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Preparation of functionalized porous nano-γ-Al_2O_3 powders employing colophony extract

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ABSTRACT

This study reports the synthesis of porous nano alumina employing carboxylato-alumoxanes $[Al(O)_x(OH)_y(O_2CR)_z]_n$ as precursors for controlling the pore size, pore size distribution and porosity of the alumina, using a new process ecofriendly. The carboxylato-alumoxanes was prepared by the reaction of boehmite with carboxylic acids. The boehmite was obtained by the hydrolysis of aluminum alkoxide in an aqueous solution. The colophony extract is employed as a source of carboxylic acids. The materials were characterized, using XRD, TGA, N_2 physical adsorption, SEM, TEM, NMR and FTIR. A mechanism was proposed for the formation of the synthesized structures. TEM measurements confirmed particle size ranged from 5 to 8 nm.

1. Introduction

Aluminas are important industrial chemicals that have found wide application as adsorbents, ceramics, abrasives, and as catalytic materials [1–3]. In particular, the class of aluminum oxides known as “transition aluminas” plays commercially important role in many chemical processes: these solids have been used as catalysts and catalyst supports for the Claus reaction, cracking, hydrocracking and hydrodesulfurization of petroleum, the steam reforming of hydrocarbon feedstocks ranging from natural gas to heavy naphthas to produce hydrogen, the synthesis of ammonia, and the control automobile exhaust emissions [1–3].

The large applications of transition aluminas in catalysis and adsorption processes can be attributed to a combination of favorable textural properties such as: appropriate pore size distributions, usually bimodal; a high surface area; and surface chemical properties that can be either acidic or basic depending on the transition alumina structure and the degree of hydration and hydroxylation of the surface [1–3]. Structurally, all transition aluminas are disordered crystalline phases. Although the oxygen atoms are arranged in regularly ordered close packed arrays, the aluminum atoms adopt different ways of occupying the tetrahedral and octahedral interstices within the oxygen lattice. In general, the variations in the relative placement of aluminum ions in the tetrahedral and octahedral positions leads to different phases that can be distinguished by NMR techniques and by X-ray diffraction [1–3].

Transition aluminas are formed through the thermal dehydration and dehydroxylation of aluminum trihydroxides or aluminum oxyhydroxides. The thermal dehydration of aluminum trihydroxide (gibbsite) can lead to the formation of χ, κ, ρ, η or θ transition aluminas, depending on the heating rate, the dwell temperature and the atmosphere in contact with the solid phase [1–3]. The thermal dehydration of boehmite can afford γ, η, δ, or θ phases, depending on the conditions of dehydration, the particle size and degree of crystallinity of the starting boehmite. Pseudoboehmite, a poorly ordered form of boehmite with a small primary particle size, is often a preferred precursor to transition aluminas, because it typically affords derivatives with relatively high surface areas and pore volumes. Particularly, γ alumina (γ-Al_2O_3) is formed from well ordered boehmite at a temperature over 500 °C, depending on the particle size. Pseudoboehmite can be transformed to η alumina upon dehydration [1–3].

Carboxylate-alumoxanes are prepared from the reaction of boehmite $[Al(O)(OH)]n$ with carboxylic acid (HO_2CR). Although, they are given the general formula, $[Al(O)_x(OH)_y(O_2CR)_z]_n$ where $2x + y + z = 3$ and $R = C_1$–C_{14} [1], carboxylate-alumoxanes are in fact

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alumina nanoparticles between 5 and 200 nm in diameter. The surface of the nanoparticle is covered with covalently bound carboxylate groups [4,5]. Some of the simple carboxylic acids which have been used are: acetic acid, methoxyacetic acid, methoxy (ethoxy) acetic acid, methoxy (ethoxy ethoxy) acetic acid, hexanoic acid etc. Some of the carboxylic acids containing other functionalized groups are: 4-hydroxybenzoic acid, 4-aminobenzoic acid, methacrylic acid, hydroxylacetic acid, aminoacetic acid, 6-aminohexanoic acid, lactic acid, L-lysine etc [4].

Carboxylate-alumoxanes have found applications in a variety of interesting fields, such as the following: synthesis of metal doped aluminum oxides, catalyst components, preparation of ceramic membranes, synthesis of hollow alumina spheres, strengthening of porous alumina ceramics, and fabrication of fiber reinforced ceramic matrix composites, fabrication of biocompatible nanocomposites, polymeric nanocomposites, performance improvements of lithium batteries, non-skid and non-flammable coatings and MRI contrast agents [6,7].

In this sense, we have developed a method for the control of the porosity and pore size distribution on the synthesis of γ-alumina: reacting boehmite with a mixture of carboxylic acids from the extract of rosin, to produce carboxylate-alumoxane nanoparticles; drying the carboxylate-alumoxane nanoparticles; and firing the dried nanoparticles at a temperature of 650 °C.

The rosin, main components of the colophony extract, is a mixture of isomeric cyclic carboxylic acids with the general formula $C_{19}H_{29}COOH$ and it is produced by heating fresh liquid oleoresin to vaporize the volatile liquid terpene components [8,9]. Oleoresins are biological materials, that exude from cuts on living pines, products of the living protoplasm and therefore referable to the original products of photosynthesis for their ultimate chemical derivation [8,9].

The rosin or “mixture of organic acids from colophony” is considered an amphipathic material because the compound contains both hydrophilic and hydrophobic parts [10,11]. For this reason, the rosin provides appropriate conditions to form highly dispersed stable colloidal suspensions [12]. These properties make it an interesting product to be used in the synthesis of materials. Fig. 1, shows the molecular structure of the main component of rosin (abietic acid) showing the hydrophobic and hydrophilic portions [10,11].

2. Materials and methods

2.1. Synthesis of carboxylate alumoxane from pine resin

A sample of 2 g of oleoresin of pine (*Pinus caribaea* spp., Fig. 1), in 60 mL of deionized water was submitted to continuous agitation for 8 h at room temperature. The sample was macerated during 24 h, centrifuged and filtered to separate the solid parts of the extract. Finally it was added under continuous agitation, 0.02 moles of aluminium isopropoxide and dilute nitric acid (10 vol%). The obtained suspension was subjected to agitation for 2 h and aged for 6 h. The resulting solid was dried at 80 °C for 12 h and calcinated at 600 °C for 6 h using a heating rate of 5 °C/min. The boehmite used for comparison was prepared by the Yoldas method [13].

2.2. Characterization

Characterization was carried out by X-ray diffraction, using a Siemens D-5005 diffractometer and CuKα radiation in the 2θ range between 5 and 70°, operating at 40 kV and 20 mA. Thermogravimetric analysis (TGA) was performed from room temperature to 750 °C in a Du Pont 990 thermogravimetric analyzer under air flow (100 mL/min) at a heating rate of 10 °C/min. Fourier transform infrared (FT-IR) spectra, of samples prepared before and after calcinations, were recorded with a Nicolet Magna 500 spectrometer in the range of 4000–400 cm^{-1}.

The textural properties of the calcined oxides were characterized by N_2 adsorption porosimetry (Micromeritics, ASAP 2010). The samples were degassed at 300 °C under vacuum. Nitrogen adsorption isotherms were measured at liquid N_2 temperature (77 K), and N_2 pressures ranging from 10^{-6} to 1.0 P/P_0. Surface area was calculated according to Brunauer–Emmett–Teller (BET) method and the pore size distribution was obtained according to the Barret–Joyner–Halenda (BJH) method [14].

The evaluation by transmission electron microscopy (TEM) was performed on a JEOL JEM-2100 microscope with LaB6 filament (accelerating voltage of 200 kV). The samples were prepared by suspending the powders in an ethanol-based liquid and pipetting the suspension onto a carbon/collodion-coated 200 mesh copper grid. ^1H- and ^{13}C-NMR spectra were measured in a Bruker 400-

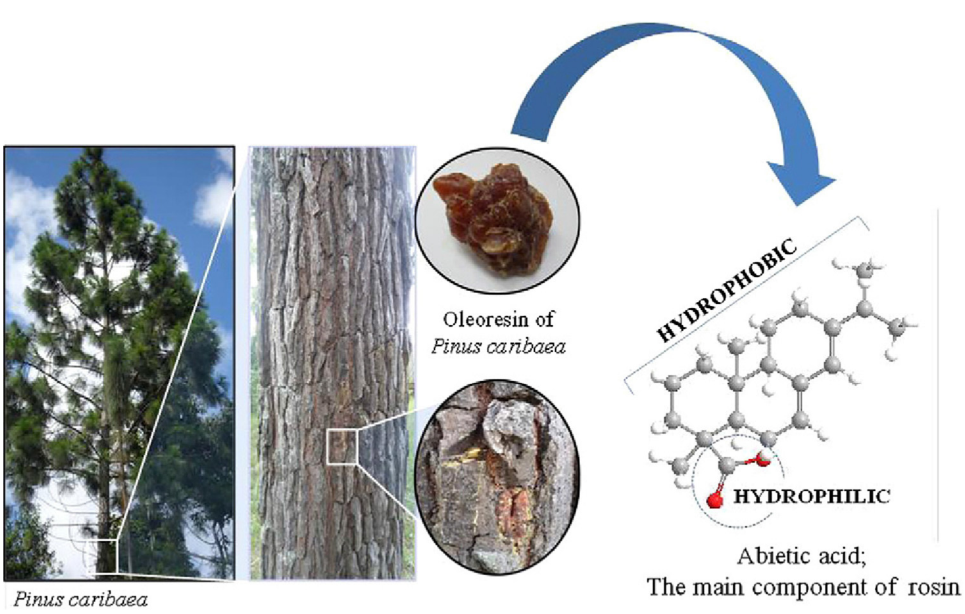

Fig. 1. Oleoresin of *Pinus caribaea* and molecular structure of abietic acid; the main component of rosin.