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Homogeneous forced hydrolysis of aluminum through the thermal decomposition of urea

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Abstract

Homogeneous hydrolysis of aluminum by decomposition of urea in solution was achieved because the urea coordinates to the Al^{3+} in solution, forming $[Al(H_2O)_5(urea)]^{3+}$ and to a lesser extent $[Al(H_2O)_4(urea)_2]^{3+}$. Upon hydrolysis more hydrolyzed monomeric species, $[Al(H_2O)_5(OH)]^{2+}$, $[Al(H_2O)_4(OH)_2]^{+}$, $[Al(H_2O)_4(urea)(OH)]^{2+}$, and $[Al(H_2O)_3(urea)(OH)_2]^{+}$, were formed, followed by trimeric species and the Al_{13} Keggin complex $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$. The ^{27}Al NMR spectra indicated the formation of other complexes in addition to the Al_{13} at the end of the hydrolysis reaction.

Keywords: Al_{13}; Keggin structure; Hydrolysis; Nuclear magnetic resonance spectroscopy; Urea

1. Introduction

The numerous studies that have been performed over the past 150 years on the hydrolysis and polymerization of aluminum in aqueous solutions have been reviewed in detail by Akitt [1]. Understanding the nature the aluminum species formed during forced hydrolysis, such as the tridecameric Al_{13} polymer $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$, is of particular concern to many research groups in the fields of catalysis, mineralogy and soil chemistry, and ceramics. The application of Al_{13} complexes as pillaring agents in clay minerals is especially important (e.g., [2–4]). By intercalating the large Al_{13} complexes between the clay platelets, the specific surface area, the porous structure, and the acidity of the clay material will be enhanced considerably. Al_{13} is a highly symmetric complex exhibiting a Keggin structure, consisting of a tetrahedrally coordinated central AlO_4 unit, surrounded by twelve octahedrally coordinated Al^{3+} ions (Fig. 1). Despite the large number of publications concerning the hydrolysis of aluminum, much confusion and controversy still exist about the formation, the breakdown, and the nature of hydroxy aluminum species.

The hydrolysis of aluminum, which is usually investigated by ^{27}Al NMR, is executed by addition of basic solutions or Na_2CO_3 to (acidified) aluminum salt solutions [5–18], by dissolving aluminum metal in a salt solution [5,19–21], or by the hydrolysis of aluminum alcoholates [22,23]. The hydroxide-to-aluminum molar ratio, n, has to be kept below 2.5 to form polyoxocations of aluminum instead of precipitating $Al(OH)_3$.

Up till now, almost all investigations reported in the literature on the forced hydrolysis of aluminum were performed with Al^{3+}-containing solutions to which hydroxyl ions were added by injection or dropwise addition of a base. These methods have the disadvantage that they establish large pH inhomogenities in the Al^{3+}-containing solutions, which makes the study of the hydrolysis of aluminum inaccurate. Furthermore, scaling up this hydrolysis procedure

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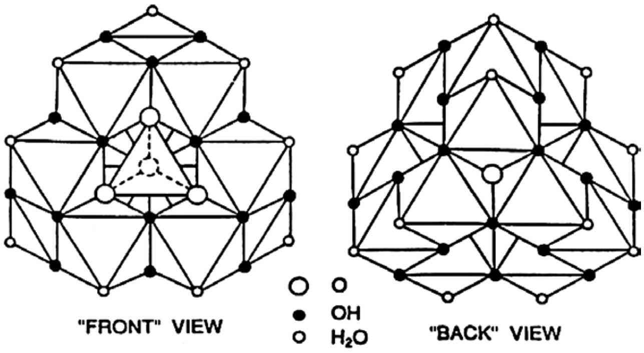

Fig. 1. Model of the Al_{13} Keggin complex.

is impossible, because faster addition of OH^- will result in the inevitable precipitation of Al-hydroxides instead of in the formation of the Al_{13} complex. Another drawback of the above-mentioned methods is that the formation of aluminum polymers during the addition of the base cannot be assessed.

This paper describes a study of forced aluminum hydrolysis in solutions by decomposition of urea. By increasing the temperature of the solution above about 70 °C, urea will slowly decompose in aqueous solutions. This will result in homogeneous generation of hydroxyls in the solution according to the overall reaction

$$CO(NH_2)_2 + 3H_2O \rightarrow 2OH^- + 2NH_4^+ + CO_2,$$

the mechanism of which was investigated by Shaw and Bordeaux [24]. Vermeulen et al. [25] and Wood et al. [26] used this method for the preparation of alumina gels. The advantage of this method is that the hydrolysis of aluminum can be followed directly with ^{27}Al NMR during the release of hydroxyl ions. More important, the procedure can be scaled up without difficulty. This work is aimed at the characterization of the species involved during hydrolysis of aluminum by the decomposition of urea at 90 °C. Furthermore, the optimum conditions for the formation of the Al_{13} complex, which will be present in these solutions, as observed by Wood et al. [26], are re-established by varying the aluminum concentration and the OH/Al ratio (n) in solution.

2. Experimental

The hydrolysis of aluminum was performed according to the procedure reported by Vermeulen et al. [25]. A 1-L solution was prepared by dissolving reagent grade $Al(NO_3)_3{\cdot}9H_2O$ or $AlCl_3{\cdot}6H_2O$ in deionized water. This solution was placed in a 3-L double-walled Pyrex vessel according to the description of Van Dillen et al. [27], heated to 90 °C, and vigorously stirred. In some cases the pH has been previously adjusted at 1.0 to prevent self-hydrolysis of the Al^{3+} ions by addition of concentrated HNO_3. Another 1-L solution was prepared by dissolving reagent grade urea in deionized water at 50 °C. This solution was added to the aluminum-containing solution in the vessel, after which the temperature was adjusted to 90 °C. The initial aluminum and urea concentrations in the combined solution were varied between 0.1 and 0.5 M and 0.3 and 2.0 M, respectively. The OH^-/Al^{3+} molar ratios ($= n$) calculated with complete hydrolysis of the urea ranged from 6 to 8. The solutions in the vessel were stirred continuously. During the reaction, a number of 10-ml samples were pipetted from the reaction vessel, sealed in flasks, and cooled with ice water to prevent further hydrolysis of the dissolved urea. All samples were measured with ^{27}Al NMR within 1 week after preparation.

^{27}Al NMR spectra were obtained on a Bruker AM500 spectrometer operated at 130.3 MHz (11.7 Tesla) using a 10-mm Bruker D-probe. For all measurements a 10-mm tube was used, in which a 5-mm tube was placed. This internal tube was held in a coaxial position by a Teflon plug and filled with D_2O, which acted as field frequency lock. The samples were placed between the inner and outer tubes. All spectra were measured at 20 °C. To prevent further hydrolysis during the measurement, no higher temperatures were used. Typically, 100–1600 free-induction decays (FIDs) were recorded. The pulse width was 32 µs with a 1.0-s relaxation delay. The spectral width was 20 kHz. The ^{27}Al chemical shifts (δ) are reported in ppm values relative to an external standard of a aqueous 0.1 M $AlCl_3$ solution, $[Al(H_2O)_6^{3+}]$. All chemical shifts reported here represent the peak maxima. Some additional ^{27}Al NMR spectra were obtained using a Bruker WP 200 spectrometer operating at 52 MHz. The samples were measured after locking with D_2O without an internal tube containing D_2O.

The pH of the solutions during the reaction was measured with a Schott–Geräde CG804 pH meter using electrodes from Ingold. The final turbid solutions were centrifuged and the resulting precipitates were washed three times and dried overnight at 130 °C. The X-ray powder diffraction (XRD) patterns of the precipitate were recorded on an Enraf Nonius FR590 diffractometer.

3. Results and discussion

3.1. pH and XRD measurements

The pH of the solutions was recorded to observe the hydrolysis of aluminum. Acidified solutions of pH 2 containing only urea at 90 °C exhibit an almost immediate sharp pH jump from 2 to 6.5. This is followed by a gradual increase to a constant value at 7.4 (Fig. 2), in accordance with the results of Vermeulen et al. [25]. The rate of change of pH of one acidified (curve a) and three nonacidified (curves b, c, d) Al^{3+} and urea-containing solutions kept at 90 °C are represented in Fig. 2. It is clear that the solutions with Al^{3+} do not show the immediate pH rise observed with solutions containing only urea, suggesting a consumption of the OH^- ions released during the hydrolysis of urea by the Al^{3+} ions in the solution.

Curve a (acidified) is divided in to four regions, denoted as I–IV. Region I exhibits an initially strong rise of the pH