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Hydrothermal synthesis of boehmite in cellular alumina monoliths for catalytic and separation applications

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Abstract

For the first time, controlled hydrothermal functionalization was performed in porous cellular α-Al_2O_3 ceramics, targeting potential separation and catalytic processes for sustainable chemistry applications. Growth of micro-nano hierarchical structures of boehmite (γ-AlOOH) with high aspect ratio was assessed by SEM/EDS/XRD/FTIR. The pH and precursors concentration determine the growth mechanism and final functionalization level. The obtained results anticipate strategies for promoting formation of boehmite at the pores surfaces and tuning its morphology, including pre-treatments of the cellular matrix to increase the concentration of the surface defects and preliminary saturation of the pores with appropriate precursors to achieve uniform functionalization. Thus grown boehmite structures can be easily converted to γ-Al_2O_3 by thermal treatment while retaining the former distribution and aspect ratio, opening new possibilities for preparation of γ-Al_2O_3 supported catalysts.

Keywords: Boehmite; Cellular alumina monoliths; Hydrothermal synthesis; γ-Alumina

1. Introduction

Functional materials with controlled dimensionality and morphology are recognized as an essential part of numerous engineering solutions for energy, food, water and environmental problems. Those possessing large surface areas, tunable pore size, appropriate thermal stability and tailored acid/basic functionalities, allowing modification with catalytically active species, are of particular interest for both technology and fundamental research. Transition aluminas, being already known and quite mature materials, are one of the most frequently used catalyst supports [1,2], especially the γ-alumina polymorph which contributes significantly to performance of supported catalysts in a variety of industries, with emphasis on petroleum, automotive sectors [1,3]. Therefore, reasonable improvements in relevant alumina properties and/or working concepts for catalytic applications are extremely challenging and expected to contribute significantly to green sustainable chemistry, encouraging the design of cheap, environmentally-safe and effective systems and processes.

A well-established route to induce the γ-alumina polymorph is based on dehydration of boehmite (AlOOH) at 400–1000 °C [4–7]. Nanostructured boehmite itself represents an interesting material for designing superhydrophobic and self-cleaning surfaces for adhesion and surface oxidation prevention, self-cleaning of windshields, antibiofouling paints, etc. [8–10]. Boehmite is also known for a fairly rare combination of superhydrophobicity, superoleophilicity and relatively good thermal stability [11], very promising for filtration or separation. Most commonly the nanostructured boehmite is synthesized by hydrothermal processes in various conditions and based on different synthesis strategies, as summarized in Table 1. As shown, these strategies are designed to yield boehmite particles of different shapes, seeking requirements of diverse applications. Boehmite can be then converted into γ-alumina powder with corresponding particle morphologies. For many catalytic applications alumina-based supports with narrow pore size distribution, uniform pore structure with appropriate pore volume are highly desired [12]. Furthermore, as an ultimate goal one may consider 3D

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Table 1
Literature data on the conditions of the hydrothermal synthesis of nanostructured boehmite.

Precursors	Hydrothermal conditions		Boehmite features	Ref.
	Temperature (°C)	Time (h)		
$Al(NO_3)_3\bullet 9H_2O$; $NaHCO_3$	200	24	2D particles with 8 μm diameter (low Al concentration, 0.1 M) 1D wire-like particles with 10 μm length (high Al concentration, 0.2 M)	[19]
$Al(NO_3)_3\bullet 9H_2O$; NH_3 Camphorsulfonic acid	160	24	Nanotubes with ~500 nm length and ~20–40 nm diameter	[20]
$NaAlO_2$; urea	160 180 200	3	Flower-like boehmite nanostructures on quartz surface	[21]
$NH_4Al(SO_4)_2\bullet 12H_2O$; Urea	150	12	Flower-like boehmite structures	[7]
$Al(OH)_3$	160 220 300	0.17 1.33 2	Plate-like boehmite particles with average particle size in range 4–25 μm	[22]
$AlCl_3$; NaOH; CTAB	160	12	Leaf-like boehmite nanosheets with aspect ratio of 2 and 60–90 nm of thickness	[4]
$AlCl_3$; C_2H_6O (ethanol)	200	72	Flowerlike nanoarchitetures	[23]
$Al(NO_3)_3\bullet 9H_2O$; $C_6H_5Na_3O_7\bullet 2H_2O$	200	24	Cantaloupe-like and hollow microspherical superstructures	[24]
Al2(SO4)3•18H_2O Urea sodium tartrate	165	3	Hollow core/shell and hollow microspheres	[25]
$Al(NO_3)_3\bullet 9H_2O$, urea and $KAl(SO_4)_2$	180	3	The morphology evolves from singe nanoflakes, nanoflakes assemblies, and flower-like structures to hollow microspheres with increasing of $KAl(SO_4)_2$ $12H_2O$	[26]
$Al_2(SO_4)_3\bullet$18H2O; NH_3	165	24	Nanorods-like structure	[27]

hierarchical structures, which are ordered in all appropriate length scales, from molecular to nano and macro [13–15]. In particular, the incorporation of macropores into mesoporous architectures can minimize diffusion barriers and potentially enhance the distribution of active sites during modification with catalyst [13]. On the other hand, such hierarchical structures are expected to tackle the challenges of the filtering applications, especially those demanding high medium flow rates.

Synthesis of mesoporous aluminas with narrow pore size distribution represents an interesting and challenging approach for the fabrication of catalyst supports [1], especially in the view of great advancements, realized for mesostructured forms of silica [14,16]. For those applications dealing with high medium flow rates and significant pressure changes (filtering of water/oil emulsions, combustion, and other catalytic reactions with volume change), introduction of larger pores is essential to support a reasonable performance, along with providing sufficient mechanical strength and appropriate interconnectivity of the pores. Recently a new facile method for processing of highly porous cellular alumina ceramics by emulsification of the liquid paraffin in ceramic suspensions was developed in our group [17,18]. The approach allows fine 3D-tuning of cavities shape and interconnectivity between pores, and results in mechanically strong ceramics (compressive strength of 10–40 MPa), with a clear potential for further improvement. Thus, to benefit from the synergy of simple and flexible processing, well-tunable pore structure and mechanical resistance, the present work focuses on the bulk modification of the monolithic cellular ceramics with boehmite/γ-alumina nanostructures via hydrothermal treatment. Thus modified monoliths are attractive for variety of catalytic applications, considering that nanostructured boehmite at the surface of the pores can be further functionalized by impregnation with various precursors, containing transition metal cations (Ni^{2+}, Cu^{2+}, $Fe^{2+/3+}$, $Co^{2+/3+}$, etc.) and converted to γ-alumina-supported catalytic layers. Those functionalities can represent a particular interest for performing catalytic combustion in monoliths, where inherent porous microstructure may be adjusted for efficient gas and thermal transport. To our best knowledge, the described strategy represents a first attempt for in situ functionalization of porous ceramic monoliths in hydrothermal conditions.

2. Experimental

Porous alumina monoliths were prepared by emulsification of molten paraffin (Merck 1.07337.2500) in aqueous alumina (Alcoa CT3000) suspension (50% vol. of solids content, stabilized with a viscosity close to 0.5 Pa s using Dolapix PC-67 (10% vol.)). Paraffin was melted at 80 °C, prior to addition of the alumina suspension in volume ratio paraffin:suspension 1.5:1, followed by addition of an anionic surfactant (sodium lauryl sulphate, Sigma-Aldrich L-6026) as emulsification agent (6% related to the emulsion volume), and collagen (OXOID LP0008) as shape stabilizer. Emulsification was promoted by mechanical stirring at 1000 rpm for 10 min, while maintaining temperature at 80 °C, to avoid paraffin solidification. After drying, the resulting ceramic emulsions was sintered at 1550 °C for 3 h with heating rate 0f 5 °C min^{-1}, and a dwell of 2 h at 200 °C to allow paraffin volatilization. Additional details about cellular alumina monoliths preparation can be founded in our recent papers [17,18,28].

The 0.5 cm thick alumina monoliths (Ø 2 cm), sintered at 1550 °C for 2 h, with ~60–70% porosity were subjected to hydrothermal synthesis in a 100 ml Teflon-lined stainless steel

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