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Journal Name

ARTICLE

Influence of the Molecular-Oriented Structure of Ionic Liquids on the Crystallinity of Aluminum Hydroxide Prepared by a Sol–Gel Process in Ionic Liquids

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The influence of the structure of ionic liquids on the crystallinity of aluminum hydroxide ($Al(OH)_3$) prepared by a sol–gel process with aluminum isopropoxide ($Al(OPr^j)_3$) in imidazolium-based ionic liquids was investigated. When the $Al(OH)_3$ was prepared in ionic liquids having long alkyl chains, such as 1-butyl-3-methylimidazolium salts and 1-methyl-3-octylimidazolium salts, highly crystalline products were obtained. In contrast, the $Al(OH)_3$ obtained using 1-ethyl-3-methylimidazolium salt was an amorphous material, indicating that hydrophobic interaction of the alkyl tail of the imidazolium cation of the ionic liquid strongly affects the crystallinity of sol–gel products and the local structure of the ionic liquid. Moreover, the crystallinity of the $Al(OH)_3$ prepared in ionic liquids increased relative to the amount of attritional water (ionic liquid/water = 1.28/2.0–3.5/0.2, w/w). In the case of a small amount of water added (ionic liquid/water = 3.5/0.2, w/w), the product was amorphous. These results implied that the presence of an ionic liquid and a sufficient amount of water were crucial for the successful synthesis of sol–gel products with high crystallinity. ^1H NMR analyses revealed a shift of the peak associated with the imidazolium cation upon the addition of water, which suggested that the molecular orientation of the ionic liquid was similar to that of a micelle.

Introduction

Ionic liquids (ILs) are ionic compounds comprising entirely cations and anions that are liquids at room temperature. ILs are nonvolatile, nonflammable, and exhibit high thermal stability; consequently, they are considered to be environmentally friendly media. Many authors have investigated the physical and chemical properties of ILs, their applications in electrochemical devices, and their use as media for chemical syntheses or separation processes.[1-13]

ILs can be designed to dissolve organic and inorganic compounds by changing the combination of anions and cations. Syntheses of inorganic materials such as silica, titania, and metal nanoparticles in ILs have been previously reported.[7,14-21] In addition to being used as solvents in such syntheses, ILs have been used as templates, surfactants, and crystal growth modifiers. The syntheses of vanadium pentoxide[17] and zirconia[19] have been reported, and the morphology of these products were observed to depend on the type of IL cations. Lian et al. demonstrated a one-step ionothermal synthesis of γ-Al_2O_3 in an imidazolium-based IL at 150°C, i.e., without high-

temperature (300°C–800°C) calcination.[22] Zhou et al. reported the direct syntheses of highly crystalline titania (rutile) nanoparticles and nanorods by sol–gel processes in an IL at 80°C without a high-temperature calcination step.[23,24] The mechanism of crystal growth processes in ILs is ambiguous; however, the authors of some reports have proposed that the mechanism of crystal growth is attributable to a molecular-orientated structure of the IL. Imidazolium-based ILs possibly form a molecular-orientated structure derived from hydrophobic interactions of the alkyl tail and electrostatic interactions of the ionic moiety.[25-27] Sol–gel products generated by hydrolysis and condensation of a precursor interact with an IL molecule through hydrogen bonding; thus, crystal growth should occur along the oriented IL molecule, which functions as a template.

Previously, we have reported a sol–gel processes for aluminum isopropoxide [$Al(OPr^i)_3$] and manganese nitrate ($Mg(NO_3)_2$) in imidazolium-based ILs 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4]) and 1-butyl-3-methylimidazolium chloride ([Bmim]Cl); the products were highly crystalline aluminum hydroxide ($Al(OH)_3$, bayerite) and

magnesium hydroxide (Mg(OH)$_2$), respectively. However, the product obtained in 2-propanol, a conventional organic solvent, was poorly crystalline.[28] Moreover, the product obtained in an ammonium-based IL, *N,N*-diethyl-*N*-methyl-*N*-(2-methoxy ethyl) ammonium tetrafluoroborate, [DEME][BF$_4$], was also crystalline Al(OH)$_3$; however, the crystallinity of Al(OH)$_3$ obtained in [DEME][BF$_4$] was lower than that obtained in [Bmim][BF$_4$].[28] With respect to crystal growth, [DEME][BF$_4$] might have been an unsuitable template in the sol–gel process because of its less-developed local structure, which is a consequence of its different molecular structure. A thorough investigation of the crystal-growth mechanism that leads to highly crystalline products in imidazolium-based ILs is needed.

In this study, we examined the influence of molecular structure and IL concentration on the crystallinity of the product obtained by a sol–gel process in an IL.

Experimental

Materials

Aluminum isopropoxide (Al(OPr^i)$_3$, 99% or greater purity; Sigma-Aldrich) and ammonium hydroxide (NH$_4$OH, NH$_3$: 28%; Nacalai Tesque, Inc.) were used as received. The ILs used were (**Scheme 1**): 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim][BF$_4$], 98% or greater purity; Alfa Aesar); 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF$_4$], 97% or greater purity; Sigma-Aldrich); and 1-methyl-3-octylimidazolium tetrafluoroborate ([Omim][BF$_4$], 97% or greater purity; Sigma-Aldrich). Prior to use, these ILs were dried in a muffle furnace at 120°C for 3 h to remove water. The amount of residual water after drying was measured by gravimetry. The weights of the ILs decreased with drying time and reached a plateau after 3 h. The dried ILs were cooled to room temperature and stored in a dry box to avoid moisture absorption. The water used in all the experiments was obtained from an Elix UV purification system (Millipore Co., Ltd.) and exhibited a resistivity of 18.2 MΩ cm.
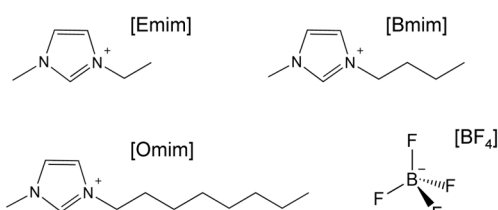
Scheme 1. Structural formula of the ions of ILs used in this study.

Sol–gel processes in ILs

The Al(OPr^i)$_3$ sol–gel processes were conducted in 10-mL glass vessels. The typical procedure was as follows: Al(OPr^i)$_3$ (0.125 g) was dissolved in the IL (2.06 mL) at 120°C and then cooled to room temperature. The reactions were initiated by adding NH$_4$OH (0.1 mol/L, 1.0 g) as a catalyst at 30°C and were performed for 24 h. Precipitated products were washed by centrifugation with methanol three times and were subsequently

vacuum dried at room temperature. To investigate the influence of the water fraction, the sol–gel processes were conducted using the same total volume of IL and water and the same amount of NH$_4$OH.

Characterization

Qualitative analyses of the products were conducted with a Fourier-transform infrared spectrometer (FT/IR-6200, JASCO Corp.) using the pressed-KBr-pellet technique and with an X-ray diffractometer (RINT-TTR, Rigaku Co., Ltd.) using a $2\theta/\theta$ method and Cu-Kα radiation (λ = 1.5418 Å) generated at 50 kV and 300 mA; the samples were scanned at 4°/min. ^{1}H NMR measurements were performed with a Bruker Avance-500 spectrometer at room temperature with the samples dissolved in D$_2$O (^{1}H resonance frequency:500 MHz). Sodium 3-(trimethylsilyl)propanesulfonic acid (DSS) was used as an internal standard. ^{1}H NMR measurements of the bulk ILs were conducted using a double tube to separate the ILs and D$_2$O.

Results and Discussion

Influence of the alkyl chain length of the imidazolium cation on the crystallinity of the sol–gel products

According to previous studies, an imidazolium-based IL forms a molecular-oriented local structure derived from van der Waals interactions of alkyl chains and electrostatic interactions of the imidazolium ring moiety.[25] The sol–gel product generated by hydrolysis and condensation of the precursor interacts with the IL through hydrogen bonding between the IL molecules and the hydroxyl group of the sol–gel product. The crystal growth of the sol–gel product occurs along the local structure of the IL, which acts as a template. As previously mentioned, the influence of the molecular structure of the IL cation on the crystallinity of the sol–gel product has been investigated using imidazolium-based IL [Bmim][BF$_4$] and ammonium-based IL [DEME][BF$_4$]. The results demonstrated
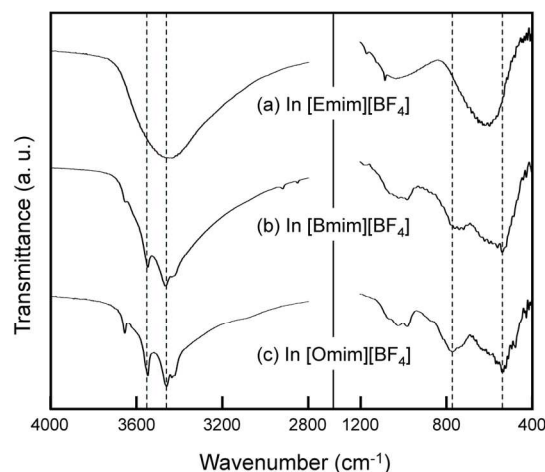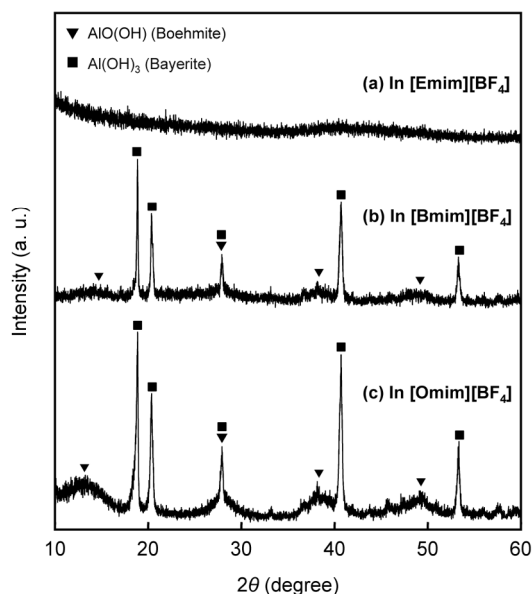

Figure 1. FT-IR spectra of products prepared by sol–gel processing of Al(OPr^i)$_3$ in (a) [Emim][BF$_4$], (b) [Bmim][BF$_4$], and (c) [Omim][BF$_4$] at 30°C using 0.1 mol/L NH$_4$OH as a catalyst.

that the cation species affect the crystallinity of the sol–gel products, which might be a consequence of the difference between the local structures of the ILs. We will now consider the influence of the alkyl chain length.

Figure 1 shows the FT-IR spectra of the products prepared by sol–gel processing of $Al(OPr^i)_3$ in $[Emim][BF_4]$, $[Bmim][BF_4]$, and $[Omim][BF_4]$. In a previous study, we determined that the product prepared by the sol–gel process of $Al(OPr^i)_3$ in $[Bmim][BF_4]$ using NH_4OH was highly crystalline $Al(OH)_3$ (bayerite).[28] In the FT-IR spectra, the products prepared in $[Bmim][BF_4]$ and $[Omim][BF_4]$ had characteristic peaks at 531, 769, 3460, and 3548 cm^{-1}, suggesting that the products obtained in $[Bmim][BF_4]$ and $[Omim][BF_4]$ were both crystalline $Al(OH)_3$. However, the spectrum of the product prepared in $[Emim][BF_4]$ exhibited no significant sharp peaks, indicating that crystalline $Al(OH)_3$ was not produced. Furthermore, the broad peak at 4000–2800 cm^{-1} is attributed to water adsorbed during the process of preparing the KBr pellet for FT-IR measurement.

Figure 2. XRD spectra of products prepared by sol–gel processing of $Al(OPr^i)_3$

in (a) $[Emim][BF_4]$, (b) $[Bmim][BF_4]$, and (c) $[Omim][BF_4]$ at 30°C using 0.1 M NH_4OH as catalyst.

Figure 2 shows the XRD spectra of the products prepared by sol–gel processes in various ILs. The spectrum of the product obtained in $[Emim][BF_4]$ exhibited no significant peaks, indicating that the product was an amorphous material. The spectra of the products obtained in $[Bmim][BF_4]$ and $[Omim][BF_4]$ had two types of peaks. The broad and weak peaks, denoted by triangles, are assigned to $AlO(OH)$, and the sharp and strong peaks, denoted by squares, are assigned to $Al(OH)_3$. The intensity of the $Al(OH)_3$ and $AlO(OH)$ peaks in the [Omim] system was as strong as that in the [Bmim] system. These results suggest that the local structure should be formed above a threshold alkyl chain length (a butyl group in this case) and that a similar structure was formed irrespective of whether

butyl or octyl groups, which have alkyl chain lengths greater than this threshold, were present.

From these results, the alkyl chain length of the imidazolium cation significantly influences the crystallinity of the sol–gel product, which might be a consequence of the local structure of the IL. An IL with a longer alkyl chain (butyl or octyl) might form a distinct local structure because of strong hydrophobic interaction between the alkyl tails. These results are analogous to those previously reported by other groups, who suggested that hydrophobic interactions occur between the alkyl chains of the imidazolium cation.[29-31]

Influence of the water fraction on the crystallinity of sol–gel products in IL/water binary mixtures

Water is essential in sol–gel processes, which is a combination of hydrolysis and condensation reactions. In a previous study, the formation of the local structure of ILs in the presence of water was investigated from both theoretical and experimental perspectives.[29,32-38] Some researchers have suggested that a sufficient amount of water promotes the alkyl chain aggregation of the imidazolium cation and that larger quantities of water induce decomposition of the structure. Thus, the amount of water in the reaction system might affect the crystallinity of the sol–gel product and local structure.

Figure 3 shows the FT-IR spectra of products prepared in ILs with various amounts of water. The spectra of the product prepared with a large amount of water ($[Bmim][BF_4]$/water = 1.28/2.0, w/w; Figure 3a) and the product ($[Bmim][BF_4]$/water = 2.5/1.0, w/w; Figure 3b; the same data shown in Figure 1b) exhibited characteristic peaks at 531, 769, 3460, and 3548 cm^{-1}. In contrast, the spectra of the products obtained with a small amount of water ($[Bmim][BF_4]$/water = 3.09/0.5 and 3.46/0.2, w/w; Figure 3c and 3d, respectively) had no characteristic sharp peaks, which indicates that crystalline $Al(OH)_3$ was not obtained.

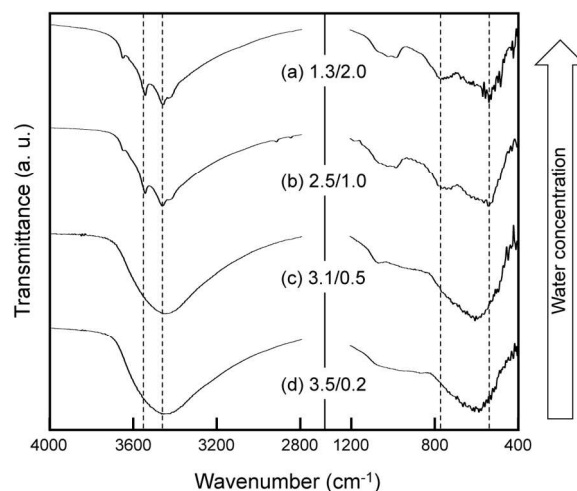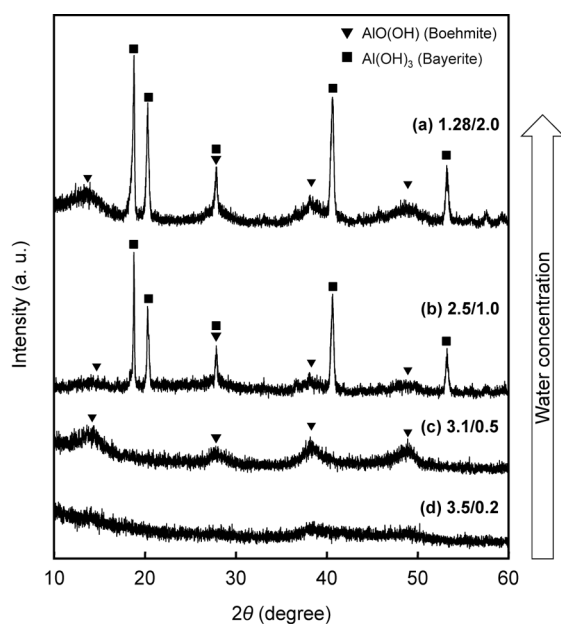**Figure 3**. FT-IR spectra of products prepared by sol–gel processing of $Al(OPr^i)_3$ in $[Bmim][BF_4]$ at 30°C using various amounts of water (added as NH_4OH aq.).

[Bmim][BF$_4$]/water (w/w), NH$_4$OH (mol/L): (a) 1.28/2.0, 0.05; (b) 2.5/1.0, 0.1; (c) 3.09/0.5, 0.2; and (d) 3.46/0.2, 0.5.

Figure 4 shows the XRD patterns of the products prepared in [Bmim][BF$_4$] with various amounts of water. The patterns of the products prepared with a large amount of water exhibited broad and weak peaks, denoted by triangles, and sharp and strong peaks, denoted by squares, which are assigned to AlO(OH) and Al(OH)$_3$, respectively. The patterns of the products obtained with a small amount of water exhibited only broad peaks (AlO(OH)) or no peaks, indicating that the materials were amorphous. These results suggest that sufficient amounts of water induced the local structure of the IL and that this structure affected the crystallinity of the sol–gel product.

To investigate the presence of a local IL structure in more detail, we performed ^{1}H NMR measurements of an IL/water binary


mixture. If the IL molecules form a local structure in the IL/water binary mixture, the electron density of the imidazolium proton should change compared to that in the bulk IL; thus, a peak shift should be observed.

Figure 4. XRD patterns of products prepared by sol–gel processes of Al(OPr^i)$_3$ in [Bmim][BF$_4$] at 30°C using various amounts of water (added as NH$_4$OH aq.). [Bmim][BF$_4$]/water (w/w), NH$_4$OH (mol/L): (a) 1.28/2.0, 0.05; (b) 2.5/1.0, 0.1; (c) 3.09/0.5, 0.2; and (d) 3.46/0.2, 0.5.

Figure 5 shows the ^{1}H NMR spectra of [Bmim][BF$_4$] with various amounts of D$_2$O in the absence of NH$_4$OH and Al(OPr^i)$_3$. The numbers associated with the spectra in Figure 5 indicate the degree of peak shift ($\Delta\delta$ [ppm]) from the peak positions in the spectrum of the bulk IL. As evident in the NMR spectra, all of the peaks of the imidazolium cation shifted to a lower magnetic field upon the addition of water; however, the $\Delta\delta$ value differed for each proton and water concentration.

The $\Delta\delta$ values of each imidazolium proton as a function of water fraction are plotted in **Figure 6**. A substantial peak shift
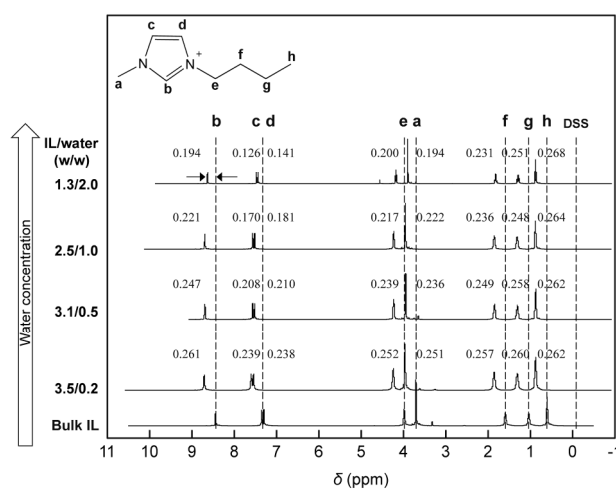
indicates a different chemical environment for the molecule. In contrast, a small peak shift indicates that the molecular dynamics are similar to those of the bulk IL. In the case of a small amount of water added ([Bmim][BF$_4$]/water = 3.46/0.2,

Figure 5. ^{1}H NMR spectra of [Bmim][BF$_4$] in the presence of various amounts of D$_2$O. [Bmim][BF$_4$]/D$_2$O (w/w), NH$_4$OH (mol/L): (a) 1.28/2.0, 0.05; (b) 2.5/1.0, 0.1; (c) 3.09/0.5, 0.2; and (d) 3.46/0.2, 0.5.

w/w), the $\Delta\delta$ values were 0.24 to 0.26 ppm. In the case of a large amount of water added, the $\Delta\delta$ values for b, c, and d, which correspond to the protons in the imidazolium ring, and the $\Delta\delta$ values for a and e, which correspond to the methyl and methylene protons combined with N atoms in imidazolium ring, drastically decreased. The $\Delta\delta$ values for f, g, and h, which correspond to protons combined with the alkyl tail moiety, remained stable at approximately 0.25 ppm. These results indicate that the imidazolium ring moiety moved freely at the same level as the bulk IL, whereas alkyl tail groups interacted hydrophobically and alkyl tail association occurred. This
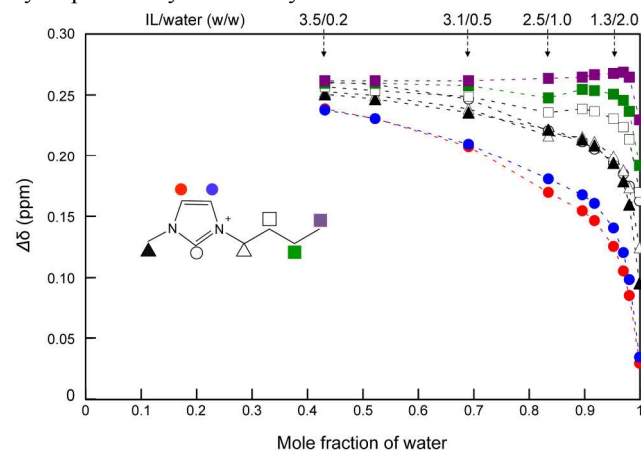
phenomenon is likely caused by the hydration of the imidazolium ring. Water molecules likely locate as neighbors of ionic moieties and trigger the formation of the local structure of the IL.

Figure 6. Degree of shift of the ^{1}H NMR spectral peak associated with the imidazolium cation of [Bmim][BF$_4$] relative to the position of the peak associated with the imidazolium cation of bulk [Bmim][BF$_4$] (mole fraction of water = 0) in the presence of various amounts of D$_2$O.

Conclusions

The crystallinity of sol–gel products prepared in imidazolium-based ILs using Al(OPr^i)$_3$ as a precursor and NH$_4$OH as a catalyst was affected by the alkyl chain length of imidazolium cation and by the IL concentrations. Water played a crucial role in forming the local structure and in the subsequent crystal growth of the sol–gel products. According to the results of the NMR analysis, water molecules should be hydrated around the ionic moieties of the IL.

We have reported the preparation of organic/inorganic composite materials, especially polymer-core/highly thermally conductive metal oxide shell composite particles as highly thermally conductive materials.[39,40] The crystallinity of the metal oxide shell correlates to the composite particles' thermal conductivity. The results observed in this study provide important information for preparing composite materials with a high thermally conductive metal oxide shell.

Acknowledgments

Notes and references

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