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Sol–gel synthesis of mesostructured γ-alumina templated by cationic surfactants

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Abstract

Sol–gel mesostructured γ-Al_2O_3 (SGAL) with pore walls largely formed by γ-Al_2O_3 nanocrystals has been synthesized by a new three step (hydrolysis, condensation and calcination) sol–gel procedure in acid medium with cationic surfactants (hexadecyltrimethylammonium chloride/bromide) and in the absence of hydrolysis retarding agents. SGAL aluminas showed BET surface areas larger than 300 $m^2 g^{-1}$, pore diameters within the 4–15 nm range and pore volumes larger than 0.40 $cm^3 g^{-1}$. Hydrogen chloride, water and surfactant contents as well as the thermal treatment deeply influence the final properties of the obtained aluminas. Hydrogen chloride/aluminium isopropoxide molar ratios larger than 1 are required to prepare uniform mesostructured aluminas of wormhole-like appearance with a narrow mesopore size distribution ($D_p \sim 4.7$–6.0 nm). A pore size decrease, accompanied by narrower mesopore size distributions has been observed when diminishing both the water/aluminium isopropoxide and template/aluminium isopropoxide molar ratios. Controlled two step thermal treatment (firstly heating under flowing nitrogen and subsequently under air flow at 550 °C for 5 h) allows to reduce the coalescence of the aluminium moieties forming the pore walls, by increasing the BET surface area values above 500 $m^2 g^{-1}$. Under special conditions, ordered mesostructured alumina with $S_{BET} \sim 626\ m^2 g^{-1}$, $D_p \sim 2.8$ nm and narrower pore walls (~3.5 nm) largely formed by γ-Al_2O_3 nanocrystals was prepared.

Keywords: Mesostructured γ-Al_2O_3; MSU; γ-Al_2O_3; Hexadecyltrimethylammonium chloride; Cationic surfactant

1. Introduction

γ-Al_2O_3 based catalysts are widely used in different industrial chemical processes such as hydrodesulfurization, metathesis, cracking, etc. [1]. These materials show high surface areas (100–250 $m^2 g^{-1}$), pore volumes (0.3–1.0 $cm^3 g^{-1}$) as well as nonuniform mesopore size distributions [2]. γ-Al_2O_3 also exhibits acid–base properties depending on the aluminium coordination, dehydration–dehydroxylation degree, presence of doping agents (e.g., chlorine), synthesis conditions and post-synthesis treatments [3–7]. In addition, the occurrence of a determined transition alumina phase plays a key role in certain catalytic processes due to structural factors, e.g., Cr/η-Al_2O_3 catalysts show higher performance than Cr/γ-Al_2O_3 for alkane dehydrogenation [8]. From a chemical viewpoint, γ-Al_2O_3 constitutes a metastable transition alumina phase, resulting in dehydration of boehmite or pseudoboehmite oxo-hydroxide AlO(OH) above 400–500 °C [9]. Traditionally, its structure has been regarded as a defective spinel similar to $MgAl_2O_4$, wherein aluminium atoms are located in both tetrahedral and octahedral positions, leaving one vacancy of every nine cationic sites. However, hydrogen has also been claimed to be present in its composition [10]. After progressive heating, γ-Al_2O_3 is transformed into a

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different transition alumina phase (δ-Al_2O_3) at roughly 800 °C and, above 1100 °C, the most stable alumina phase (α-Al_2O_3) is finally obtained [9]. Nevertheless, neither δ-Al_2O_3 nor α-Al_2O_3 show such remarkable textural properties as γ-Al_2O_3, since both the surface area and pore volume diminish on heating, giving finally rise to a network of interconnected macropores [2].

The synthesis of γ-Al_2O_3 with a uniformly ordered mesoporous structure is a long standing goal. In 1992, the discovery of the uniformly mesoporous M41S silicate/aluminosilicate materials by Mobil Oil researchers [11] opened up the way for the preparation of a wide variety of templated mesoporous oxides. Huo et al. [12] reported the first attempts through several electrostatic self-assembly mechanisms but they led mostly towards the formation of unstable lamellar structures. The first templated mesoporous alumina (pore size about 2.0 nm) was obtained by Vaudry et al. [13] using different carboxylic acids (e.g. caproic acid, lauric acid) as templates and aluminium *sec*-butoxide as the aluminium source, the formation taking place through a S–I mechanism (S = acid; I = alkoxide). Yada et al. [14] synthesized thermally unstable hexagonal mesoporous alumina according to an electrostatic mechanism (S^-I^+) using an homogeneous precipitation route with urea, sodium dodecyl sulphate as template and $Al(NO_3)_3$ as the aluminium source. Examples of the preparation of mesoporous alumina using cationic surfactants (hexadecyltrimethylammonium bromide) are scarce [15–17] and sometimes, as in the case of the Cabrera et al. method [15], the addition of hydrolysis retarding agents (triethanolamine) is required. On the other hand, Bagshaw et al. [18] synthesized mesoporous alumina molecular sieves, named MSU-X, by using nonionic polyethylene oxide surfactants (N^0) and aluminium *sec*-butoxide (I^0) through a N^0I^0 mechanism. MSU aluminas exhibited BET surface areas above 350 $m^2\,g^{-1}$, pore sizes ranging from 4.0 to 8.0 nm and a thermal stability that might be increased above 600 °C by adding cerium or lanthanum [19]. Unfortunately and unlike their equivalent silica mesostructures (e.g. MCM-41 or SBA-15), mesostructured aluminas show a final pore size distribution that cannot be simply tailored by a judicious choice of the template. Instead, other variables such as the presence of hydrolysis delaying agents [15], composition of the synthesis gel [20] and calcination conditions [21] (among others) are of the utmost importance. In addition, most mesostructured aluminas contain largely amorphous pore walls giving rise to materials with a low stability and limited applications. Yang [22,23] succeeded in preparing several metal oxides (titanium and zinc oxides) with crystalline domains inside the pore walls. However, these attempts failed in the case of alumina. Zhang et al. [3,4] have recently reported a three step procedure for the preparation of mesostructured alumina with their pore walls made up of crystalline γ-Al_2O_3 nanoparticles (named MSU-γ). They used both nonionic diblock and triblock copolymers as templates and the preparation of an intermediate MSU-S/B phase employing pseudoboehmite nanoparticles as building blocks was required.

Sol–gel techniques [24–26] have been widely applied for the synthesis of highly porous aluminas and according to procedures directly related to that originally developed by Yoldas [25]. These methods allow to control the pore size and the surface area by adjusting the main synthesis variables (e.g. pH, water content and solvent nature). Surprisingly, to the best of our knowledge, only one synthesis example of the preparation of mesostructured alumina using the sol–gel techniques has been reported [27], despite the remarkable features of Yoldas procedure [25] for the preparation of highly porous aluminas (e.g. acidic medium, solvent evaporation). In this work, a novel sol–gel procedure for the preparation of mesostructured alumina with pore walls largely formed by γ-Al_2O_3 nanocrystals (2–5 nm size) using an acid medium and cationic surfactants (hexadecyltrimethylammonium chloride/bromide) is reported. In addition, the influence of the main synthesis variables (hydrogen chloride, water and template content) as well as the thermal treatment procedure is described.

2. Experimental section

2.1. Chemicals

Aluminium isopropoxide, (AIP, 99 wt%), hexadecyltrimethylammonium bromide (C_{16}TMABr, 99 wt%), and hexadecyltrimethylammonium chloride (C_{16}TMACl, 25 wt% aqueous solution) were purchased from Aldrich. 2-propanol (99 wt%) and hydrogen chloride (35 wt% aqueous solution) were provided by Scharlau.

2.2. Characterization techniques

The chemical composition of the samples was determined by X-ray fluorescence (XRF) in a Philips PW 1404 spectrometer. CHN elemental analyses were performed in a Varian EL III Elementar apparatus equipped with a double oven system and using a 5 mg sample. TG analyses were carried out in a SDT 2960 TA instrument heating the sample up to 600 °C with a rate of 5 °C min^{-1} under a 100 NmL min^{-1} air flow. XRD patterns were taken in a Philips X'PERT MPD diffractometer using Cu K_α radiation. XRD pattern scanned within the $2\theta \sim 0.5$–$10°$ range were obtained using a step size of 0.02° and a counting time of 10 s. XRD patterns at higher angles ($2\theta \sim 15$–$80°$) were taken with a step size and a counting time of 0.1° and 2 s, respectively. The identification of the different crystalline phases was performed by comparison with the corresponding JCPDS diffraction data cards.