

Self-assembly of saponite nanoparticles originated from nano-layered structure

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Abstract. The mechanism of self-assembly induced by H₂O molecules is studied for layered saponite nanoparticles and zeolite with the cage structure by means of positronium (Ps) annihilation spectroscopy together with thermogravimetry and differential thermal analysis (TG-DTA). Prior to hydration the saponite exhibits two kinds of open spaces with their sizes of ~ 3 Å and ~ 9 Å, whereas open spaces with their sizes of ~ 3 Å and ~ 5 Å corresponding to β and α cages are obtained for the zeolite. The occupation of both α and β cages by H₂O molecules proceeds along with hydration up to 2.5 h, which well synchronizes with the weight gain in TG data. On the contrary, the angstrom-scale open spaces for the saponite vary with hydration in the time scale with ~ 100 h much longer than that of TG-DTA with ~ 8 h. The present results suggest that the long-term self assembly originates from not the cage but the nanolayered structures.

1. INTRODUCTION

Nanoparticle self-assembly is a phenomenon, in which nanoscale particles spontaneously agglomerate with well-defined local structures through their mutual interactions [1]. Self-assembly often leads to specific properties and functionalities that cannot be accessible by the conventional technique of material synthesis [2,3]. The application of self-assembly to material synthesis could be thus currently one of the most straightforward strategies that allow the design of new multifunctional nanocomposites [4], though the phenomenon of self-assembly itself has not been understood yet. In addition, the self-assembly of nanoparticles is increasingly of importance for dealing with the global environmental issues. It has been reported that dynamical functionality in the soil environment emerges as a consequence of self-assembly in the soil-microbe system [5].

In the present study, we employed inorganic layered compound saponite known as clay minerals. The layered saponite is typical material that exhibits self-assembly in the presence of H₂O molecules [6,7]. The self-assembly of saponite nanoparticles is explored by positronium (Ps) annihilation spectroscopy coupled with thermogravimetry and differential thermal analysis (TG-DTA). We focus on the long-term self-assembly ranging from the onset of H₂O adsorption at the interlayer cations to far after complete hydration.

2. EXPERIMENTS

Synthetic Na-type saponite nanoparticles (54.71% SO₂, 5.02% Al₂O₃, 0.03% Fe₂O₃, 30.74% MgO, 2.15% Na₂O, 0.07% CaO, 0.67% SO₃, 6.64% H₂O) produced by Kunimine Industries Co. Ltd., Japan were employed in this study. The particle size is approximately 45 nm in diameter. A-type zeolite powder produced by Tosoh Co. Ltd., Japan was employed as well. All the samples were dehydrated at 423 K for 12 h under the vacuum condition of $\sim 10^{-5}$ Torr, which are referred as the starting saponite samples.

Adsorption of H₂O molecules was investigated with respect to the weight gain by means of TG-DTA (TG-DTA 2020SA, BRUKER AXS Co. Ltd.) at room temperature with α corundum (α Al₂O₃) as an internal standard. The starting samples were exposed to the humidity of $\sim 35\%$ at the temperature of ~ 300 K, where the time-dependent data were obtained.

The sizes of open spaces and their fractions were investigated by Ps annihilation lifetime spectroscopy [8–10]. A fraction of energetic positrons injected into samples forms the bound state with an electron, positronium (Ps). Singlet *para*-Ps (*p*-Ps) with the spins of the positron and electron antiparallel and triplet *ortho*-Ps (*o*-Ps) with parallel spins are formed at a ratio of 1 : 3. Hence, three states of positrons: *p*-Ps, *o*-Ps, and free positrons exist in samples. The annihilation of *p*-Ps results in the emission of two γ -ray photons of 511 keV with lifetime ~ 125 ps. Free positrons are trapped by negatively-charged parts such as polar elements and annihilated into two photons with lifetime ~ 450 ps. The positron in *o*-Ps undergoes two-photon annihilation with one of the bound electrons with a lifetime of a few ns after localization in angstrom-scale pores. The last process is known as *o*-Ps pick off annihilation and provides information on the free volume size R through its lifetime τ_{o-Ps} based on the Tao-Eldrup model [11, 12]:

$$\tau_{o-Ps} = 0.5 \left[1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin \left(\frac{2\pi R}{R_0} \right) \right]^{-1}, \quad (1)$$

where $R_0 = R + \Delta R$, and $\Delta R = 0.166$ nm is the thickness of homogeneous electron layer in which the positron in *o*-Ps annihilates. The positron source (²²Na), sealed in a thin foil of Kapton, was mounted in a sample-source-sample sandwich. The starting samples were exposed to the humidity of $\sim 35\%$ at the temperature of ~ 300 K, where the Ps lifetime spectra were obtained at the time interval of 45–52 min. The validity of our lifetime measurements and data analysis was confirmed with certified reference materials (NMIJ CRM 5601-a and 5602-a) provided by National Metrology Institute of Japan, National Institute of Advanced Industrial Science and

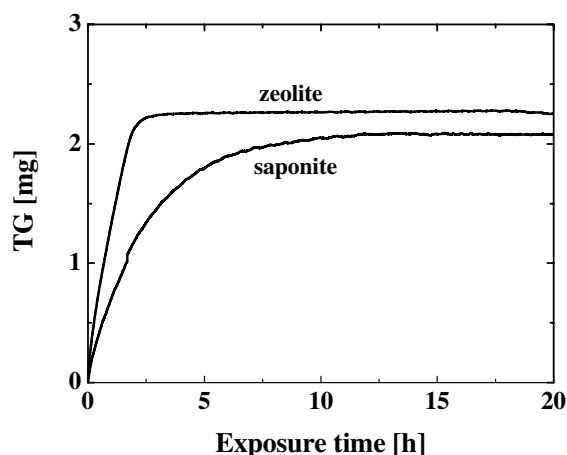


Figure 1. Thermogravimetry (TG) data of saponite and zeolite as a function of exposure time.

Technology (AIST) [13, 14]. Positron lifetime spectra were numerically analyzed using the POSITRONFIT code [15].

3. RESULTS AND DISCUSSION

Figure 1 shows thermogravimetry (TG) as a function of exposure time. The TG data for saponite gradually increases with increasing exposure time up to ~ 8 h owing to hydration in the interlayer spaces and is saturated thereafter. The TG data for zeolite increases more rapidly with exposure time up to ~ 2.5 h and stays constant thereafter. This demonstrates that H_2O molecules adsorb more easily for zeolite than saponite.

Ps annihilation spectroscopy for both the saponite and zeolite reveals two kinds of open spaces denoted as A and B. The size of small open space A for saponite is consistently ~ 3 Å without any significant change along with exposure time, whereas the size of large open space B significantly decreases from ~ 9 Å to ~ 6 Å. For the zeolite sample, small and large open spaces with their sizes of ~ 3 Å and ~ 5 Å corresponding to β and α cages, respectively, are obtained.

In Fig. 2, the fractions of small and large open spaces obtained for the saponite and zeolite are presented as a function of exposure time. The fraction of small open space for the zeolite quickly increases from $\sim 7\%$ to $\sim 13\%$ with increasing exposure time along with the decrease of large open space from $\sim 12\%$ to $\sim 0\%$. The large open space is not obtained anymore after the exposure time of 2.5 h, which is well synchronized with TG data (see Fig. 1). This is typical behavior that Ps annihilation occurs in water-filled α and β cages [16]. The present results of Ps annihilation spectroscopy together with TG-DTA clearly capture the picture that the weight increase due to hydration observed for the zeolite solely arises from the occupation of α and β cages by H_2O molecules.

In sharp contrast with the zeolite, the fraction of small open space for the saponite gradually increases from $\sim 5\%$ to $\sim 9\%$ with exposure time with the decrease of large open space from $\sim 10\%$ to $\sim 4\%$. They are well synchronized in the time scale with ~ 100 h much longer than that of TG-DTA with ~ 8 h. We conclude that the

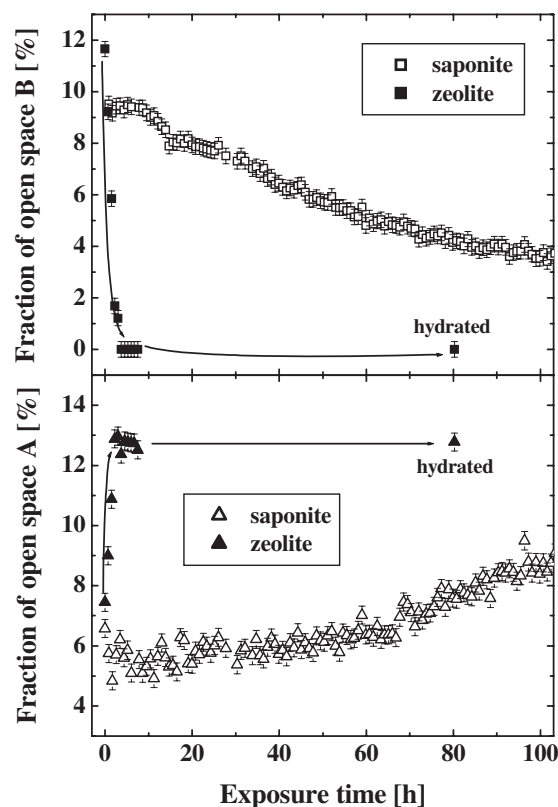


Figure 2. Fractions of open spaces A and B obtained for saponite and zeolite as a function of exposure time. The data of well hydrated zeolite are added at the exposure time of ~ 80 h.

long-term molecular dynamics probed by Ps annihilation spectroscopy originates from the self-assembly of saponite nanoparticles rheologically caused by H_2O molecules. The present finding demonstrates that the long-term self-assembly is caused by not the cage but the nanolayered structures.

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References

- [1] G.M. Whitesides, B. Grzybowski, *Science* **295**, 2418 (2002).
- [2] L. Wu, J. Lal, K.A. Simson, E.A. Burton, Y.Y. Luk, *J. Am. Chem. Soc.* **131**, 7430 (2009).
- [3] L.M. Toma, R.Y.N. Gengler, D. Cangussu, E. Pardo, F. Lloret, P. Rudolf, *J. Phys. Chem. Lett.*, 2004 (2011).
- [4] G. Garnweitner, B. Smarsly, R. Assink, W. Ruland, E. Bond, C.J. Brinker, *J. Am. Chem. Soc.* **125**, 5626 (2003).
- [5] I. M. Young, J. W. Crawford, *Science* **304**, 1634 (2004).

- [6] E. Balnois, S. Durand-Vidal, P. Levitz, *Langmuir* **19**, 6633 (2003).
- [7] B.V. Lotsch, G.A. Ozin, *ACS Nano* **2**, 2065 (2008).
- [8] K. Sato, H. Murakami, K. Ito, K. Hirata, Y. Kobayashi, *Macromolecules* **42**, 4853 (2009).
- [9] K. Sato, K. Fujimoto, M. Nakata, and T. Hatta, *J. Phys. Chem. C* **115**, 18131 (2011).
- [10] K. Sato, *J. Phys. Chem. B* **115**, 14874 (2011).
- [11] S. J. Tao, *J. Chem. Phys.* **56**, 5499 (1972).
- [12] M. Eldrup, D. Lightbody, J. N. Sherwood, *Chem. Phys.* **63**, 51 (1981).
- [13] K. Ito, T. Oka, Y. Kobayashi, Y. Shirai, H. Saito, Y. Honda, Y. Nagai, M. Fujinami, A. Uedono, K. Sato, T. Hirade, A. Shimazu, H. Hosomi, K. Sakaki, *J. Appl. Phys.* **104**, 0261021 (2008).
- [14] K. Ito, T. Oka, Y. Kobayashi, Y. Shirai, K. Wada, M. Matsumoto, M. Fujinami, T. Hirade, Y. Honda, H. Hosomi, Y. Nagai, K. Inoue, H. Saito, K. Sakaki, K. Sato, A. Shimazu, A. Uedono, *Mater. Sci. Forum* **607**, 248 (2009).
- [15] P. Kirkegaard and M. Eldrup, *Comput. Phys. Commun.* **7**, 401 (1974).
- [16] A.M. Habrowska, E.S. Popiel, *J. Appl. Phys.* **62**, 2419 (1987).