Photocatalytically active molecular sites introduced by mechanochemical decomposition in saponite nanoparticles

K.Numata, K.Sato, K.Fujimoto

Abstract—Photocatalytically-active molecular sites introduced by mechanochemical decomposition and long-term rheological self-assembly were studied for saponite nanoparticles by means of positronium annihilation spectroscopy. Two kinds of open spaces with sizes of ~ 0.3 nm and ~ 0.9 nm were identified for as-receivedsaponitenanoparticles. Thermogravimetry and differential thermal analysis (TG-DTA) conducted for mechanochemically-decomposed nanoparticles supported with TiO_2 indicated the relative weight decrease of ~ 1 % at the ultraviolet rays (UV)-irradiated time of 300 h. The result suggest that the local molecular structures introduced by mechanochemical decomposition act as photocatalytically-active sites.

Index Terms—photocatalysaponite nanoparticle, positronium

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1 INTRODUCTION

Saponite layered nanoparticles, known as clay mineral, are inorganic compounds consisting of two-dimensional (2D) nanosheets with angstrom-scale interlayer spaces. The 2D nanosheets are negatively charged due to the compositional and structural fluctuation. The negative layer charge is compensated by interlayer cations such as Na^+ which attract to polarized H_2O molecules. Saponite layered nanoparticles can thus contain a large amount of H_2O molecule in the angstrom-scale interlayer spaces, which is characteristic for the swelling property [1]. The 2D nanosheets of minimum structural unit spontaneously agglomerate with well-defined local structures through their mutual interactions in the time scale more than 10 days [2-4]. This agglomeration process toward structural densification, so-called self-assembly of 2D nanosheets, is increasingly of importance in the field of environmental science, such as e.g., specific Cs adsorption [5-6].

In saponite layered nanoparticles, there exists a large surface area exceeding ~ 800 m²/g owing to highly porous structure with interlayer spaces [7]. Saponitenanoparticles are thus promising materials for supporting TiO_2 particles with a high photocatalytic performance for the degradation of organics. A uniform dispersion of TiO_2 particles on the matrix of layered nanoparticles as clay-TiO_2 composite and the resulting improvement of photocatalytic performance has been reported [8-9]. In these reports, the photocatalytic reaction is exclusively associated with the intrinsic molecular structures of clay minerals as e.g., the surface of 2D nanosheet and open space created by 2D nanosheets called as a clay pore. Here, photocatalytically active molecular sites newly developed upon mechanochemical decomposition is explored.
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2 EXPERIMENTS

Synthetic Na-type saponite nanoparticles produced by Kuni-

mine Industries Co. Ltd., Japan were employed in this study. The sample was mechanochemically milled with tungsten carbide balls for9 h under dry atmosphere at ambient temperature, which is referred as mechanochemically decomposed sample hereafter. As-received and mechanochemically decomposed samples were dehydrated at 423 K for 12 h under a vacuum of ~ 10^{-3} Pa, and then exposed to the humidity of ~ 35 % at the temperature of ~ 300 K for self-assembly.

The sizes of open spaces and their fractions were investigated by positroniumu (Ps) annihilation lifetime spectroscopy [10]. A fraction of energetic positrons injected into samples forms the bound state with an electron, 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 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 $\tau_{o\text{-}Ps}$ based on the Tao-Eldrup model [11-12]:

$$\tau_3 = 0.5\left[1 - \frac{R}{R_0} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R_0}\right)\right]^{-1}$$

whereR_0 = R + ΔR, and ΔR = 0.166 nm is the thickness of homogeneous electron layer in which the positron in *o*-Ps annihilates. The positron source (^{22}Na), sealed in a thin foil of Kapton was mounted in a sample-source-sample sandwich.Ps lifetime spectra were obtained at the time interval of 45-52 min during self-assembly. The spectra were numerically analysed using the POSITRONFIT code [13].

3 RESULTS AND DISCUSSION

Ps lifetime spectroscopy for the as-received sample revealed two kinds of open spaces, a smaller one labeled A and a larger one labeled B, whereas only a kind of open space labeled A' slightly larger than the open space A was observed for the mechanochemically decomposed sample. The smaller open space A had a radius of ~ 0.3 nm for the as-received sample which was unchanged with self-assembly, whereas the size of open space A' slightly decreases for the mechanochemically decomposed sample. The radius of the larger open space B for the as-received sample decreased significantly from ~ 0.9 nm to ~ 0.6 nm with self-assembly.

Fig. 1 shows the measured fractional intensity of each open space obtained for the as-received and mechanochemically decomposed samples as a function of exposure time. The fraction of the smaller open space A (IA) for the as-received sample slowly increases from ~ 5 % to ~ 9 % with increasing exposure time together with a decrease of the larger open space from ~ 9 % to ~ 5 %, as indicated by arrows. The change takes place on a time scale of ~ 100 h, much longer than that generally observed by TG-DTA with a time scale of ~ 8 h [4]. It is thus concluded that the long-term molecular dynamics probed by Ps lifetime spectroscopy originates from the self-assembly of 2D nanosheetsrheologically caused by H_2O molecules. The mechanochemically decomposed sample indicates a completely different time variation for the fractions of the smaller open space A. The fraction of the smaller open space A is ~ 15 % before hydration, which is significantly higher than for the as-received sample. It decreases from ~ 15 % to ~ 10 % with a time scale of ~ 100 h.

Previously, we conducted molecular dynamics (MD) calculations to figure out the location of the two kinds of open spaces for as-received saponite sample [4]. One of the simulated molecular structures is called type A, in which one 2D nanosheet is inserted into the interlayer spaces forming a open space with a size of ~ 0.3 nm. Another is type B, in which two 2D nanosheets are inserted into the interlayer spaces forming a large open space with a size of ~ 0.9 nm. The sizes of open spaces simulated by MD calculations are in agreement with those observed by Ps annihilation spectroscopy. The results of Ps lifetime spectroscopy thus demonstrate that the local molecular structure denoted as type A with the smaller open space increases maintaining its size along with self-assembly. On the other hand, the local structure of type B disappears with self-assembly shrinking this larger open space. Type A could be an intrinsic local molecular structure of as-received sample, whereas the type B could be a metastable structure present dominantly prior to self-assembly. It is reasonably inferred for the as-received sample that the metastable structure of type B is

gradually altered to the intrinsic structure of type A together with self-assembly.
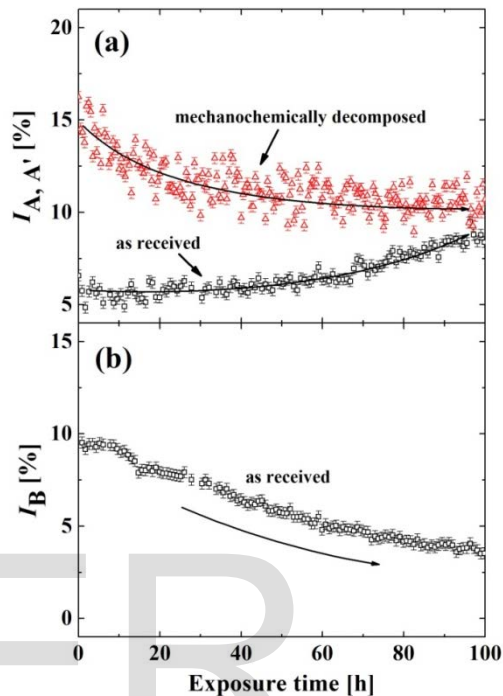

Fig. 1: The fractional intensity of small and large open spaces (IA, A' and IB) obtained for as-received (black squares) and mechanochemically decomposed (red triangles) saponite samples as a function of exposure time.
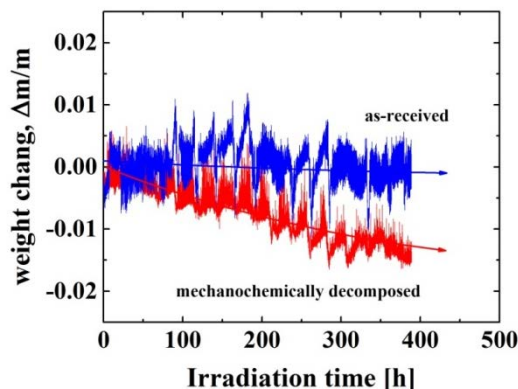

Fig. 2: Weight changes obtained in the TG-DTA experiments as a function of UV-irradiation time for as-received (blue) and mechanochemically decomposed (red) saponite samples.

It is of interest that the large open space B disappears upon mechanochemical decomposition. Furthermore, a open space

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is introduced as a result of decomposition, as deduced from the increase of the fraction of the smaller open space A (see Fig. 1). As mentioned above, the size of the open space A' introduced upon decomposition is slightly larger than that of the smaller open space A. Our next interest is that the above-mentioned local molecular structures introduced upon mechanochemical decomposition act as chemically active sites for photocatalytic reactions. For testing it, photocatalytic degradation of methylene blue with ultraviolet rays (UV) was conducted for TiO2 supported both by the as-received and mechanochemically decomposed samples. Fig. 2 shows weight changes obtained in the TG-DTA experiments as a function of UV-irradiation time for both the samples. Obviously, the weight change decreases due to the photocatalytic degradation of methylene blue with increasing UV-irradiation time for TiO2 supported by the mechanochemically decomposed sample, whereas the weight decrease is hardly observed for TiO2 supported by the as-received one. It is expected that the photocatalytic performance is enhanced by the photochemically active sites introduced upon mechanochemical decomposition.

Conclusions

Mechanochemical milling with tungsten carbide balls under dry atmosphere at ambient temperature was conducted for saponite layered nanoparticles. This treatment efficiently decomposes the local structure of 2D nanosheets yielding new kinds of molecular sites. The weight changes caused by photocatalytic degradation of methylene blue obtained by TG-DTA suggest that the local molecular structures introduced by mechanochemical decomposition act as photocatalytically active sites.

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