



Mechanochemical synthesis of low-fluorine doped aluminum hydroxide fluorides

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ABSTRACT

Different aluminum hydroxide fluorides with varying Al/F molar ratios from 1:1.5 up to 1:0.05 were successfully synthesized by mechanochemical reactions. The characterization of the products by XRD, ^{27}Al and ^{19}F MAS NMR, thermal analysis, nitrogen adsorption and zeta potential techniques allows a detailed understanding of the structure and surface properties of the products. Using $\gamma\text{-Al}(\text{OH})_3$ and $\beta\text{-AlF}_3 \cdot 3\text{H}_2\text{O}$ as OH- and F-sources, respectively, strongly disordered products were obtained with an Al: F molar ratio higher than 1:0.25. The fluorination degree has affected the amount of 4- and 5-fold coordinated Al sites, not present in the reactants. An evolution of the sub-coordinated Al-species has been detected also as a consequence of annealing processes. Obviously, these species affect the phase transition to alumina, by decreasing the transition temperature of the formation of $\alpha\text{-Al}_2\text{O}_3$. Synthesis conditions (milling time, fluorination degree) play a crucial role for the product composition.

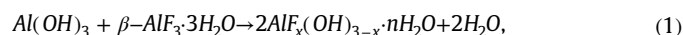
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1. Introduction

One of the most important goals in materials science is the design and modification of solids to obtain functionalized materials for industrial applications. A general approach to the modification of the macroscopic properties of these materials is to incorporate species with the desired functionalities. Currently, nanomaterials are an area of intense scientific research: their physical and chemical properties are different from the same materials at larger scales. In many cases, the particle-forming material, the shape and the size determine the applicability of the desired nanomaterials. Because of their small particle size, high surface area, and catalytic activity of their surfaces, nanosized metal oxide powders (especially transition aluminas) find many applications in industry as adsorbents, catalysts or catalyst supports, coatings and drug delivery systems [1–3]. Mechanical treatment to increase the reactivity of solids is known in the ceramics industry for a long time as a method capable to remarkably modify the atomic-scale structure, generating new surfaces and various defects [4,5]. Compared to the precipitation methods and the sol-gel synthesis, the mechanochemical synthesis entails several benefits. The use of solvent is completely prevented as well as the handling of toxic fluorine sources. Also with nonconventional preparation techniques such as mechanosynthesis, non-equilibrium metastable transition aluminas are accessible [6,7]. Understanding their formation processes

might help to improve their properties so that highly functionalized alumina nanoparticles can be made available.

In this work our attention is focused on the alteration of properties of aluminum hydroxides by fluoride doping on a mechanochemical route. This is because simultaneously present Lewis-acid and Brønsted-acid sites make aluminum hydroxide fluorides very interesting for many different applications in the field of catalysis [8–10]. As a consequence of combined action of milling and fluoride doping the number of introduced defects will be high. For instance, by applying a combination of both, high-energy ball milling and fluoride doping, the phase transition temperature to corundum can be reduced to 900 °C [11]. In addition, previously synthesized aluminum hydroxide fluorides prepared on the fluorolytic sol-gel route with aqueous hydrofluoric acid led to nanostructured, X-ray amorphous compounds with high surface areas. Their stoichiometry can be adjusted, which was done in previous studies with F/Al ratios larger than 1 [1,12]. Moreover, the successful mechanochemical synthesis of nanocrystalline aluminum hydroxide fluoride samples $\text{AlF}_x(\text{OH})_{3-x} \cdot 3\text{H}_2\text{O}$ with pyrochlore structure was also previously shown by our group [1]. For $x=1.5$ the reaction was almost complete according to Eq. (1).



Optimal conditions for the synthesis were achieved using $\gamma\text{-Al}(\text{OH})_3$ and $\beta\text{-AlF}_3 \cdot 3\text{H}_2\text{O}$ as reactants with a molar ratio Al:F of 1:1.5. Starting from the same reference system, in the present study we reduced the fluorine supply from Al:F=1:1.5 down to

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1:0.05 in order to prepare highly distorted aluminum oxide/hydroxide fluorides. The introduction of even low dopant amounts modifies the chemical composition and causes a disruption of the crystalline atomic structure of the reactants. Following that, as prepared aluminum hydroxide fluorides are expected to show altered local structures as well as an altered chemical behavior, especially concerning their reactivity and solubility in water. In the present study mechanochemical reactions of these two reactants, γ -Al(OH)₃ and β -AlF₃·3H₂O, were performed with different Al: F ratios down to 1:0.05 without further subsequent chemical treatment. The influence of the mechanical impact and the F-doping was evaluated by X-ray powder diffraction, ¹⁹F and ²⁷Al MAS NMR and FT-IR spectroscopies. The thermal behavior of the samples was studied by DTA-TG, the characterization of the specific surface areas was performed using the BET method and the analysis of their dissolution behavior and stability in aqueous solution was made by zeta potential measurements. In order to be able to distinguish the distortion introduced by milling and the one introduced by fluorine doping, a detailed characterization of each reference sample was peculiar.

2. Experimental

2.1. Preparation

γ -Al(OH)₃ (Fluka) and β -AlF₃·3H₂O (Sigma Aldrich) were used for milling experiments as commercially delivered, without further purification. Samples were milled in a commercial planetary mill "Pulverisette7-premium line" (Fritsch, Germany) under access of air applying a milling time of 4 h. Zirconium oxide (ZrO₂) vials equipped with five zirconium oxide balls were used at a rotation speed of 600 rpm. The weight ratio of the milling media to the sample was 15:1.

2.2. XRD

XRD measurements were performed using the FPM 7 equipment (Rich, Seiffert & Co., Freiberg) with Cu K α radiation (Cu K α _{1,2}, λ = 1.542 Å, 2 θ range: 5° < 2 θ < 90°, step scan: 0.05°, step time: 5 s). Phases were identified by comparison with JCSd powder diffraction file [13].

2.3. Solid state NMR (¹⁹F, ²⁷Al)

¹⁹F and ²⁷Al MAS NMR spectra were recorded on a Bruker AVANCE 400 spectrometer (Larmor frequencies: ν_{19F} = 376.4 MHz, ν_{27Al} = 104.6 MHz) using 2.5 mm double-bearing magic angle spinning (MAS) probe (Bruker Biospin) and applying a spinning speed of 20 KHz if not otherwise indicated. ¹⁹F MAS NMR (I = 1/2) spectra were recorded with a $\pi/2$ pulse duration of 3.6 μ s, a spectrum width of 400 kHz, and a recycle delay of 5 s. Isotropic chemical shifts of ¹⁹F are given with respect to the CFCl₃ standard. Background signals of ¹⁹F could be completely suppressed with the application of a phase-cycled depth pulse sequence according to Cory and Ritchey [14]. ²⁷Al MAS NMR (I = 5/2) spectra were recorded with an excitation pulse duration of 1 μ s. A 1 M aqueous solution of AlCl₃ was used as reference for the chemical shift of ²⁷Al. The recycle delay was chosen as 1 s and the accumulation number was 2000. Quantitative reconstruction of the central lines of the ²⁷Al MAS NMR spectra was made using DMFIT software [15].

2.4. DTA/TG

The thermal behavior was studied by conventional thermal analysis (TA) in air. A NETZSCH thermoanalyzer STA 409C

Skimmer, being additionally equipped with a conventional high-temperature SiC oven, was used to record the thermoanalytical curves (DTA, TG, DTG).

2.5. FT-IR

IR spectra were recorded on a Digilab Excalibur Series FT IR spectrometer using KBr disks (4000–400 cm⁻¹) in transmission mode. 1 mg of sample was ground with 500 mg KBr and pressed for 5 min with a load of 10 t.

2.6. BET

The specific surface area of each sample was determined applying the Brunauer-Emmett-Teller (BET) method using a Physiosorption Analyzer ASAP 2020 (Accelerated Surface Area and Porosimetry System) by Micrometrics. Each sample was first heated at 125 °C for 72 h in order to remove the physisorbed water. After heating, a 12 h-long degassing process of each sample at room temperature was done. Pore size distribution was determined by the Barret-Joyner-Halenda (BJH) method, applied to the desorption branch of the isotherm.

2.7. Zeta potential

Zeta potential (ζ) measurements were performed using a Malvern Instruments Zeta-sizer Nano ZSP. The velocity of the particles under electric field is measured using a patented laser interferometric technique M3-PALS (Phase analysis Light Scattering). This enables the calculation of electrophoretic mobility and from this the zeta potential and zeta potential distribution. The samples were diluted in water (0.1 wt%) and the mixture was ultrasonicated (Sonotrode: Bandelin Electronics) for 2 min prior to measurements. The zeta potential was determined as a function of pH. Titration was performed using a Malvern Instruments MPT-2 Autotitrator. The pH of the suspension was adjusted using NaOH or HCl.

3. Results

3.1. XRD measurements

Milling of γ -Al(OH)₃ essentially causes the disruption of the pillar-like structure of the matrix of γ -Al(OH)₃, producing the characteristic broad features of an almost X-ray amorphous material (Fig. 1(f)). On the other hand, β -AlF₃·3H₂O remains, after milling, nearly unchanged as indicated by XRD (Fig. 1(a) and (b)), showing only a small broadening of the individual reflections accompanied by a slight decrease of their amplitudes. Although β -AlF₃·3H₂O itself contains theoretically all the elements (Al, F, O, H) necessary for a mechanically initiated transformation into AlF_x(OH)_{3-x}·nH₂O without any impurities, this does not occur at milling. Table 1 gives an overview on the products identified by XRD measurements obtained from the mechano-synthesis applying different Al:F molar ratios.

For lower Al:F ratios, well resolved reflections of aluminum hydroxide fluoride with pyrochlore structure (PDF-number: 41-0381) can be observed immediately, as already demonstrated [1]. These reflections are observable with a really good resolution for a molar ratio Al:F = 1:1.5, (Fig. 1(c)). Increasing the Al: F ratio (that corresponding with decreasing F-content) results in broad reflections that indicate a higher degree of disorder in the products. However, in all mechanochemical reactions of the two reactants the reflections of β -AlF₃·3H₂O disappear completely (Fig. 1 and Table 1).

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