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Preparation of Aluminum Hydroxide and Alumina Particles in an Ionic Liquid

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Highly crystalline $Al(OH)_3$ particles were successfully prepared by the sol–gel process of aluminum isopropoxide ($Al(OPr^i)_3$) in a hydrophilic ionic liquid (IL), 1-butyl-3-methylimidazolium tetrafluoroborate ($[Bmim][BF_4]$) at 30 °C using NH_4OH as catalyst. Moreover, crystalline alumina particles were prepared from the $Al(OH)_3$ particles by heat treatment at 300 °C. When 2-propanol was used as medium for comparison, obtained particles were low crystalline AlO(OH). This difference seemed to arise from the difference in the local structure of $Al(OPr^i)_3$ in IL.

Ionic liquids (ILs) are a class of solvents which consist of entirely organic cation and organic or inorganic anion and are liquid at ambient temperature. ILs are used as environmentally friendly solvents because of their nonvolatility, nonflammability, and thermal stability.[1] Many researchers have focused on these properties and have devoted much attention to use of these as media for chemical reactions.[2] Ogoshi et al. reported that green polymerization of phenol with sulfuric acid as catalyst in ILs and without catalyst using an IL with a Brønsted acid site.[3] Landfester et al. prepared polyimide nanoparticles in IL taking advantage of the nonvolatility and thermal stability of IL.[4]

Recently, we succeeded in preparing polystyrene (PS) particles by dispersion polymerization in an IL, *N*,*N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)amide ([DEME][TFSA]).[5] We also prepared PS particles by thermal polymerization in [DEME][TFSA] at 130 °C without radical initiator. Moreover, Nylon-6 particles[6] and poly(acrylic acid) (PAA) particles[7] were successfully prepared in ILs. Moreover, the preparation of composite polymer particles, which consist of PS (hydrophobic) core and PAA (water-soluble) shell by seeded dispersion polymerization in [DEME][TFSA] using PS particles as seed, was demonstrated.[8]

Furthermore, the chemical and physical properties of ILs can be easily tuned by changing the counter anions. ILs exhibit unusual solvent power for organic compounds and inorganic compounds. The syntheses of inorganic materials such as silica, metal, and metal oxide nanoparticles in ILs are also studied by many researchers.[9,10] Antonietti and co-workers reported direct syntheses of highly crystalline titania particles and nanorods by sol–gel process in IL at 80 °C without high-temperature ($\geq$1000 °C) calcination.[10,11] This would suggest the possibility of preparation of polymer/highly crystalline metal oxide composite materials. Generally, highly crystalline metal oxide requires high-temperature calcination, and organic polymers such as PS particles are easily decomposed at high temperature. However, only a few papers report the preparation of alumina (Al_2O_3) in ILs. Endres and co-workers reported the synthesis of alumina by the sol–gel process in hydrophobic ILs, in which IL was immiscible with water for hydrolysis reaction.[12,13] In their work, crystalline alumina particles were obtained after calcination of the sol–gel products at 500 to 1000 °C, which is above the decomposition temperature of PS (ca. 400 °C).

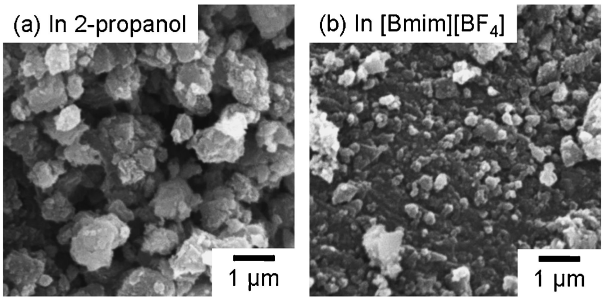

Figure 1. SEM photographs of particles prepared by the sol–gel process of $Al(OPr^i)_3$ in 2-propanol (a) and $[Bmim][BF_4]$ (b) at 30 °C using NH_4OH as catalyst.

In this study, we report preparation of crystalline aluminum hydroxide and alumina particles by the sol–gel process of aluminum isopropoxide ($Al(OPr^i)_3$) using hydrophilic IL, 1-butyl-3-methylimidazolium tetrafluoroborate ($[Bmim][BF_4]$), as medium without high-temperature calcination prior to preparation of PS/crystalline alumina composite particles.

The sol–gel reaction of $Al(OPr^i)_3$ in $[Bmim][BF_4]$ was conducted in a 10-mL glass vessel. $Al(OPr^i)_3$ (0.13 g) was dissolved in $[Bmim][BF_4]$ (2.1 g) at 120 °C and then cooled at room temperature. The reactions were started by adding 0.1 M NH_4OH (1.0 g) as catalyst at 30 °C and were carried out for 24 h. The sol–gel reactions in 2-propanol were carried out, for comparison, under the same conditions except that the IL was replaced with 2-propanol (1.4 g).

Figure 1 shows the SEM photographs of the samples prepared in 2-propanol and $[Bmim][BF_4]$ at 30 °C. All the samples were nonregular shaped particles having rough surface, and sizes of the particles in 2-propanol and $[Bmim][BF_4]$ were micrometer- and submicrometer-sizes, respectively. This difference might be based on the difference of viscosities between 2-propanol (1.77 mPa s) and $[Bmim][BF_4]$ (118 mPa s). High viscosity media tend to depress the coagulation of nuclei.

Figure 2 shows the FT-IR spectra of the samples prepared in 2-propanol (a) and $[Bmim][BF_4]$ (b) at 30 °C. The FT-IR spectra show that neither sample had the characteristic broad peaks of alumina at 585 and 763 cm^{-1} (Figures 2a and 2b). The XRD pattern of the sample prepared in 2-propanol showed less crystalline profile and some broad peaks (Figure 3a), which was identified as boehmite, [AlO(OH)] (JCPDS File Card No. 21-1307). On the other hand, the XRD pattern of $[Bmim][BF_4]$ systems was observed (Figure 3b) as two types of peak, in which broad and weak peaks (▼) and sharp and strong peaks (■) can be assigned to AlO(OH) and bayerite, $[Al(OH)_3]$ (JCPDS File Card No. 20-0011), respectively.

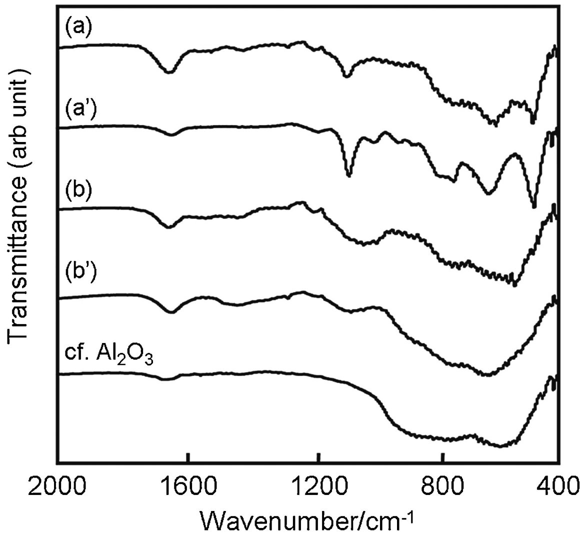

Figure 2. FT-IR spectra of samples before (a, b) and after (a′, b′) heat treatment at 300 °C for 24 h in N_2 atmosphere prepared by the sol–gel process of $Al(OPr^i)_3$ at 30 °C in 2-propanol (a, a′) and $[Bmim][BF_4]$ (b, b′) using NH_4OH as catalyst.

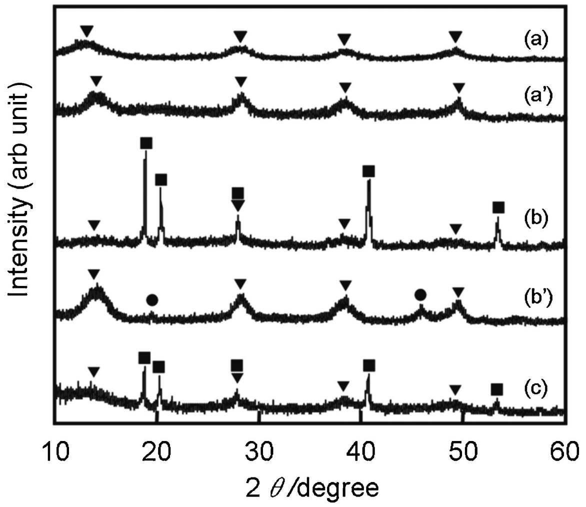

Figure 3. XRD spectra of samples before (a, b, c) and after (a′, b′) heat treatment at 300 °C in N_2 atmosphere prepared by the sol–gel process of $Al(OPr^i)_3$ in 2-propanol (a, a′), $[Bmim][BF_4]$ (b, b′), and $[DEME][BF_4]$ (c) at 30 °C using NH_4OH as catalyst.

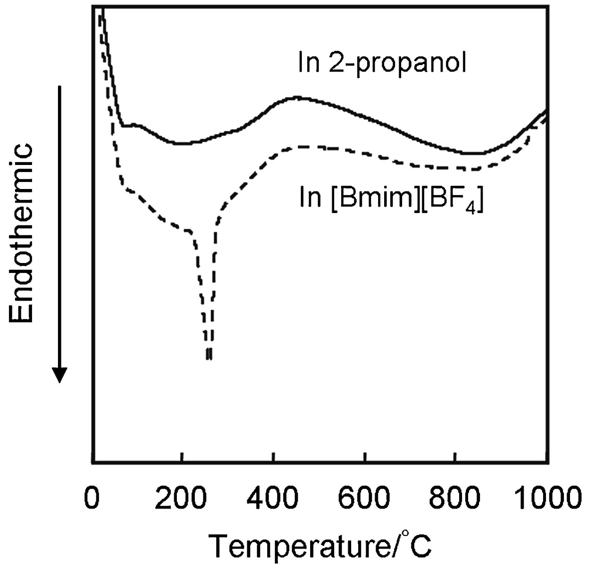

Figure 4. DTA curves of samples prepared by sol–gel process of $Al(OPr^i)_3$ in 2-propanol (—) and $[Bmim][BF_4]$ (----) at 30 °C for using NH_4OH as catalyst measured at a heating rate of 10 °C min^{-1} in N_2 atmosphere.

In the case of $[Bmim][BF_4]$, highly crystalline aluminum hydroxide obtained though alumina could not be prepared. These results were actually similar to Antonietti's work, in which alkylimidazolium-based ILs worked as a template, resulting the formation of highly crystalline products. They suggested that hydrogen bonding formed between the anion of IL and the hydroxy group of the sol–gel product along the local structure of IL by using imidazolum-based IL.[14] Hamaguchi and co-workers reported that alkylimidazolium cations form liquid crystal-like local structures based on π–π stacking interaction between imidazolium rings and hydrophobic interaction between alkyl chains.[15,16] In order to confirm this phenomenon, alkylammonium-based hydrophilic IL, *N*,*N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium tetrafluoroborate ($[DEME][BF_4]$) was used as medium, in which regularity of the local structure would be lower than $[Bmim][BF_4]$. XRD analysis of the sample prepared in $[DEME][BF_4]$ is shown in Figure 3c. XRD spectra exhibit that the sample obtained in $[DEME][BF_4]$ had the same peaks as that prepared in $[Bmim][BF_4]$; thus, these samples are the same components ($AlO(OH)$ and $Al(OH)_3$). However, values of diffraction intensity of $Al(OH)_3$ of $[Bmim][BF_4]$ system were twice larger than that of $[DEME][BF_4]$ system, indicating that yielding sample was highly crystalline $Al(OH)_3$ in $[Bmim][BF_4]$ compared to the case of $[DEME][BF_4]$. These results suggest that local structure of $[Bmim][BF_4]$ resulting from the interaction of alkylimidazolium cation worked as template.

It is well known that aluminum hydroxides transform to alumina by heat treatment. There are several crystal structures of alumina dependent on treatment temperature such as η-, χ-, γ-, δ-, θ-, and α-alumina.[17] It has been reported that $AlO(OH)$ and $Al(OH)_3$ transform to γ-alumina and η-alumina at calcination temperatures of 450 and 230 °C, respectively,[17] which indicated that $Al(OH)_3$ can be transform to alumina at comparatively low temperature.

From the differential thermal analysis (DTA) data of $AlO(OH)$ and $Al(OH)_3$ prepared by the sol–gel process at 30 °C in 2-propanol and $[Bmim][BF_4]$ (Figure 4), the curves show that the sample obtained in 2-propanol ($AlO(OH)$) has no peaks in the measuring range, while the sample obtained in $[Bmim][BF_4]$ (mainly $Al(OH)_3$) has a strong endothermic peak at 250 °C. This indicates that $Al(OH)_3$ should transform into η-alumina.

Figure 5 shows the SEM photographs of samples after heat treatment at 300 °C, which prepared in 2-propanol and $[Bmim][BF_4]$, respectively. Both samples were nonregular shaped particles having rough surface. The size of these particles becomes larger than that of samples before heat

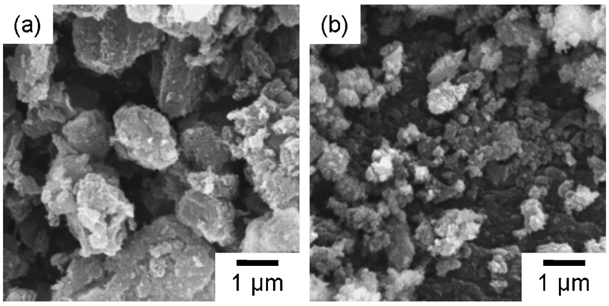

Figure 5. SEM photographs of samples after heat treatment at 300 °C for 24 h prepared by sol–gel process of $Al(OPr^i)_3$ in 2-propanol (a) and $[Bmim][BF_4]$ (b) at 30 °C using NH_4OH as catalyst.

treatment. This might be derived from sintering and aggregation of the AlO(OH) and $Al(OH)_3$ particles during heat treatment.

FT-IR and XRD analyses of samples after heat treatment at 300 °C are shown in Figures 2a′, 2b′, 3a′, and 3b′. After heat treatment, the FT-IR spectrum of sample obtained in 2-propanol did not display peak shift, on the other hand, the sample obtained in $[Bmim][BF_4]$ showed small peak shift from 540 to 620 cm^{-1} (Figure 2). XRD spectra show that there was no change for the sample obtained in 2-propanol. In the case of $[Bmim][BF_4]$, the highly crystalline peaks of $Al(OH)_3$ (■) disappeared and new small peaks (●) appeared indicating η-alumina. These results indicate that although the crystallinity was low, crystalline alumina was successfully synthesized under mild conditions.

From the above results, it was concluded that highly crystalline $Al(OH)_3$ particles were prepared by the sol–gel process of $Al(OPr^i)_3$ using $[Bmim][BF_4]$ with NH_4OH as a catalyst, which transform to η-Al_2O_3 at the consecutive heat treatment at calcination temperature of 300 °C. The results illustrated that preparation of polymer/crystalline metal oxide composite materials using $[Bmim][BF_4]$ as medium can be anticipated. The preparation of composite particles will be reported in a near future publication.

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References

1 T. Welton, *Chem. Rev.* **1999**, *99*, 2071.
2 P. Wasserscheid, W. Keim, *Angew. Chem., Int. Ed.* **2000**, *39*, 3772.
3 T. Ogoshi, T. Onodera, T.-A. Yamagishi, Y. Nakamoto, *Macromolecules* **2008**, *41*, 8533.
4 H. Frank, U. Ziener, K. Landfester, *Macromolecules* **2009**, *42*, 7846.
5 H. Minami, K. Yoshida, M. Okubo, *Macromol. Rapid Commun.* **2008**, *29*, 567.
6 H. Minami, Y. Tarutani, K. Yoshida, M. Okubo, *Macromol. Symp.* **2010**, *288*, 49.
7 H. Minami, A. Kimura, K. Kinoshita, M. Okubo, *Langmuir* **2010**, *26*, 6303.
8 H. Minami, K. Yoshida, M. Okubo, *Macromol. Symp.* **2009**, *281*, 54.
9 K.-I. Okazaki, T. Kiyama, K. Hirahara, N. Tanaka, S. Kuwabata, T. Torimoto, *Chem. Commun.* **2008**, 691.
10 H. Kaper, F. Endres, I. Djerdj, M. Antonietti, B. M. Smarsly, J. Maier, Y. S. Hu, *Small* **2007**, *3*, 1753.
11 Y. Zhou, M. Antonietti, *J. Am. Chem. Soc.* **2003**, *125*, 14960.
12 H. K. Farag, F. Endres, *J. Mater. Chem.* **2008**, *18*, 442.
13 H. Farag, M. A. Zoubi, F. Endres, *J. Mater. Sci.* **2009**, *44*, 122.
14 Y. Zhou, J. H. Schattka, M. Antonietti, *Nano Lett.* **2004**, *4*, 477.
15 S. Hayashi, R. Ozawa, H. Hamaguchi, *Chem. Lett.* **2003**, *32*, 498.
16 H. Hamaguchi, R. Ozawa, *Adv. Chem. Phys.* **2005**, *131*, 85.
17 M. Digne, P. Sautet, P. Raybaud, H. Toulhoat, E. Artacho, *J. Phys. Chem. B* **2002**, *106*, 5155.