naked eye. The acid strength was then estimated using Table 1. For example, a sample that gave a red coloration with methyl yellow but was yellow with aminoazatoluene was estimated to have acid strength of  $\text{H}_0 = 3.3$  to 2.0 or rank III.

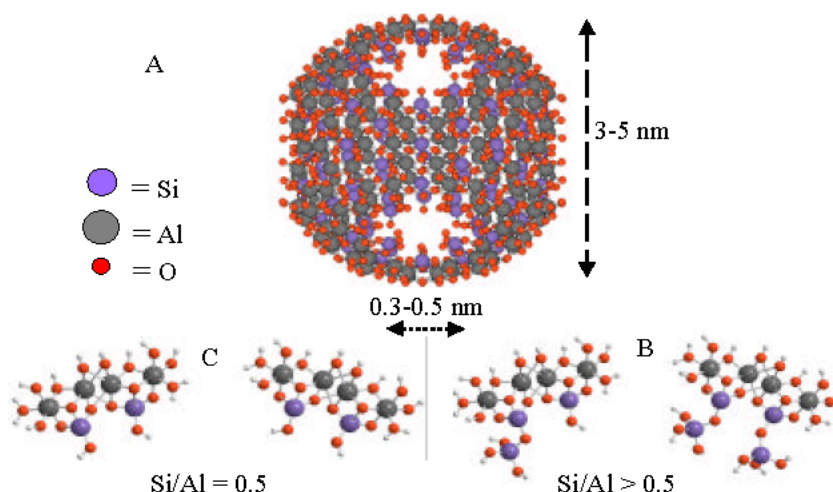


Fig. 1: Scheme of chemical structure of a unit particle of nano-ball allophane (A: Complete structure; B and C: atomic arrangement in the cross section at the pore region)

Table 1: List of Hammet indicators used for surface acidity measurements and ranking to express  $H_0$  values

Indicators	Color		pKa	$H_0$	Rank
	Basic	Acidic			
4-Dimethylaminoazobenzene	Yellow	Red	5.0		
2-Carboxylic acid (Methyl Red)				+5.0 ~ +4.0	I
4-Phenylazo-1-naphthylamine (Naphthyl Red)	Yellow	Purple	4.0	+4.0 ~ +3.3	II
N, N-dimethyl-4-(Phenylazo)-Benzenamine (Methyl Yellow)	Yellow	Red	3.3		
2-Methyl-4-(2-ethylphenyl)-azo benebamino-amino azotoluene	Yellow	Red	2.0	+3.3 ~ +2.0	III
4-Phenylazodiphenylamine (4-Benzeneazo diphenylamine)	Yellow	Purple	1.5	+2.0 ~ +1.5	IV
1, 9-Dipheeryl-1, 3, 6, 8-nonatetraene	Yellow	Red	-3.0	+1.5 ~ -3.0	V
5-one (Dicinnamalacetone)					
1, 3-diphenyl-2-propene-1-one	Colorless	Yellow	-5.6	-3.0 ~ -5.6	VI

## RESULTS AND DISCUSSION

### Change in Acid Strength

The results generally showed that the acidity of the allophane sample with a higher Si/Al ratio (KnP) was stronger than for the KyP sample with lower Si/Al ratio (Table 2). This trend was observed under the RH between 0 and 76% and then the acid strength for the two nano-ball samples was the same at the RH of 100%. The stronger acidity of the KnP sample is attributed to its a higher number of accessory polymeric silanol groups attached to the main frame as shown in Fig. 1 which cause the enhancement of the Brønsted acidity (Henmi *et al.*, 1997). For the lower Si/Al ratio KyP sample, the result indicated that with increasing RH from 31 to 100%, there was no apparent change in the acid strength ( $H_0 = \text{II}$ ). This results is attributed to the water molecules occupying the same number of the acid sites, however heating the allophane samples up to 105 °C, led acid strength increase up to  $H_0$  values of (+ 3.3 ~ + 2.0) or rank III. It is well known that, when the mineral surfaces become drier the Brønsted acidity and protons are concentrated in a smaller volume of water resulting in more extreme surface acidity (Huang, 2000). Even very weak bases, i.e., poor proton acceptors can be protonated

Table 2: Measured acid strength ( $H_0$ ) of the allophane samples with and without zinc adsorption

Sample	Relative humidity levels (%)			
	0	31	76	100
KyP without Zn	III	II	II	II
Zn adsorbed ( $\mu\text{mol g}^{-1}$ )*				
148.0	V	IV	IV	IV
153.0	V	IV	IV	IV
156.0	V	IV	IV	IV
KnP without Zn	V	III	III	II
Zn adsorbed ( $\mu\text{mol g}^{-1}$ )*				
190.0	V	V	V	IV
230.0	V	V	V	IV
245.0	V	V	V	IV

(\*): above data indicated amounts of Zn adsorbed  $\mu\text{mol g}^{-1}$

on the surfaces of such mineral. On the other hand, at RH of 100%, the both original allophane samples in 10.0 mM NaCl background solution have the same rank II ( $H_0 = 4.0 \sim 3.3$ ). These results are attributed in part to the 100% moisture level, the water molecules engaged almost all the available sites for the acidity, resulting in the very weak Brønsted acidity. In addition, when the nano-ball allophane samples become wetter, the  $H^+$  ions are concentrated in large volumes of the water and subsequently resulting in weak Brønsted acidity.

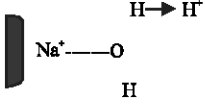
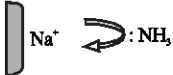
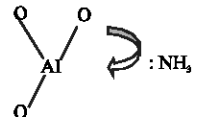
### Effect of Zinc Adsorption

The effect of zinc adsorption on the acid strength of nano-ball allophane samples at different RH levels is presented in Table 2. In general, after zinc adsorption there are increases in the surface acidity of the two nano-ball allophane samples except for the KnP sample with a higher Si/Al at RH of 0%. The increase in the acid strength after adsorption is the same magnitude regardless the amounts of zinc adsorbed (Table 2). For example, the KyP allophane sample with a lower Si/Al ratio, the acid strength increased from rank II to rank IV at the RH between 31 and 100%, however after heating the samples up to 105°C, the acid increase to the rank V. In case of allophane sample with a higher Si/Al ratio (KnP) at the RH of 31 and 76% levels, the acid strength increased from rank III to V (+ 1.5 ~ -3.0). At the 100% moisture level, the two samples have the same acidity of rank II. Also the results showed that no change in the acid strength was observed for the KnP sample at 0%, this may be due to the sample after heating up to 105°C losses almost all the water adsorbed on its surfaces, in addition the rank V is regard as wider range (e.g.,  $H_0 = +1.5 \sim -3.0$ ). The increase in the acid strength after zinc adsorption on the two samples at the RH between 31 and 76% is attributed to the  $H_2O$  coordinated the exchangeable sodium on the allophane surface. The stronger acid strength observed after zinc adsorption for the KnP at RH between 31 and 76% is probably due to the higher inherent  $Na^+$  content for the KnP allophane sample. The higher increase in the acid strength of the higher Si/Al ratio (KnP) could be also attributed to its higher adsorptive capacity for zinc (Ghoneim *et al.*, 2001, 2006; Ghoneim, 2002). The surface acidity of the clay minerals arises from two main sources: the Brønsted acidity and the Lewis acidity. The Brønsted acidity comes from the deprotonation of the  $H^+$  on the constant charge, water molecules, which coordinated to surface bound cations and also from the dissociation of functional groups. On the other hand, the Lewis acidity originates from un-saturated structural silicon and aluminum, from constituent ions such as aluminum and iron that exposed at the edges of the minerals (Sposito, 1984; Wu *et al.*, 1992; McBride, 1994). Table 3 shows the possible origins of the surface acidity of nano-ball allophane before Zn adsorption.

### Molecular Orbital Analysis

The increase in the Brønsted acidity of the nano-ball allophane samples after phosphate adsorption was explained by the dissociation of  $H^+$  from the silanol (Si-OH) groups near the adsorption site (Johan, 1999), but Elhadi *et al.* (2001) reported that the increase in the surface acidity

Table 3: The possible origins of the surface acidity of nano-ball allophane samples before zinc adsorption

Origin of acidity	Type	Relative acid strength
(1) Functional groups		
Al-OH <sub>2</sub> <sup>+</sup> → Al-O <sup>-</sup> + H <sup>+</sup>	Brønsted	Medium-strong
Si-OH → Si-O <sup>-</sup> + H <sup>+</sup>	Brønsted	Medium-strong
(2) Water on exchangeable Na at Si-ONa or Al-ONa	Brønsted	Weak
		
(3) Exchangeable Na <sup>+</sup> Si-ONa or Al-ONa	Lewis	Medium-strong
		
(4) Coordination unsaturated Si or Al	Lewis	Very strong
		

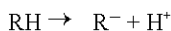
of nano-ball allophane samples was attributed to the dissociation of the proton from the adsorbed molybdate (Mo-OH). For that reason the molecular orbital calculations were carried out to know and determine the sources of increase in the surface acidity of the allophane samples upon zinc adsorption.

The gas acidity of a molecule is determined from the difference in energy between that of the anion and the neutral molecule by the following equation (Siggel and Thomas, 1986).

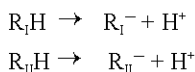
$$A = E_a - E_m$$

Where A is the gas acidity of the molecule, E<sub>a</sub> and E<sub>m</sub> is the total energy of the anion and neutral molecule, respectively. The Brønsted acidity can be estimated either from the equilibrium constant pK<sub>a</sub> value or from the change in the free energy value (ΔG°) of the reaction of (Siggel *et al.*, 1988). The ΔG value can be calculated from the difference in the heat of formation (ΔH) between the products and reactants (ΔH = H<sub>products</sub> - H<sub>reactants</sub>).

The dissociation reaction is expressed as:



Where RH is the neutral molecule and R<sup>-</sup> is the anion. The principle of the calculations is when the dissociation of two compounds, R<sub>I</sub>H and R<sub>II</sub>H, with a similar molecular weight occurs, therefore only the heat of formation (H) of the products and the reactants are required.



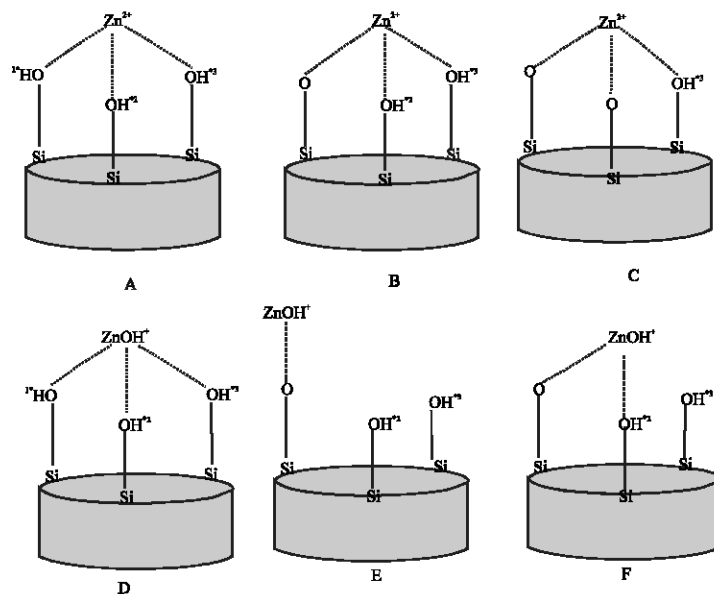


Fig. 2: Model clusters used for molecular orbital calculations. Models A and D shows allophane with undissociated Si-OH; models B, C, E and F simulates zinc species adsorption with one or two Si-O<sup>-</sup> groups

However, the heats of formation of proton is canceled out and therefore only the heats of the formation of the dissociated and undissociated forms are needed. Lower value for  $\Delta H$  indicates the stronger Brønsted acidity.

Figure 2 shows the zinc adsorption on the silanol groups. Model A depict allophane model with no dissociated Si-OH; protons with the asterisk marks in the three models shows those can dissociate and cause the acidity. Models B and C simulates the zinc adsorption with one or two dissociated Si-O<sup>-</sup> groups, respectively. Even when the allophane model had no dissociated silanol group, the Zn<sup>2+</sup> ions was adsorbed and positioned between the three O atoms of the three silanol groups. The O-H bond lengths of the three Si-OH bonded to the Zn<sup>2+</sup> (0.097 nm) was longer than those of the other silanol groups (0.095 nm). This means that the protons of the silanol groups bonded to Zn<sup>2+</sup> ions were easily dissociated, resultant in a release of the protons into the bulk solution as observed experimentally (Ghoneim *et al.*, 2001; Ghoneim, 2002). For the allophane model with one Si-O<sup>-</sup> dissociated, the monomeric Zn<sup>2+</sup> adsorbed strongly by the dissociated Si-O<sup>-</sup> and also weakly adsorbed by the two near Si-OH groups (model B). The O-H bond length of the two Si-OH groups, which bonded to Zn<sup>2+</sup> were longer than for the other silanol groups. These results indicate that, the Zn<sup>2+</sup> ions have the possibility to accelerate the deprotonation of the Si-OH near the adsorption site. For adsorption of ZnOH<sup>+</sup>, the molecular orbital calculation also carried out (models D, E and F). The monohydroxylated species ZnOH<sup>+</sup>, also could be adsorbed between three silanol groups but the Zn-O bond length was longer than those for Zn<sup>2+</sup> adsorption.

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