



Thermal stabilization of alumina modified by lanthanum



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ABSTRACT

Transition alumina, with different La loadings, were synthesized from boehmite (AlOOH) hydrosols containing a PEO/PPO/PEO triblock copolymer (Pluronic® P123) and lanthanum nitrate. After calcination at 500 °C, the xerogels prepared from these sols have large specific surface area (≈ 400 m²/g) and very large porous volumes, increasing with the amount of La to reach 2.5 cm³/g for La/(La + Al) = 0.036. This material still kept a surface area close to 180 m²/g and a pore volume of 2.3 cm³/g when it was calcined at 1000 °C. However, after calcination at 1200 °C, the best textural properties (70 m²/g and 0.6 cm³/g) were observed for La/(La + Al) = 0.015. Larger La loadings led to the formation of LaAl₁₁O₁₈ and LaAlO₃ and the detection of these mixed oxides was associated with a decrease of surface area and pore volume.

The improvement of the thermal stability of these materials can be explained by the synergy of two effects: (i) the adsorption of copolymer onto fiber-like boehmite nanoparticles, preventing their compact rearrangement during the drying and maintaining a large porosity after calcination; (ii) the inhibition of the sintering process through the formation of thermally stable species between reactive surface sites (strong Lewis acid sites) and lanthanum atoms.

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1. Introduction

γ -Alumina is without doubt one of the most important material in catalysis. It is used both as catalyst and catalyst support because of its high specific surface areas and its exceptional surface properties [1]. However γ -alumina is metastable and, heated above 800 °C, it starts to transform in δ -alumina, then in θ -alumina and finally into the thermodynamically stable α -alumina [2,3]. These transformations are accompanied by a progressive loss of residual hydroxyl groups and a severe decrease of specific surface area. Schaper et al. [4,5] showed that the final transformation in α -alumina is not the cause of the drastic drop of specific surface area but actually results from the sintering of transition alumina.

Because thermal stability in the high temperature range is mandatory for processes like catalytic combustion, automotive emission control, methane steam reforming or oxidative coupling of methane, thermal stabilization of alumina-supported catalysts has been extensively studied [6]. Sintering of gamma alumina proceeds via surface diffusion [4] thus the sintering rate can be decreased by addition of elements that prevent the atomic diffusion. Among the additives reported in the literature, lanthanum appears to be one of the best elements for inhibiting the sintering

of high-surface-area alumina [7–13]. Besides its stabilizing effect lanthanum generates Lewis and Bronsted acid sites [12]; a decrease of this acidity with the lanthanum content has been observed [14,29].

On the other hand, because the sintering occurs especially at the contact between primary particles, the thermal stability can be improved through the control of the arrangement in order to minimize the number of contact point between the particles. Indeed Burtin et al. showed that alumina with the highest surface area exhibits the highest rate of transformation into α -alumina [9]. Conversely enhanced thermal stability has been reported for loosely packed fibrous [15,16] or platelet [17] alumina.

In a recent work [18] we reported the remarkable enhancement of γ -alumina porosity prepared from a boehmite hydrosol containing a triblock copolymer, the Pluronic® P123 and a metal nitrate (Al, Mn, Cu). This simple process can give materials with outstanding pore volume (up to 2.6 cm³/g) associated with high surface areas (in the range 300–500 m²/g). Besides it has the advantage of producing highly stable colloidal sols giving crack free coatings thanks to the presence of copolymer.

Even more recently Jiang et al. [19] reported that the addition of lanthanum nitrate in a boehmite sol containing Pluronic® P123 gives mesoporous alumina with high thermal stability retaining a specific surface area of 100 m²/g and a pore volume of 0.66 cm³/g after a thermal treatment at 1200 °C for 1 h. However these authors did not mention the effect of lanthanum addition on the

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pore size distributions of La-modified alumina and they did not follow the effect of lanthanum concentration on the thermal stability.

In this paper, we study the effect of P123 and La concentration on the textural properties and the crystal structure of these mesoporous alumina modified by lanthanum, after calcination at 500, 1000 and 1200 °C.

2. Experimental

2.1. Synthesis of boehmite sols

Boehmite sols were synthesized according to the method reported by Yoldas [20–22]. In a typical procedure, 185 mL of hot water (85 °C) were added very fast, under vigorous stirring, to 25.3 g (0.1 mol) of aluminum tri-sec-butoxide (ASB) [Al(OC(CH₃)₃)₃, Acros Organics]. The hydrolysis ratio, $h = [\text{H}_2\text{O}]/[\text{Al}] \approx 100$. After 15 min, the white precipitate was peptized by adding 0.474 mL (0.1 mol) of nitric acid (HNO₃, 68%, Fluka) ([HNO₃]/[Al] = 0.07). The mixture was stirred and maintained at 85 °C for 24 h; the white suspension changed gradually to a transparent sol. During the first 3 h, the reaction flask was kept uncovered in order to allow the isobutanol formed during hydrolysis to evaporate. The concentration of aluminum in the final sol was about 0.8 mol L⁻¹ with a pH in the range 4.5–5.3.

Pluronic® P123 (Sigma–Aldrich) was added in the sol and the mixture was kept under gentle stirring for 24 h at 25 °C to approach the adsorption–desorption equilibrium. Then lanthanum nitrate [La(NO₃)₃, 6H₂O, 99.999% Acros–Organics] was added and the sol was stirred again for at least 12 h at room temperature. The transparency of the boehmite sols was not changed after addition of copolymer or lanthanum nitrate. The polymer amount, expressed by its weight/weight percent (w/w%) concentration in the sol, was fixed at 17% because we observed in a previous work [18] that the largest pore volume was obtained by using this value. The lanthanum content is expressed by the atomic ratio (in percent) of La/(La + Al). This content ranged from 0% to 3.6%.

Xerogels were made by drying the sols in PTFE plates at 70 °C for 12 h. This gave a glassy material which was fired in air at 500 °C for 2 h. The AlOOH concentration in the sols was determined by weight loss on ignition at 1000 °C for 2 h.

2.2. Powder X-ray diffraction (PXRD)

The crystal structure was investigated via powder X-ray diffraction. Data was collected, at room temperature, with a Bruker AXS D4 0-2θ diffractometer, in the Bragg–Brentano geometry, using filtered Cu Kα radiation and a graphite secondary-beam monochromator. Diffraction intensities were measured by scanning from 20 to 80° (2θ) with a step size of 0.02° (2θ).

2.3. Specific surface area, pore size distribution

Specific surface area and pore size distribution were calculated from nitrogen adsorption–desorption isotherms collected at 77 K, using an adsorption analyzer Micromeritics Tristar II 3020. The specific surface areas were computed from adsorption isotherms, using the Brunauer–Emmett–Teller (BET) method [23]. The pore size distributions (PSD) were computed from desorption isotherms by the NLDFT method [24] (with Quantachrome Autosorb-1 software using silica equilibrium transition kernel at 77 K, based on a cylindrical pore model).

Pore volume (V_{pore}) was calculated from the adsorbed volume at a relative pressure of 0.995 (V_{sat}) by:

$$V_{\text{pore}} = \frac{N_2 \text{ gas density}}{N_2 \text{ liq. density}} V_{\text{sat}} = 0.00155 V_{\text{sat}}$$

The relative errors associated with adsorption–desorption analysis were estimated to be the followings: S_{BET} , 5%; P_V , 5%. Prior to analysis, to remove the species adsorbed on the surface, the samples (0.02–0.5 g) were degassed for 1 h at 90 °C, then for 1 h at 150 °C and finally at 350 °C overnight (≈ 15 h).

2.4. Electron microscopy

Transmission electron microscopy analyses were performed with a JEOL JSM-2100F operating at 200 kV. Samples were prepared by putting a drop of an ethanol suspension of particles on a carbon-coated copper grid.

3. Results

3.1. Nitrogen-adsorption

3.1.1. Specific surface area and pore volume

The effect of addition of lanthanum on surface area and porous volume for the xerogels fired at 500, 1000 and 1200 °C is summarized in Table 1 and plotted in Fig. 1. Firstly, if we consider the xerogels fired at 500 °C, the top two rows of Table 1 shows that, for samples free of lanthanum, P123 addition produced an increase of S_{BET} of approximately 30% but especially an expansion of the pore volume of 370%. The addition of lanthanum had a minor effect on S_{BET} , which decreased linearly with lanthanum content but with a slope of about 7 m² for each %La (Fig. 1). In contrast the pore volume increased significantly with lanthanum content so that, for 3.6% lanthanum, the volume has expanded more than 60%.

The little impact of lanthanum nitrate addition on the BET surface area of xerogels fired at 500 °C is comparable to the effect already reported for other metal nitrates like Al, Mn and Cu [18].

Table 1

Surface area and porosity of xerogels prepared with addition of P123 and lanthanum nitrate, after calcination at 500, 1000 and 1200 °C. The polymer amount corresponds to its weight/weight percent (w/w%) concentration in the sol. The lanthanum content is expressed by the atomic ratio (in percent) of La/(La + Al). S_{BET} is BET specific surface area; V_{sat} is the adsorbed volume at $P/P_0 = 0.995$ and V_{pore} is the pore volume calculated by $V_{\text{pore}} = 0.00155 \cdot V_{\text{sat}}$. The surface coverage of lanthanum (last column) was calculated from S_{BET} .

La/(La + Al) (%)	%P123	Calcination temperature (°C)	S_{BET} (m ² /g)	V_{sat} (cm ³ /g)	V_{pore} (cm ³ /g)	La coverage (La/nm ²)
0	0	500	306	212	0.33	0
0	17	500	405	1002	1.55	0
0.3	17	500	389	1111	1.72	0.1
0.6	17	500	391	1190	1.84	0.2
0.9	17	500	393	1221	1.89	0.3
1.5	17	500	391	1405	2.17	0.4
2.5	17	500	375	1463	2.26	0.8
3.6	17	500	377	1640	2.53	1.0
0	0	1000	82	132	0.20	0
0	17	1000	174	712	1.10	0
0.3	17	1000	174	708	1.09	0.2
0.9	17	1000	174	687	1.06	0.6
1.5	17	1000	188	841	1.30	0.9
2.5	17	1000	191	1063	1.64	1.7
3.6	17	1000	176	1084	1.67	2.3
0	0	1200	5	11	0.02	0
0.9	0	1200	23	79	0.12	4.5
1.8	0	1200	28	87	0.13	6.2
2.5	0	1200	23	85	0.13	12.3
0	17	1200	32	173	0.27	0
0.3	17	1200	51	289	0.45	0.7
0.9	17	1200	60	341	0.53	1.8
1.5	17	1200	71	414	0.64	2.5
2.5	17	1200	61	395	0.61	4.9
3.6	17	1200	49	298	0.46	8.3

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