SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

Preparation of Mesoporous Aluminum Hydroxide and Oxide in Ionic Liquids

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Abstract—Mesoporous aluminum hydroxides and oxides were synthesized using ionic liquids (ILs) as templates. The influence of various factors (the nature of the IL, pH, ultrasonication, surfactants, reagent ratio, and the nature of the aluminum precursor) on the specific surface area and pore volume was analyzed.

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Ionic liquids (ILs) are used as templates for preparing mesoporous inorganic oxides [1-7]. However, the preparation of mesoporous Al_2O_3 in ILs has not been described. Micellar template is now the main method for preparing mesoporous oxides, including Al₂O₃ [8]. In particular, mesoporous Al₂O₃ with $S \ge 550 \text{ m}^2/\text{g}$ was prepared by this method [9]. Below, we report the results of our study of the preparation of mesoporous $Al(OH)_3 \cdot nH_2O$ and Al_2O_3 in systems where the template used was one of the following ILs: 1-butyl-3methylimidazolium bromide (bmimBr), 1-butyl-3methylimidazolium bis(trifluoromethylsulfonyl)amide $(bmimNTf_2)$, 1-decyl-3-methylimidazolium bromide (dmimBr), or 1-butyl-3-methylimidazolium chloride chloroaluminate with varied AlCl₄⁻ concentrations (bmimCl and bmimAlCl₄).

EXPERIMENTAL

Synthesis of Halide ILs (bmimCl and bmimBr)

The synthesis procedure is described in works [10, 11]. Butyl halide taken in a 20% excess was mixed with *N*-methylimidazole, and acetonitrile was added to the mixture in provide uniform boiling. The mixture was refluxed for 2–4 h, acetonitrile was distilled off in vacuo, the residue was rinsed three times with equal volumes of ethyl acetate to remove unreacted reagents, and finally ethyl acetate and water were removed from the product in vacuo. The yield was 65–80%; most loss was during ethyl acetate rinsing.

Example synthesis: butyl bromide (32.9 g, 0.24 mol), *N*-methylimidazole (16.4 g, 0.2 mol), and acetonitrile (30 mL) were refluxed for 2.5 h. The product was rinsed with three 30-mL portions of ethyl acetate. The yield was 31.5 g bmimBr (72%). The product was a thick light yellow liquid which crystallized upon standing. Thus-prepared bmimCl was virtually colorless.

Synthesis of bmimNTf₂

The synthesis procedure is described in work [10]. BmimNTf₂, which is incompletely miscible with water, was produced by an exchange reaction between bmimBr and LiNTf₂ in aqueous solution and separated. BmimNTf₂ remaining in the aqueous phase was extracted with methylene chloride in virtually quantitative yield.

Synthesis of an IL Containing $AlCl_4$ Anions

Inasmuch as bmimAlCl₄ crystallizes at room temperature, we used near-eutectic mixtures of bmimAlCl₄ and bmimCl that contained 40 or 60 mol % AlCl₄⁻. To bmimCl (3 g), a calculated amount of freshly distilled AlCl₃ was added; the reaction mixture was strongly heated, and a clear liquid was formed.

Preparation of Mesoporous $Al(OH)_3 \cdot nH_2O$

From Al(O-iPr)3. Aluminum isopropoxide was dissolved in benzene. The cosolvent used was freshly prepared and dried acetonitrile or dimethylformamide. The solutions were mixed with an IL. Then, the solvents were distilled off in vacuo at temperatures not higher than 80°C. Very fine solid particles of aluminum isopropoxide were formed and uniformly distributed over the bulk of in the IL. The particle diameter was not greater than 100 µm. To this mixture, water was added in an amount sufficient for Al(OH)₃ formation. The mixture was stirred and left to stand at room temperature for 1 week for hydrolysis and gel formation. Gel formation started soon when, after water addition, the mixture of IL, aluminum isopropoxide, and H₂O was ultrasonicated (a UZDN-A instrument, 300 W, 22 ± 1.65 kHz). After 7 days, the IL and isopropanol were extracted from the gel with acetonitrile or ethanol (two times for 4 h each in a flask with a refluxer). The solid precipitate was filtered with a porous-bottomed funnel, and the IL

| IL + Al-precursor systems | | | | | | | |
|---------------------------|------------------|-------------|---|---|------|-----------------------|--|
| Run | Properties of IL | | Specific surface area, pore volume* | IL and water amounts per 1.5 g Al(O- <i>i</i> Pr) ₃ | | | Notos |
| no. | | | | IL volume, mL | | H ₂ O (mL) | - Notes |
| 1 | | Hydrophilic | 325/1.03 | bmimBr | 1 | 0.1985 | |
| 2 | | | 326/1.24 | The same | 1 | 2.0 | |
| 3 | | | 606/1.88 | " | 4 | 2.0 | |
| 4 | sous | | 423/1.36 | " | 4 | 2.0 | Ultrasonication during gel formation |
| 5 | gen | | 362/1.10 | dmimBr | 1 | 0.1985 | |
| 6 | letero | | 278/0.66 | The same | 1 | 0.1985 | Addition of NH ₄ OH to pH 9 |
| 7 | Щ | Hydrophobic | 589/1.75 | bmimNTf ₂ | 1.5 | 0.1985 | |
| 8 | | | 528/1.14 | The same | 4 | 2.0 | |
| 9 | | | 313/0.67 | " | 1.25 | 0.1975 | Addition of 3 wt % PEG |
| 10 | leous | Hydrophilic | 390/0.26 | bmimCl : AlCl ₃ , AlCl ₃ weight fraction = 0.2 | | - | Addition of NH ₄ OH** |
| 11 | moger | | 333/0.26 | bmimCl : AlCl ₃ , AlCl ₃ weight fraction = 0.4 | | - | The same |
| 12 | ЮŅ | Hydrophobic | 399/0.20 | bmimNTf ₂ | 1 | 0.1985 | |

Characteristics of aluminum hydroxide samples

Notes: * In the numerator, $Al(OH)_3 \cdot nH_2O$ specific surface areas (m^2/g) ; in the denominator, pore volumes (cm^3/g) with pore diameters less than 40 nm.

** In the amount required for $Al(OH)_3 \cdot nH_2O$ precipitation.

was recovered. The solid residue was dried in air for 1-2 h at 100–120°C.

From AlCl₃. To the chloride–chloroaluminate IL, an aliquot of 25% aqueous ammonia required for hydrolyzing tetrachloroaluminate ions was added under vigorous stirring:

 $A1C1_{4}^{-} + 3NH_{3} + 3H_{2}O = Al(OH)_{3}\downarrow + 3NH_{4}Cl + Cl^{-}.$

The precipitate was left to age for 1 week; the last day, it was heated for 4 h to 100°C to enhance aging, cooled, and centrifuged. The precipitate was washed alternately with ethanol and water to remove the IL and NH_4Cl and dried at 150°C.

From $Al(acac)(O-iPr)_2$. To obtain homogeneous solutions of the aluminum derivative in a hydrophobic IL, one of the three isopropoxide moieties was substituted by an acetyl acetone moiety (acac). The resulting $Al(acac)(O-iPr)_2$ was dissolved in the bmimNTf₂ IL. The hydrolysis and separation of porous aluminum hydroxide were performed as with aluminum isopropoxide.

The pore-structure parameters for $Al(OH)_3$ were derived from low-temperature nitrogen adsorption/desorption isotherms. The isotherms were recorded on an ASAP 2010 Micromeritics automated sorption meter. Standard instrumental software was used in isotherm processing.

The phase composition of products $(Al_2O_3 \cdot nH_2O)$ was studied on a DRON-3 diffractometer $(2\theta = 5^\circ - 60^\circ, CuK_\alpha \text{ radiation}).$

RESULTS AND DISCUSSION

The rate of aluminum isopropoxide hydrolysis in hydrophilic or hydrophobic ILs was expected to be different because of different solubilities of water in these ILs. However, one week of structuring led to complete hydrolysis in all samples. It appeared that from heterogeneous IL + aluminum precursor + H₂O systems, aluminum hydroxide was obtained with higher specific surface areas (up to $600 \text{ m}^2/\text{g}$) and greater specific pore volumes (up to $1.88 \text{ cm}^3/\text{g}$) than from initially homogeneous IL + aluminum precursor + H₂O systems; compare runs 3 and 7 with runs 10-12 (table). Ultrasonication in the beginning of gel formation decreased both the specific surface area and the pore volume, despite the enhancement of gel formation; compare run 3 with run 4 (table). When the pH of the system was increased to 9 by adding aqueous NH₃ in order to complete hydrolysis, both the specific surface area and the pore volume decreased; compare runs 5 and 6 (table). Addition of 3 wt % PEG decreased the specific surface area and pore volume; compare runs 7 and 9 (table). The following fact is interesting. When the ratios between the IL and water that gave the best results for hydrophilic ILs were used for hydrophobic ILs, the pore volume decreased; compare runs 3, 7, and 8 (table).

In hydrophilic ILs that formed homogeneous systems, aqueous ammonia was used for hydrolyzing AlCl₃. One could think that the use of aqueous NH₃ is the reason of the low specific surface areas and low pore volumes of Al(OH)₃ \cdot *n*H₂O; compare runs 10 and 11 (table). This was inferred from the low specific surface area and low pore volume obtained in run 6 (table). Although water was used for hydrolyzing a homogeneous Al(acac)(O-iPr)₂ in a hydrophobic IL, the specific surface area and pore volume in this case were low (table, run 12). This signifies that the heterogeneity of the IL + aluminum precursor system enhances the development of the specific surface area and pore volume in Al(OH)₃ \cdot *n*H₂O. Likely, the domain structure of the IL, which was discovered in works [12–21], has an effect in heterogeneous systems. Solid aluminum isopropoxide particles in heterogeneous systems can be accommodated only in interdomain spaces. Therefore, newly formed Al(OH)₃ \cdot *n*H₂O should also reside in interdomain spaces; i.e., IL domains form pore volumes. Ultrasonication in the beginning of structuring, apparently, spoils this process, deteriorating the results (see above). Possibly, PEG changes the domain structure of the IL, which also deteriorates the results (see above).

The Al(OH)₃ \cdot *n*H₂O obtained in run 7 after extracting the IL was calcined in air in stages to convert it to Al₂O₃ as follows: heating rate, 1 K/min; exposure at 300°C for 2 h, at 400°C for 2 h, and at 500°C for 2 h. The resulting sample had a specific surface area of 453 m²/g and a specific pore volume of 1.74 cm³/g. Because IL bmimNTf₂ in an inert medium withstands heating to 400°C, an Al(Al(OH)₃ \cdot *n*H₂O gel in IL bmimNTf₂ was heated in flowing argon as follows: from 25 to 100°C for 1 h; at 100°C, 1 h; from 100 to 200°C, 2 h. After heating, the ILs were extracted and the solid residue was dried. The specific surface area and pore volume were equal to 363 m²/g and 1.16 cm³/g. All samples were amorphous to X-rays.

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