Solid State Ionics 267 (2014) 16–21

Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

Selective intercalation of ionic liquid in montmorillonite and influence of water molecules

Chisato Takahashi, Takashi Shirai, Masayoshi Fuji *

Advanced Ceramics Research Center, Nagoya Institute of Technology Honmachi 3-101-1, Tajimi, Gifu 507-0033 Japan

A R T I C L E I N F O

Article history:
Received 14 May 2014
Received in revised form 25 July 2014
Accepted 1 September 2014
Available online 20 September 2014

Keywords:
Clay
Ionic liquid
Composite materials
Electron microscopy
Raman spectroscopy

A B S T R A C T

The influence of water molecules on ionic liquid (IL; 1-butyl-3-methylimidazolium tetrafluoroborate) intercalated montmorillonite (M_{IL}) and the selectivity of IL have been studied. The intercalation behavior of IL into an IL-intercalation compound containing various amounts of water (M_{ILW}) was investigated by X-ray diffraction (XRD), transmission electron microscopy (TEM) and a selected area electron diffraction pattern (SAED). The structural change of M_{IL} influenced by the water was also confirmed by a TEM study. Based on the amount of interlayer exchangeable cations as measured by inductively coupled plasma (ICP), the extent of the intercalation and arrangement of cations in the interlayers of M_{IL} treated by different amounts of water was studied. In addition, the Raman spectroscopy results showed that the water molecules do not interact with both the IL and the montmorillonite. These results suggest that the IL-intercalation compound can maintain its property in water due to its high water resistance. Moreover, this technique would be useful for the adsorption reaction and fabrication of montmorillonite composite materials using non-polar organic molecules.

1. Introduction

Clay minerals are well known and used in daily life because of their low cost, abundant resources, high sorption and ion exchange properties. Clay materials exist as a layered structure and used as host materials for fabricating composite materials [1]. These clays can be classified as smectites, kaolinite, mica, vermiculite, pylophyllite, sepiolite, etc. In particular, the montmorillonite clay has a high surface area and high cation exchange capacity. Due to its properties, the inorganic clay–organic intercalation compounds have been researched for several decades. The inorganic clay–organic intercalation compounds that could have specific properties, such as mechanical strength, thermal stability, photoluminescence and catalysis, have been fabricated by many researchers [2–8]. In these methods, the organic molecules containing cations can easily infiltrate into the interlayer of the inorganic clays.

Ionic liquid (IL) modified clays have recently been paid attention due to the IL's unique properties, such as negligible vapor pressure, nonflammability and electrical conductivity, for fabricating inorganic clay–organic intercalation compounds with a high thermal stability and composite materials with an improved flame retardant property [9,10]. The applications of IL intercalated clays, such as catalysis [11] and nanocomposites, have been the focus of some researchers [12,13].

Room temperature ionic liquids are organic fused salts that consist of cations and anions and remain fluid below 100 °C [14,15]. The first RTIL (1-ethyl-3-methylimidazolium tetrafluoroborate; [emim][BF_4]) was reported in 1992. ILs are frequently used as a solvent in various chemical reactions [16–19], an electrolyte in batteries [20], a dispersant [21], etc. They show a high electric conductivity. In our previous studies, we have evaluated the fabrication and observation method of the montmorillonite intercalation compounds using various kinds of ILs [22–24]. Additionally, they are expected to be used for the fabrication of transparent thin films.

However, it has been observed that the addition of a small amount of water to the IL can change their properties due to the interaction of the water molecules. This interaction affects the noble properties of the IL, such as the electric conductivities, viscosity and polar characteristic [25–27]. Thereby, it is expected that the properties of the IL modified clay will be drastically changed. Nevertheless, there is no report about the interaction of water into the IL-modified clay. Therefore, we need to confirm the influence of water molecules on the IL-modified clay and selective intercalation of IL into the montmorillonite in the presence of water for practical applications using the IL-modified clay.

In this study, the influence of water molecules on the IL-intercalated montmorillonite was studied. We used a hydrophilic IL, which has alkyl chain cations (1-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF_4]), for the fabrication of the IL-intercalation compound (abbreviated M_{IL}). Subsequently, various amounts of water were added to the M_{IL} (abbreviated M_{ILW}). Behaviors of the IL within the silicate layer of montmorillonite in the presence of various amounts of water were confirmed by an XRD analysis. Moreover, the structures of the M_{IL} samples treated with various amounts of water were characterized using TEM and SAED analyses, which were then compared to the XRD results in order to

---

* Corresponding author. Tel.:+81 572 24 8110; fax: +81 572 24 8109.
E-mail address: fuji@nitech.ac.jp (M. Fuji).

http://dx.doi.org/10.1016/j.ssi.2014.09.001
0167-2738/

confirm the crystal structures. The interaction between IL into M_{IL} and water was determined by Raman spectroscopy studies in order to understand the adsorption selectivity of the IL. In addition, from the amount of exchanged alkali metal cations, the intercalation behavior of IL and water molecules was investigated.

2. Experimental section

2.1. Materials

Na-montmorillonite (Kunipia-F®, Kunimine Industries Co., Japan) was prepared after being dried in an oven at 130 °C for 3 days. The density, CEC and electric conductivity of the montmorillonite were 2.65 g/cm^3 (Ultrapicnometer1000, Qurntachrome Instruments Co., Japan), 119 mEq/100 g clay and 3.43 mS/cm, respectively [1,28]. The structural formula of the purified montmorillonite can be written as $Na_{2/3}Si_8(Al_{10/3}\,Mg_{2/3})O_{20}(OH)_4$.

The ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF_4] (Kanto Chemical Co., Japan), was used after drying in a vacuum desiccator at 60 °C for 1 day; the water content was less than 128 ppm. The montmorillonite and the IL (M_{IL}) were initially prepared by mixing both of them in the weight ratio of 1:2. Subsequently, water was added to the M_{IL} (weight ratio; M_{IL}:water = 1:1, 1:2, 1:10 and 1:50). In this study, we abbreviated the intercalation compounds (montmorillonite-IL) + water as M_{ILW}. The four kinds of M_{ILW} samples indicate as M_{11}, M_{12}, M_{110} and M_{150} in the present study. The weight ratio of the montmorillonite–IL–water = 1:2:3, 1:2:6, 1:2:30 and 1:2:150. The mass of montmorillonite, IL and water for each measurement is kept as follows: M_{11}, 1:2:3 (g); M_{12}, 1:2:6 (g); M_{110}, 1:2:30 (g); and M_{150}, 1:2:150 (g). The mass concentration of water in the IL solution is 60.00%, 75.00%, 93.75% and 98.68%. The molar concentration is 94.96%, 97.41%, 99.47% and 99.89%.

2.2. Methods

The phase compositions of the montmorillonite and M_{ILW} samples were observed by X-ray diffraction (XRD) (Ultima 5, Rigaku Co., Japan) in the 2θ range of 5° to 60° at a scan speed of 2°/min using Cu Kα radiation ($\lambda = 0.1542$ nm, 40 kV, 40 mA) and a proportional counter detector. The four kinds of M_{ILW} samples were prepared by mixing the IL and the montmorillonite, placing them in desiccator for 1 min, subsequently mixing with various amounts of water as described in Section 2.1, putting them in desiccator for 24 h. Excess IL and water were wiped away.

Thus, the four kinds of prepared M_{ILW} samples were observed using a TEM (JEM2010, JEOL Co., Japan) operated at 120 kV. For comparison, the dried montmorillonite was also observed under similar conditions by TEM. The montmorillonite powder for the TEM observation was dispersed in ethanol and skimmed off by a copper mesh with carbon-coated plastic microholes, while the four kinds of M_{ILW}s were mixed with ethanol (weight ratio; M_{ILW}–ethanol = 1:50), and only the supernatant was chosen. The process was repeated 5 times then skimmed off by a copper mesh for the organic samples.

The Raman spectra of M_{ILW} solutions with respect to the water ratios after storing in a desiccator for 2 h and maintaining a vacuum at 60 °C for 24 h were measured in order to understand the interaction between IL and water. It is well known that water can exist under vacuum condition due to the interaction between hydrophilic IL and water [29,30]. In this study, we focused on the specific water bonded with the hydrophilic IL because of the difficulty of removal the excess water (which was not intercalated) around M_{ILW}. For the Raman measurement, the solutions were kept in a Pyrex tube of 5.0 mm φ, 0.8 mm wall thickness. The Raman spectra were measured at room temperature by a JASCO NRS-3100 (JASCO Co, Japan) laser Raman spectrophotometer equipped with a single monochromator and a CCD detector. The Raman spectrum was taken in the range of 2800 to 3800 cm^{-1} at the 1.0 mm depth from the Pyrex surface and averaged 5 times. The Raman spectrum was taken using 2.5 mW of the 514.5 nm line of an Ar ion laser as the excitation source.

The amount of alkali metal cations substituted by IL and water molecules was determined following Schollenberger's procedure [31]. In the present study, the exchanged cations of the four kinds of M_{ILW}s through the intercalation process were measured. The exchanged cations, such as Na, K, Ca and Mg, were leached by filtration using a 1-N ammonium acetate solution and measured by inductively coupled plasma (ICP) (SPS-7800, SII Co., Japan).

3. Results and discussion

3.1. Intercalation behavior of ILs into the M_{ILW}

Fig. 1 shows the XRD patterns of the dried montmorillonite powder as a reference and the four kinds of M_{ILW} samples. The (001), (002) and (020) reflections at 9.67 Å, 4.78 Å and 4.44 Å, respectively, are a constituent of the montmorillonite powder. and the sharp reflections at the 2θ value of 26.76 (3.33 Å) correspond to the quartz that was used as an external component are shown in Fig. 1a. The result is in good agreement with the XRD data of the dried montmorillonite [32]. From Fig. 1b, the (001) reflection (13.93 Å), the (002) reflection (6.95 Å) and the (020) reflection (4.68 Å) were clearly observed. Compared to the dried montmorillonite powder, the (001) d-spacing values of the four kinds of M_{ILW}s showed a remarkable increase from 9.68 Å. This type of swelling, which shows a limited d-spacing increase, has been called crystalline swelling. Based on our previous studies, it is expected that the [BMIM]$^+$ cation was intercalated into the interlayer of montmorillonite [22].

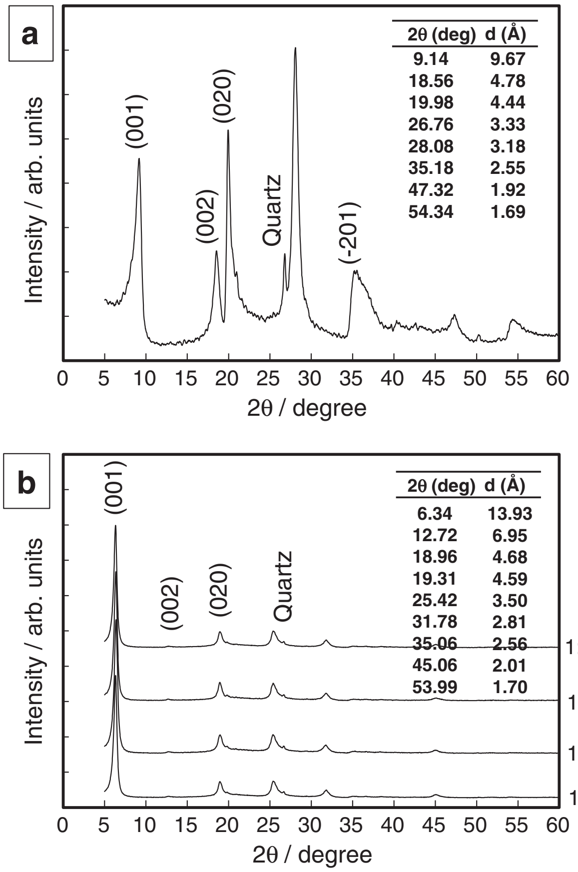

Fig. 1. XRD patterns of (a) the dried montmorillonite and (b) the four kinds of M_{ILW}s. The 1:1, 1:2, 1:10 and 1:50 indicates the amounts weight ratio of IL–water. The list shows the d-spacing of each XRD peaks.