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Silica promoted self-assembled mesoporous aluminas. Impact of the silica precursor on the structural, textural and acidic properties

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ABSTRACT

This paper investigates the effect of silica addition on the structural, textural and acidic properties of an evaporation induced self-assembled (EISA) mesoporous alumina. Two silica addition protocols were applied while maintaining the EISA synthesis route. The first route is based on the addition of a Na-free colloidal silica suspension (Ludox®), and the second method consists of the co-hydrolysis of tetraethyl orthosilicate (TEOS) with aluminium tri-*sec*-butoxide, to favour a more intimate mixing of the Al- and Si-hydrolysed species. The properties of the so derived materials were compared to the SiO_2-free counterpart. The SiO_2 addition was always beneficial from a structural and textural standpoint. TEOS appears to have a truly promoting effect; the ordering, surface area and pore volume are all improved. For Ludox®, the enhancement comes from the formation of smaller pores by a densification of the structure. The crystallization of γ-alumina depends on the interaction between the Al- and Si-species in the mesophase. Ludox®-based materials achieved crystallization at 750 °C but the intimate mixing in the TEOS-based mesophases shows a suppression of the phase transformation by 50–100 °C, with respect to the SiO_2-free counterpart. This reduces the textural features substantially. For all SiO_2-modified materials, the enhancement in the surface area is not accompanied by a concomitant improvement of total acidity, and the formation of weak Lewis acid sites was promoted. These effects were ascribed to SiO_2 migration to the surface that blocks part of the acidity.

1. Introduction

Gamma alumina is a widely employed material in adsorption and as a catalyst support [1,2]. The surface area of a conventional alumina [3] originates from the interparticle space of the crystallites. Thus, the pore size distribution is typically broad and the surface areas are not especially high. Mesostructured gamma aluminas with crystalline walls and enhanced surface areas have been a challenge in the last decade. The use of supramolecular surfactants in sol–gel routes has succeeded in enhancing the textural properties; several examples have been reported on mesostructured γ-aluminas with atomically well-crystallized walls [4–18].

The surfactant-induced fibre formation [4–8,16] gives rise to γ-Al_2O_3 with high surface areas ranging between 250 and 450 $m^2\ g^{-1}$, obtained at relatively low crystallization temperatures around 330–550 °C. An aspect of attention is the relatively broad pore size distribution where the small pores contribute most to the surface area. Nanocasting using hard templates (SBA-15 or mesoporous carbon) has been reported as well [12,18] yielding γ-aluminas with extremely narrow pore size distributions. The evaporation-induced self-assembly route proposed by Niesz et al. [19], and followed by Yuan et al. [14], was the first example of a mesoporous alumina with intracrystalline mesoporosity using soft templates.

Yuan et al. [14] proposed an upgrading route to get more stable walls. The addition of carboxylic acids (such as citric, tartaric and DL-malic) enables control of the hydrolysis rate by chelating reactive sites in the alkoxide, or partially hydrolysed Al species, or both. In this way, the crystallization can take place without pore collapse. This approach produced stable and ordered structures with narrow pores. The crystallization of the walls was obtained at 800 °C, with a reduction of the surface area from 434 to 226 $m^2\ g^{-1}$. In a different approach, López Pérez et al. [20] reported that the controlled hydrolysis and evaporation of Aluminum tri-*sec*-butoxide (ATSB) at specific conditions in the presence of *sec*-BuOH was able to produce a mesophase that upon thermal activation rendered 300 $m^2\ g^{-1}$ of γ-Al_2O_3 (denoted as OM-5 material). The controlled

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hydrolysis and formation of low-polymerized Al species are probably responsible for the adequate assembly onto the surfactant. Among the various solvents studied, *sec*-BuOH produced a regular distribution of relatively size-uniform nanoparticles in the mesophase. The other solvents yielded particle heterogeneity in the mesophases, with random packing of fibrous and wormhole morphologies attributed to a higher hydrolysis rate. Such a low particle coordination favours coarsening with enlargement of the pore size distribution upon thermal treatment; explaining the lower surface area. On the contrary, the high particle coordination in the *sec*-BuOH-based mesophase prevents coarsening and favours densification upon thermal treatment. This maintains a relatively uniform pore size distribution and gives rise to an enhanced surface area [20].

Additionally, chemical additives can be applied to further enhance the structural stability of organized aluminas. For instance to the optimal *sec*-BuOH-derived OM-5 mesophase reported previously [20]. Among the various reported additives, silica at low loadings (1–10 wt.% [21]) has been found to be an effective agent in retarding the sintering of various alumina phases [21–30]. Various effects of the silica addition have been reported, such as the delayed formation of α-Al_2O_3 up to 1200 °C [22], 1380 °C [21] or 1500 °C [23]; the retention of the θ phase at 1400 °C [24,25] or 1200 °C [26]; improved hydrothermal stability of γ-alumina and its precursors [27,28]; retention of the γ-Al_2O_3 up to 1200 °C [26] or 1000 °C [29], the latter with 60% enhancement of the surface area compared to the SiO_2 free counterpart. Daniel et al. [30] systematically studied a number of silica-modified aluminas, ranging from pure silica to pure alumina; they observed an enhancement of the surface areas for all SiO_2 compositions. At SiO_2 loadings >10 wt.% Brønsted sites were formed. Kosuge and Ogata [29] reported that silica insertion improved the γ-Al_2O_3 texture derived from a sol–gel EISA route, with a concomitant reduction of the acid sites strength. Besides these studies, the combined effect of the silica insertion on the structure, texture and acidity of sol–gel derived aluminas has received little attention.

In this study, we have investigated the effect of silica as promoter on the structural, textural and acidic properties of the OM-5 mesophase. The concentration of silica was chosen below 10 wt.% to avoid forming mixed aluminosilicates [30]; within this range, a low (2.5 wt.%) and high concentration (9 wt.%) was selected. Two silica addition protocols were investigated. The first is based on the addition of a Na-free colloidal silica suspension (Ludox®) after the ATSB hydrolysis. In the second method, tetraethyl orthosilicate (TEOS) was co-hydrolysed with the ATSB in order to favour an intimate mixing of the Al- and Si-hydrolysed species. In both cases, the overall EISA synthesis route is maintained.

2. Experimental

2.1. Mesophases preparation

2.1.1. Chemicals

Pluronic P123 (M = 5800, $EO_{20}PO_{70}EO_{20}$), aluminium tri-*sec*-butoxide (97%), tetraethyl orthosilicate (TEOS, $Si(OC_2H_5)_4$, 98.0%) and Ludox® AS-40 colloidal silica (40 wt.% suspension in H_2O) from Sigma-Aldrich; *sec*-butyl alcohol (99%) from Acros Organics; hydrochloric acid (37 wt.%) from Merck, were used in this study.

2.1.2. Synthesis

Silica promoted alumina mesophases were synthesized based on the OM-5 pure-alumina mesophase reported by López Pérez et al. [20], that consists of a gel that was hydrolysed in the presence of a non-ionic surfactant (Pluronic P123, $EO_{20}PO_{70}EO_{20}$), aluminium tri-*sec*-butoxide (ATSB) as aluminium source, *sec*-butanol as solvent, $H_2O/Al = 6$ and a synthesis temperature of 60 °C. The amount of silica was chosen in two loadings, 2.5 and 9.0 wt.% using either Ludox® or TEOS. Approximately 170 μmol (0.986 g) of Pluronic P123 was dissolved in 150 mmol of alcohol (14 ml of *sec*-BuOH) and stirred for 15 min at the synthesis temperature. In a second solution, 18 mmol of HCl (1.49 ml of HCl 37 wt.%), 150 mmol of alcohol (14 ml) and the corresponding amount of silica source (TEOS or Ludox®), to achieve 2.5 or 9.0 wt.% as $gSiO_2/[gSiO_2 + gAl_2O_3]$ in the final activated oxide, were mixed at room temperature; the necessary water was supplied by the HCl source. Aluminum tri-*sec*-butoxide (10 mmol, 2.54 g) was slowly added to the latter solution under stirring. After 15 min the two solutions were mixed and further stirred at 60 °C. The stirring speed in all pre-evaporation steps was set at 100 rpm. The homogeneous solution was left three days at the synthesis temperature under N_2 flow (30 ml STP min^{-1}) resulting in a white gel. The condensation was induced by evaporating the solvent at 60 °C by increasing the nitrogen flow at 200 ml STP min^{-1} and the stirring speed at 250 rpm until dryness. The samples were coded as L2.5, L9, referring to 2.5 or 9 wt.% SiO_2 using Ludox® and T2.5, T9 referring to 2.5 or 9 wt.% SiO_2 using TEOS. Table 1 summarizes the synthesis variables and materials nomenclature. The term 'mesophase' corresponds to the dried material containing the pluronic template after the sol–gel process; the sample codes are suffixed with a 'P' indicating that it contains the pluronic.

Table 1
Synthesis variables and template content of the silica-promoted alumina mesophases.

Material	Silica source	SiO_2 (wt.%)	Template (wt.%)[a]
OM-5/P	None	–	82
L2.5/P	Colloidal silica, Ludox®	2.5	87
L9/P	Colloidal silica, Ludox®	9.0	86
T2.5/P	TEOS co-hydrolysis	2.5	88
T9/P	TEOS co-hydrolysis	9.0	87

[a] Calculated as ΔW 30–900 °C from the TGA patterns.

2.2. Thermal activation

The resulting dry materials were calcined at 750 °C in a conventional oven at 1 °C min^{-1} with an intermediate step at 400 °C for 4 h to decompose the organic template, based on the TGA patterns shown in Fig. 1a. This was followed by a second step at 1 °C min^{-1} up to 750 °C, which was maintained for 4 h after which the sample was cooled down. In some instances, the calcination of the mesophase was carried out at higher temperatures; when applicable, this temperature will be indicated. The sample codes are suffixed with a number that corresponds to the applied calcination temperature in °C (example: L2.5/750).

2.3. Characterization

Thermogravimetric analysis (TGA) was carried out in a Mettler–Toledo analyzer (TGA/SDTA851e) using a flow of synthetic air of 80 cm^3 min^{-1} STP. The samples were heated from 30 to 900 °C at 10 °C min^{-1}.

TGA with evolved gas analysis was carried out in the same instrument by continuously analyzing the gases in a Hiden Quadrupole analyser using 20 vol.% O_2/Ar and Ar as purge gas. The intensities were normalized to inert gas (Ar^+, m/z = 40).

Small angle X-ray scattering (SAXS) measurements were performed using a Bruker NanoStar instrument. A ceramic fine-focus X-ray tube, powered with a Kristallflex K760 generator at 35 kV and 40 mA, has been used in point focus mode. The primary X-ray flux is collimated using cross coupled Göbel mirrors and a pinhole of 0.1 mm in diameter providing a Cu $K\alpha$ radiation beam with a full