



Self-functionalization of cellular alumina monoliths in hydrothermal conditions



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ABSTRACT

Alumina-based open cellular microstructures with highly interconnected porosity attract much interest as supports for catalytic applications, with emphasis on petroleum and automotive sector. This work reports a novel route for *in-situ* functionalization of the sintered porous α -Al₂O₃ ceramics by micro/nano structures of boehmite (γ -AlOOH), promoted by hydrothermal treatment in alkaline conditions. The mechanism of the process includes slow dissolution of the matrix, which acts as an aluminum precursor, and transport of Al-containing species inside the pores, resulting in growth of boehmite fibers and clusters of various morphologies, as confirmed by combined SEM/EDS/XRD/FTIR. These results suggest that deliberate variation of the pH and ionic strength of the hydrothermal medium may represent a promising strategy for controlling the spatial distribution, morphology and dimension scale of the grown boehmite. A complementary approach implies pre-treatment of cellular monoliths in highly-reducing conditions to increase the concentration of surface defects and dangling bonds, facilitating the matrix dissolution and probably acting as nucleation centers, and thus to boost the functionalization level.

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1. Introduction

Industrial growth in the last decades, especially in the chemical manufacturing sector, makes the catalysis one of the most important topics in research. Catalytic processes are used for more than 20% of all industrial and 90% of chemical products. Heterogeneous catalysis is highly desirable to minimize environmental impact and to comply with green chemistry principles, including low-energy consumption routes and facilitated catalyst recovery [1]. Although many catalytic processes and related materials have already been discovered and improved during the last century, still many opportunities exist both for development of new approaches and even for new solutions in mature technologies [1]. A representative example is the catalyst supports based on transition aluminas, especially the γ -alumina polymorph, with many applications in various industries, petroleum and automotive sectors [2–4]. Transition aluminas can be obtained by topotactic dehydration/decomposition of (oxi)hydroxides, in particular, boehmite AlOOH [5], boehmite contains terminal groups that provide high reactivity to the surface, in recent years has also attracted much

interest both in terms of fundamental and application viewpoint ([6–10] and references therein). Thus, a reasonable improvement in properties and/or working concepts for alumina-based materials, with particular emphasis on catalytic and separation applications, will be a significant step toward green sustainable chemistry.

Many catalytic applications, especially those dealing with high medium flow rates and significant volume changes (e.g., combustion...), require appropriate mechanical properties of the supports, which can be ensured by sintering at relatively high temperatures. In this context, the introduction of specific porosity within bulk alumina often represents a challenge for processing, allowing the tuning of the flow rate, imposed by the process, and adjusting the amount of accessible active sites. The diffusion barriers and the distribution of the active sites can be further enhanced in hierarchically porous architectures [11]. In such materials the macropores usually are formed by emulsion templating [12] or colloidal crystal templating [13]. Recently, a new flexible and facile method for processing of α -Al₂O₃ based monoliths with high bimodal interconnected porosity by emulsification of liquid paraffin in ceramic suspensions was developed in our group. The catalyst itself can be loaded into the porous structure of support by variety of methods, including simple impregnation, sol-gel, precipitation, co-precipitation and grafting [16–19], followed by drying, calcination and reduction. An alternative solution, recently developed in

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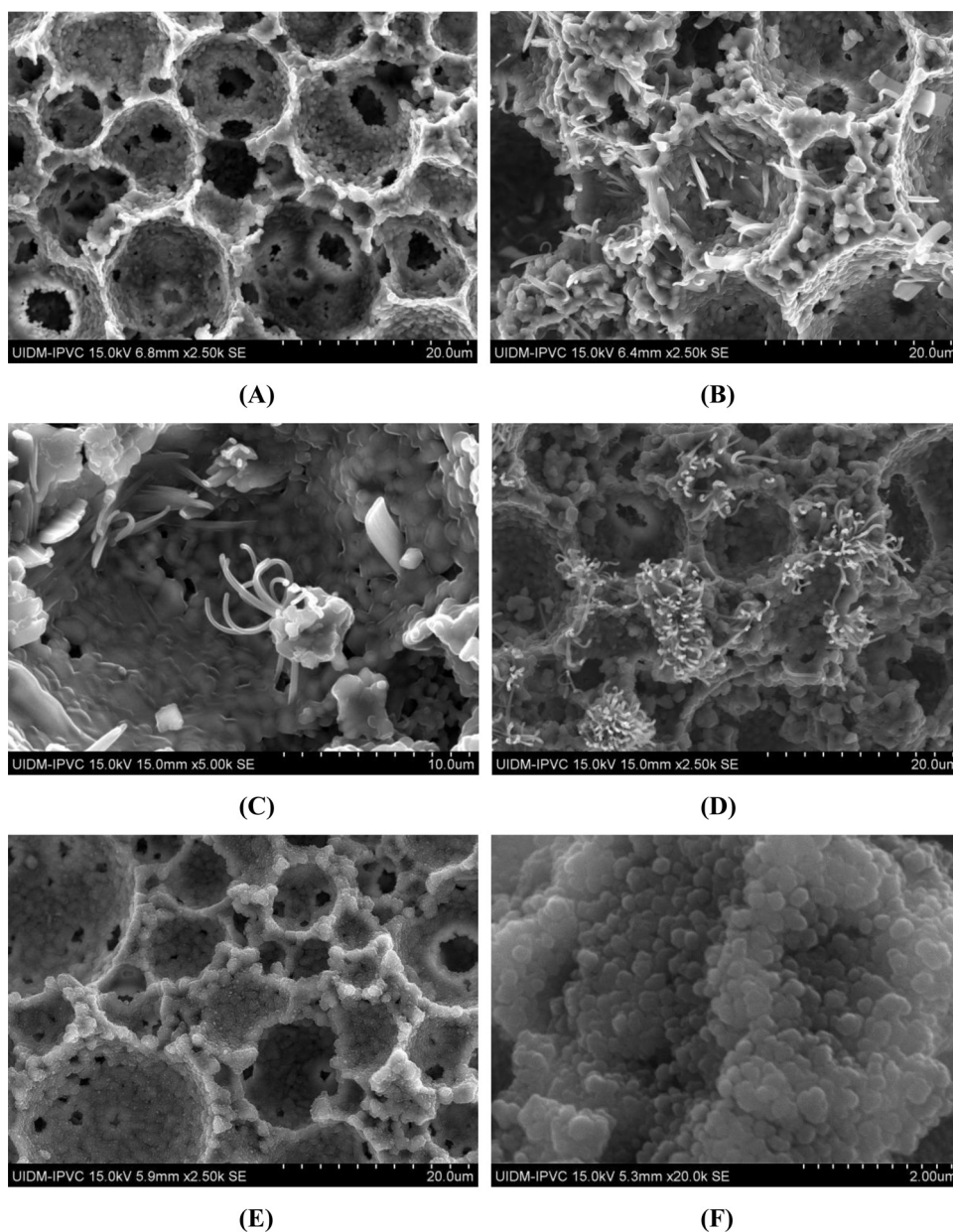


Fig. 1. Representative SEM micrographs of the fractured non-modified monolith (A), Na₂-0.93 (B,C), NaH-0.93 (D) and NaH-0.93(H₂) (E,F) samples.

our group, is based on hydrothermal synthesis of boehmite at the pore surface of already sintered cellular alumina monoliths with sufficient mechanical strength, using $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and NaHCO_3 precursors [20]. That was a first attempt for *in-situ* functionalization of porous densely sintered ceramic monoliths in hydrothermal conditions. Inspired by these results, the present work intends to demonstrate that submicro- and nanostructured boehmite can be grown *in-situ* in cellular $\alpha\text{-Al}_2\text{O}_3$ monoliths without additional use of aluminum-containing precursors, by controlled dissolution of alumina matrix, promoted by hydrothermal treatment in alkaline conditions.

2. Experimental part

Cellular alumina monoliths were prepared by emulsification of molten paraffin in aqueous alumina suspension, followed by consolidation, drying and final sintering at 1550 °C for 3 h. Further details on the processing conditions and microstructural proper-

ties of the prepared monoliths can be found elsewhere [14,15]. After sintering, 0.5 cm thick alumina monoliths (ϕ 2 cm), with porosity of 60–70% were subjected to hydrothermal treatment in a 100 ml Teflon-lined stainless steel autoclave, with an aqueous solution volume fraction of 40% at room temperature. Hydrothermal treatments were performed at 190 °C for 19 h in the solutions, containing various amount of NaHCO_3 (Merck K25746929 843) and Na_2CO_3 (Panreac Cod., 141647) addition, such as to provide alkaline conditions at different pH. Corresponding sample denominations, additions and their concentrations, and calculated pH values are listed in Table 1. The maximum concentration of additives (0.93 M) corresponds to the saturation point of NaHCO_3 at room temperature. After hydrothermal synthesis the samples were washed by several immersions in deionized water and dried at 373 K. To assess the effect of pre-processing in reducing conditions prior to hydrothermal synthesis, a set of the samples was annealed in $\text{H}_2(10\%)/\text{N}_2(90\%)$ mixture at 1500 °C for 2 h ($p(\text{O}_2) = 1.2 \times 10^{-12}$ atm).

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