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Thermal stabilization of alumina modified by lanthanum

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A B S T R A C T

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.

Keywords:
Boehmite
Alumina
Lanthanum
Poloxamer
Thermal stabilization

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) ($[\text{HNO}_3]/[\text{Al}] = 0.07$). 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

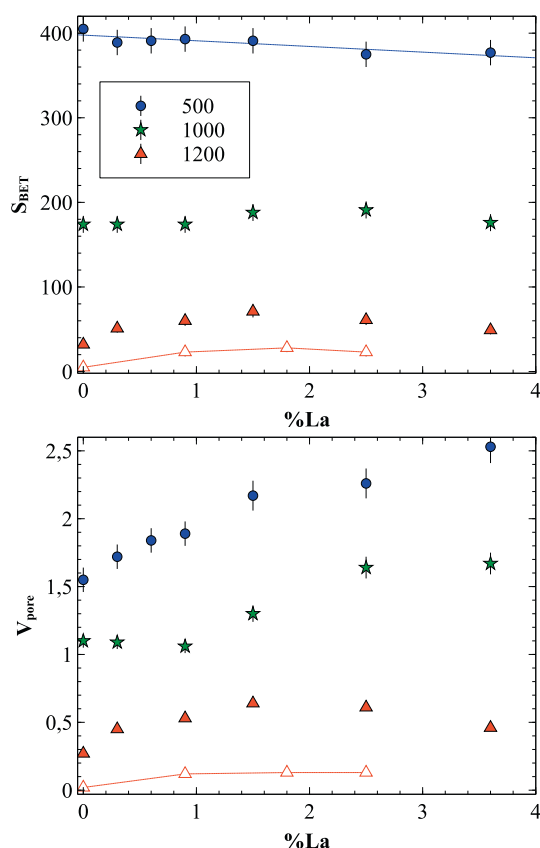


Fig. 1. Effect of lanthanum content and calcination temperature on the specific surface area and porosity of alumina xerogels. The empty symbols (red triangle) correspond to samples prepared without addition of P123. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Concerning the increase in porosity resulting from the addition of lanthanum nitrate, it is more marked with La compared to other metal nitrates. For example, the pore volume of the xerogel containing 3.6% La exceeds $2.5 \text{ cm}^3/\text{g}$ whereas for the other additives, the pore volume did not go beyond $2.2 \text{ cm}^3/\text{g}$ for the same concentration.

Heating these xerogels at $1000 \text{ }^\circ\text{C}$ induced a large decrease of S_{BET} . For samples prepared without additives the drop in surface area exceeded 70%. After addition of P123 the reduction was still larger than 60%. For low lanthanum content ($<1\%$) the loss in surface area remained close to 60% whereas for higher content it decreased to 50%. Thus, at $1000 \text{ }^\circ\text{C}$, the stabilizing effect of the lanthanum on S_{BET} seems rather limited. The shrinkage of pore volume due to heating at $1000 \text{ }^\circ\text{C}$ corresponded to about 40% without additives. After addition of P123 it became about 30% for lanthanum free samples. Surprisingly, in samples containing 0.3% La, the shrinkage of pore volume was larger, at more than 40%, than in the lanthanum free xerogel. Then the pore shrinkage decreased to about 30% when lanthanum content increased, the best stabilization being obtained for 2.5% La.

Calcination of the xerogels prepared without additives at $1200 \text{ }^\circ\text{C}$ induced a huge decrease, both of S_{BET} and V_{pore} , which dropped respectively at $5 \text{ m}^2/\text{g}$ and $0.02 \text{ cm}^3/\text{g}$. Addition of P123 resulted in a significant stabilization with a S_{BET} of $30 \text{ m}^2/\text{g}$ and a V_{pore} of $0.3 \text{ cm}^3/\text{g}$, but it was clearly the addition of both P123 and lanthanum which provided the best stabilization, with a S_{BET} of $70 \text{ m}^2/\text{g}$ and a V_{pore} exceeding $0.6 \text{ cm}^3/\text{g}$ for xerogels containing 1.5% La. As already pointed out by Pijolat et al. [25] the best stabilizing effect, for both S_{BET} and V_{pore} , was observed near 1% La.

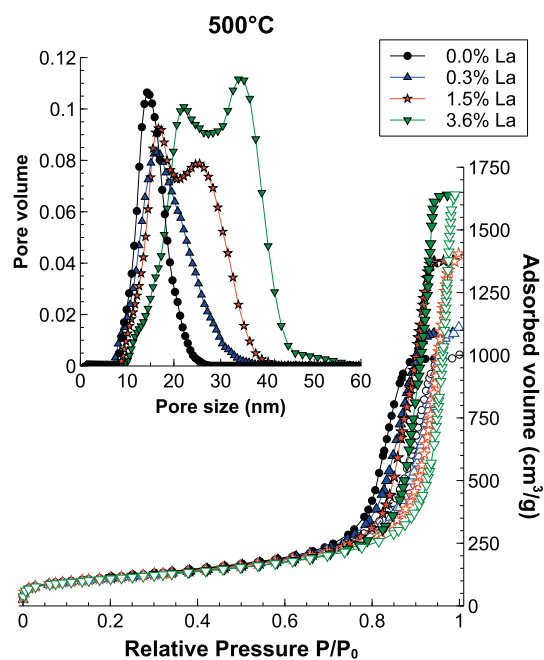


Fig. 2. Effect of addition of P123 and lanthanum nitrate on the nitrogen adsorption-desorption isotherms and PSD of xerogels prepared from the sols by drying and calcination at $500 \text{ }^\circ\text{C}$ for 2 h.

3.1.2. Pore size distribution (PSD)

Some representative isotherms, recorded with xerogels fired at $500 \text{ }^\circ\text{C}$, and their associated PSD, calculated using NLDFT method, are plotted in Fig. 2. These isotherms were all of the same type IV with an H1 hysteresis loop [26].

The PSD of the lanthanum free sample can be fitted rather accurately with a Gaussian curve centered at 15 nm and with half height of 7 nm (Fig. 3, top-left). This indicates that essentially one family of pore was present in this sample. After addition of 0.3% of lanthanum the PSD broaden and became unsymmetrical. Now it can be fitted correctly with two Gaussian peaks, the first still centered at about 15 nm with a half height of 7 nm and the second centered at 20 nm with a half height of 13 nm (Fig. 3, top-right). This evidences that the lanthanum addition created a new kind of pore. When the amount of lanthanum was increased the PSD can still be correctly fitted with two Gaussian peaks. Up to 2.5% of lanthanum, the first peak shifted slightly from 15 to 17 nm and the second peak more markedly from 20 to 28 nm. However for 3.6% of lanthanum a notable shift toward larger pore size was observed with the first peak being centered at 23 nm and the second at 35 nm (Fig. 3, bottom-right).

In summary the addition of lanthanum both created a new kind of pore with larger size and also increased the size of the pores generated by the copolymer. This could be explained by the diminution of repulsion barrier between boehmite nanoparticles because lanthanum nitrate addition increased the ionic strength, rising the sticking probability between particles and leading to the formation of less compact aggregates during the drying.

The effect of calcination temperature on the PSD, for xerogels prepared with P123 and containing various content of lanthanum, is shown in Fig. 4. For all the samples the calcination at 1000 and $1200 \text{ }^\circ\text{C}$ induced a shrinkage, a broadening and a shift of the PSD toward larger pore size. The stabilizing effect of lanthanum is clear even for the lower content. As already pointed out, despite the very large pore volume of the xerogels containing 3.6% of lanthanum when fired at 500 and $1000 \text{ }^\circ\text{C}$, such lanthanum content led to a reduced thermal stability at $1200 \text{ }^\circ\text{C}$. This point will be addressed in the discussion.

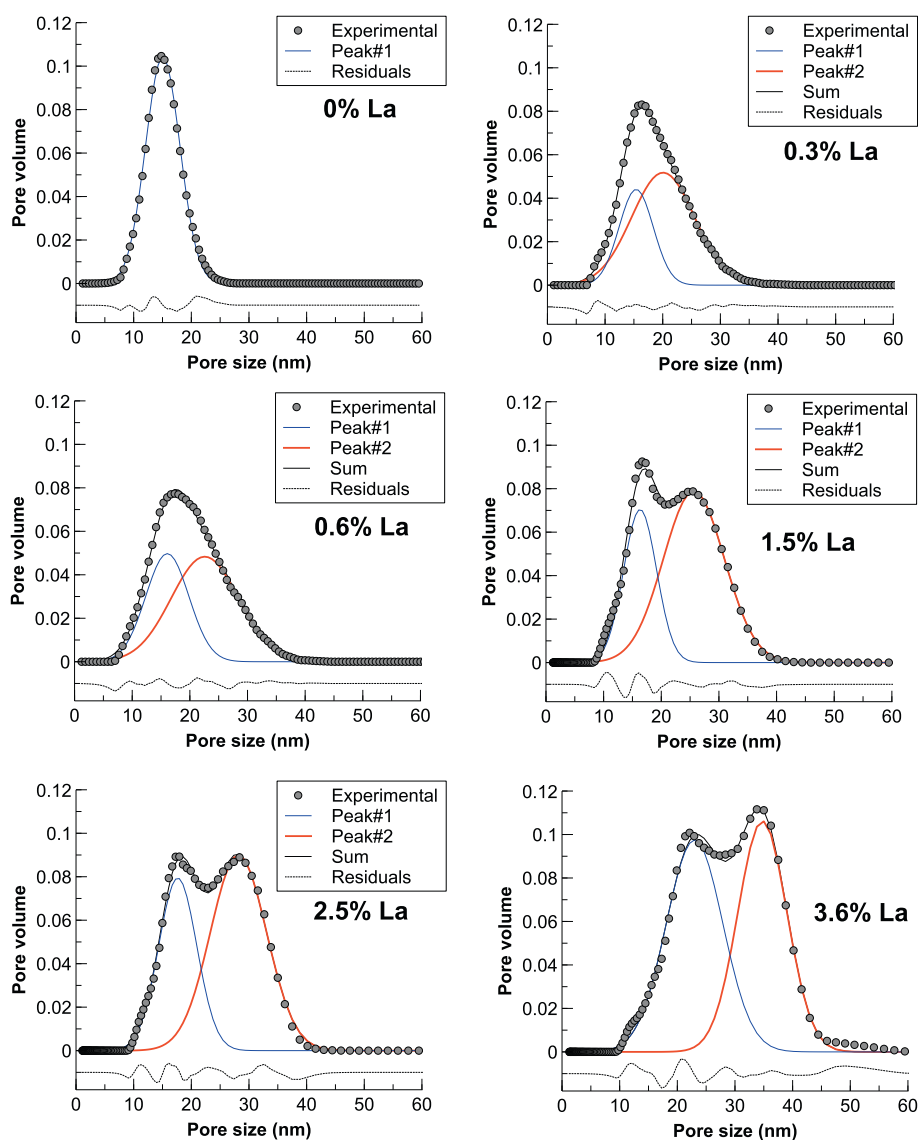


Fig. 3. Fitting with Gaussian peaks of the PSD of xerogels (fired at 500 °C) containing increasing amount of La. Residuals plot corresponds to the difference between the sum of the peaks and the experimental data (symbols). To improve the figure clarity this line was slightly shifted (-0.01).

3.2. XRD

For all the samples the XRD powder patterns of xerogels fired at 500 °C show only γ -alumina (PDF No. 10-425). XRD patterns of xerogels heated at 1000 °C and 1200 °C for 4 h are summarized respectively in Figs. 4 and 5.

The main crystalline phases detected in the XRD patterns of the xerogels fired at 1000 °C, prepared without any additives (Fig. 5a, left), were δ -alumina (PDF No. 00-056-1186) and θ -alumina (PDF no 00-035-0121). A small amount of α -alumina (PDF No. 01-070-5679) was also detected. After firing at 1200 °C, the XRD patterns of these xerogels showed only α -alumina (Fig. 6a, left).

Addition of 1.5% of lanthanum suppressed the formation of α -alumina in the xerogels fired at 1000 °C and decreased the amount of θ -alumina (Fig. 5c, left). However a significant amount of α -alumina was still formed when these xerogels were fired at 1200 °C (Fig. 6b, left). Besides a small amount of hexagonal $\text{LaAl}_{11}\text{O}_{18}$ (PDF No. 00-033-0699) was also detected. Most of the studies reported in literature did not mention the formation of this lanthanum hexaaluminate phase but the formation of LaAlO_3 and La_2O_3 . Actually it was shown that the growth of $\text{LaAl}_{11}\text{O}_{18}$ is very slow even at temperatures exceeding 1400 °C [27]. However MacKenzie

et al. [28] have evidenced that $\text{LaAl}_{11}\text{O}_{18}$ can be prepared by firing at 1200 °C a gel produced by hydrolysis of aluminum-sec-butoxide in presence of lanthanum acetate.

Increasing the amount of lanthanum to 2.5% did not improve the stabilizing effect; actually it was quite the reverse as the quantity of α -alumina formed after firing at 1200 °C was clearly larger compared to the sample containing 1.5% of lanthanum (Fig. 6c, left). The proportion of $\text{LaAl}_{11}\text{O}_{18}$ formed when the xerogels containing 2.5% of lanthanum were fired at 1200 °C did not seem larger than with the sample containing 1.5% of lanthanum.

When the La free xerogels were prepared with P123, γ -alumina was fully transformed in a mixture of δ and θ -alumina after firing at 1000 °C but no α -alumina was detected (Fig 5a, right). Nevertheless after firing at 1200 °C, almost all the transition alumina was transformed into α -alumina. Thus the stabilizing effect induced by P123 at 1000 °C was no longer effective at 1200 °C (Fig 6a, left).

Addition of 0.3% of lanthanum in the xerogels prepared with P123 did not seem to change the crystalline phase composition for the samples fired at 1000 °C. However, when the xerogels were fired at 1200 °C, a stabilizing effect of lanthanum was observed because these samples contained less α -alumina than the free lanthanum sample. When the amount of lanthanum was increased to

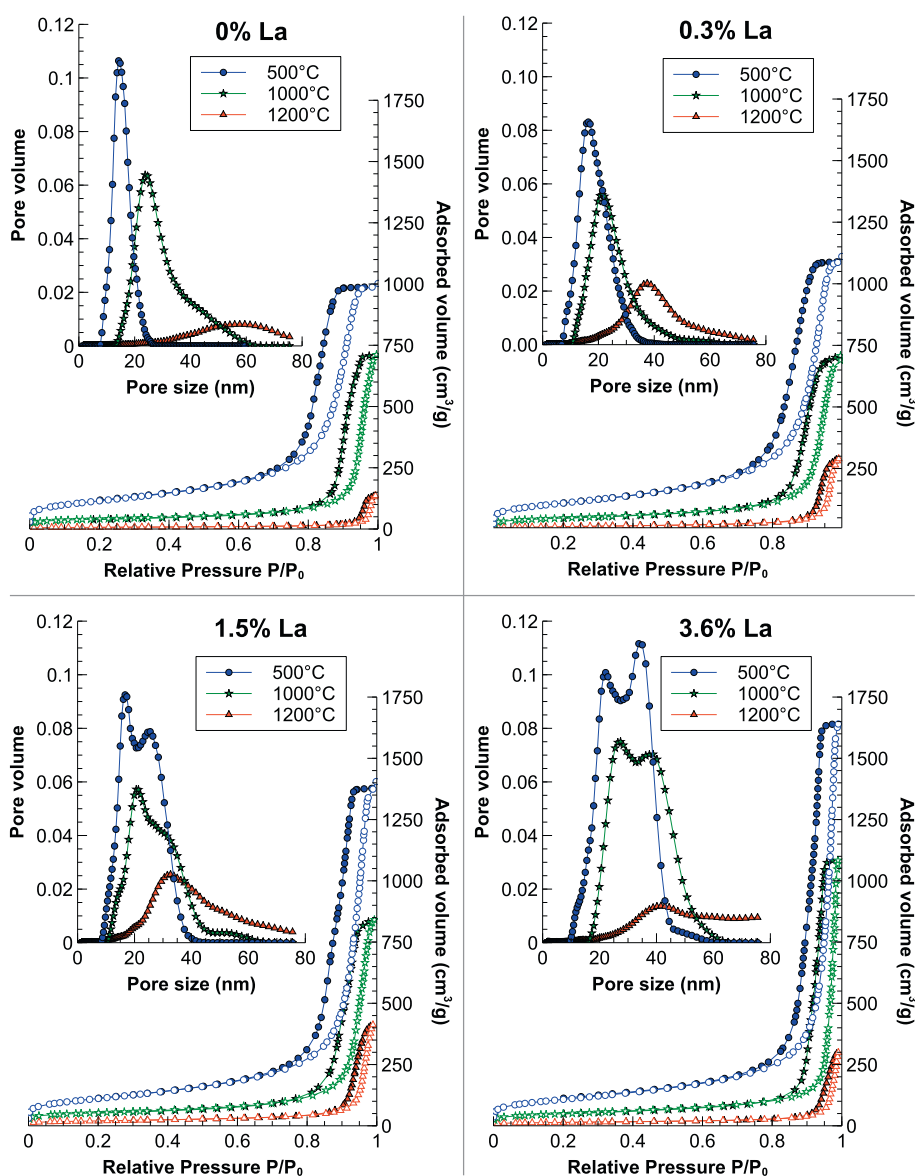


Fig. 4. Effect of lanthanum nitrate content on the nitrogen adsorption–desorption isotherms and PSD of alumina xerogels after calcination at 500 °C for 2 h (blue dot), 1000 °C for 4 h (green star) and 1200 °C for 4 h (red triangle). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

0.9% the stabilizing effect of lanthanum was improved, nevertheless the samples fired at 1200 °C still contained a significant amount of α -alumina. Actually the stabilizing effect of lanthanum became very clear for 1.5% of lanthanum. No phase transformation was detected when the samples were fired at 1000 °C, their γ -alumina structure was retained (Fig. 5c, right). Firing at 1200 °C induced phase transformation into a mixture of δ and θ -alumina but no α -alumina was detected (Fig. 6b, right). When the lanthanum amount was increased more, the formation of La–Al mixed oxides was observed for xerogels fired at 1200 °C. The XRD patterns of the samples containing 2.5% of lanthanum showed the lines of $\text{LaAl}_{11}\text{O}_{18}$ (Fig. 6c, right) while the patterns of the samples containing 3.6% of lanthanum showed additionally some lines of LaAlO_3 (PDF No. 01-073-3684) (Fig. 6d, right).

3.3. Transmission electron microscopy

Fig. 7a shows a TEM image of a xerogel prepared with P123 and La (1.5%) after calcination at 500 °C. The primary particles of boehmite self-organize in mono-dimensional objects (rods or

laths) and, thanks to the additives, this structure is maintained after the transformation in γ -alumina. After calcination at 1200 °C, when no lanthanum was added (Fig. 7b) all these objects collapsed to give thin plates connected by large neck. Comparison with a xerogel containing 1.5% La (Fig. 7c) clearly evidences that the lanthanum addition has delayed the sintering process. The image of the xerogel prepared with both P123 and 1.5% La (Fig. 7d) shows that this sample has kept a very porous structure; no large particles can be seen like in Fig. 7c.

4. Discussion

Schaper et al. assumed that the cause of sintering is neck formation at contact points between the crystallites via surface diffusion, and that the stabilizing effect of lanthanum is due to the decrease of the rate of surface diffusion by the formation of lanthanum aluminate surface layer [4,5]. Bettman et al. [8] assumed that, up to a concentration of $8.5 \mu\text{mol La}/\text{m}^2$, the lanthanum forms a two-dimensional lanthana overlayer invisible by XRD. For larger lanthanum concentrations, the excess forms crystalline La_2O_3 at

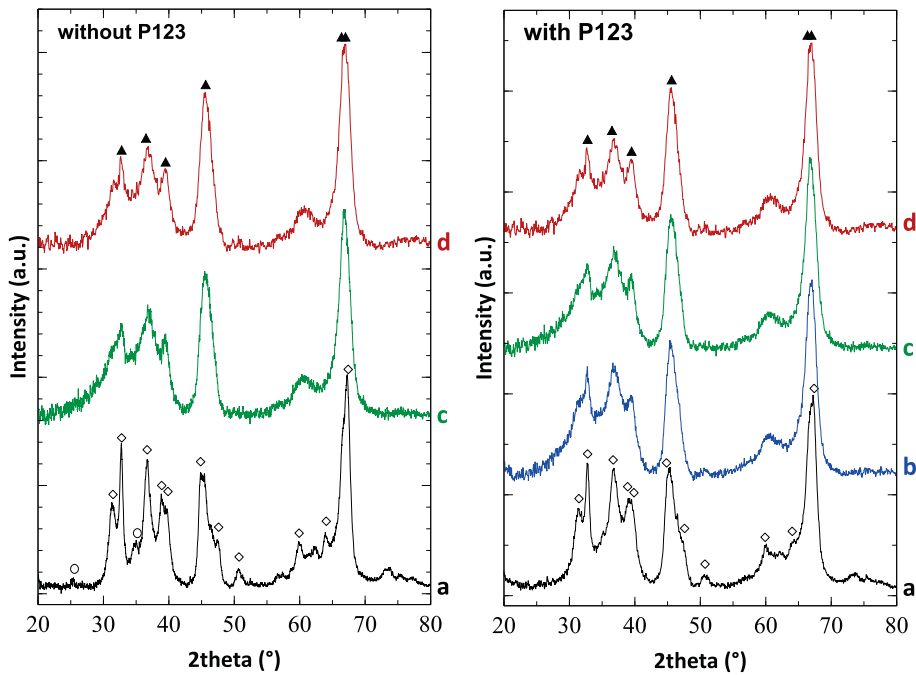


Fig. 5. X-ray powder patterns of xerogels, after calcination at 1000 °C. These samples were prepared without (left plot) and with (right plot) P123 addition and with a La content of (a) 0%, (b) 0.9%, (c) 1.5% and (d) 2.5%. (O) Shows positions of α -alumina, (\diamond) of θ -alumina and (\blacktriangle) of δ -alumina reflections.

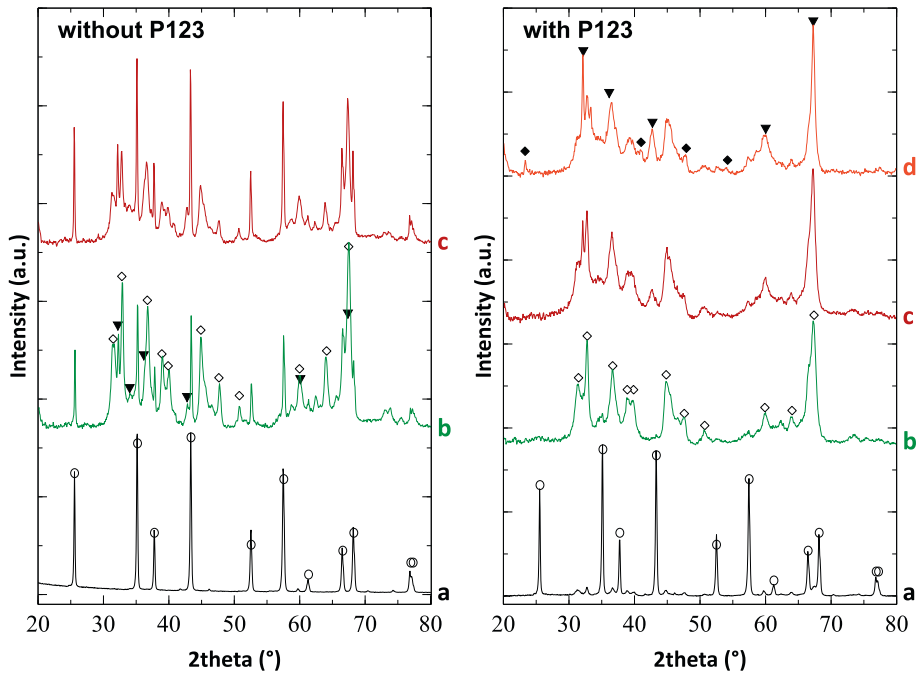


Fig. 6. X-ray powder patterns of xerogels, after calcination at 1200 °C. These samples were prepared without (left plot) and with (right plot) P123 addition and with a La content of (a) 0%, (b) 1.5%, (c) 2.5% and (d) 3.6%. (O) Shows positions of α -alumina, (\diamond) of θ -alumina, (\blacktriangledown) of $\text{LaAl}_{11}\text{O}_{18}$ and (\blacklozenge) of LaAlO_3 reflections.

650 °C and LaAlO_3 at 800 °C detectable by XRD. These authors proposed that the stabilizing effect of lanthanum is due to the lowering of the surface energies of transition alumina by the lanthana overlayer.

Since the sintering of transition alumina occurs on surface defects corresponding to the most reactive sites i.e., edges and corners of the particles, where the aluminum atoms are not fully coordinated (strong Lewis acid sites), Oudet et al. [7] then Beguin

et al. [10] proposed that the thermal stabilization provided by lanthanum nitrate addition could be explained by the anchoring of the lanthanum precursor on these reactive sites, blocking these ions into a thermally stable structure and thus inhibiting the sintering process.

This interpretation was supported by the study of Yamamoto et al. [29] who show that the addition of lanthanum transforms the strong Lewis acid sites on γ -alumina original surface in acid

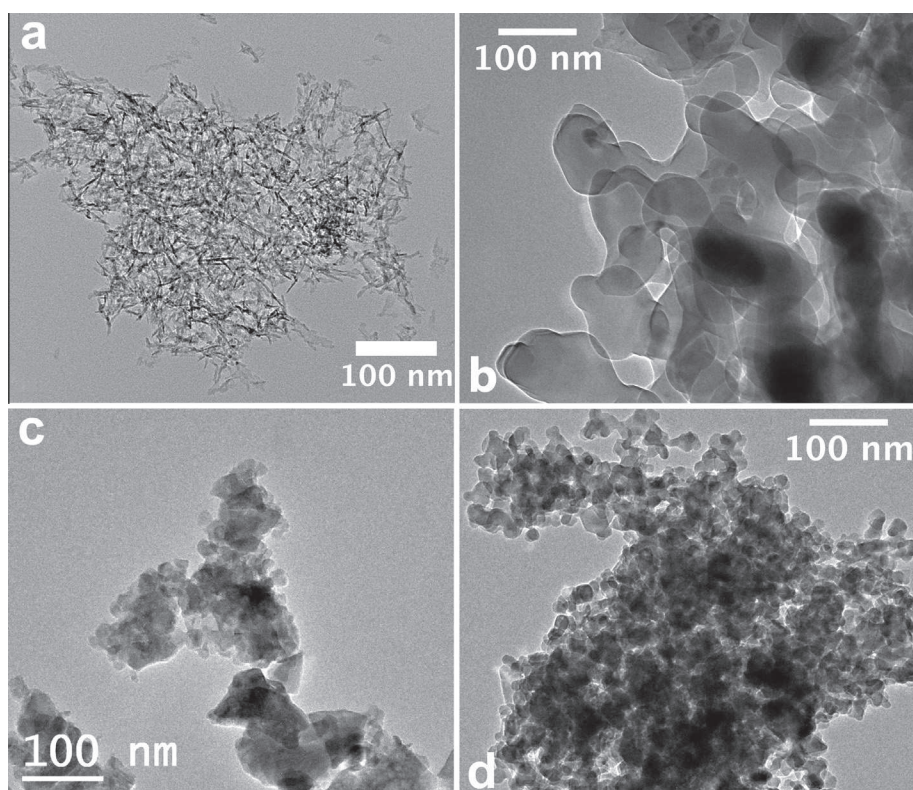


Fig. 7. TEM images of xerogels prepared with: (a) P123 and La (1.5%), after calcination at 500 °C. (b) P123 only, after calcination at 1200 °C. (c) La (1.5%) only, after calcination at 1200 °C. (d) P123 and La (1.5%), after calcination at 1200 °C.

sites with lower strength. These authors also demonstrated that, below 1000 °C, when the lanthanum amount is low, isolated La–Al surface species are stable, whereas on samples containing lanthanum excess, formation of LaAlO_3 perovskite was observed. Moreover they conclude that the formation of LaAlO_3 did not enhance the thermal stability of alumina. This observation was already reported by Beguin et al. [10] for the formation of $\text{LaAl}_{11}\text{O}_{18}$.

This interpretation explains why there is an optimum lanthanum concentration, which corresponds to the situation where all the nucleation sites are blocked. Beyond this concentration the lanthanum excess will lead to the formation of LaAlO_x compounds (involving La–O–La configurations), precursors of La–Al mixed oxides. Since the density of aluminum atoms on γ -alumina surface is about 5 atoms/nm² [30], the formation of a LaO_x monolayer will require about 5 La atoms/nm². It is interesting to note that 5 La atoms/nm² corresponds to about 8 $\mu\text{mol La/m}^2$ which is very close to the value found by Bettman et al. (8.5 $\mu\text{mol La/m}^2$) for the saturation of their 2D overlayer.

In our case the surface coverage of lanthanum, calculated from S_{BET} by assuming a uniform distribution of lanthanum on the surface, is listed in the last column of Table 1. For the samples fired at 1000 °C, the maximum coverage is 2.6 La atom/nm² which is about half the monolayer value. Indeed, whatever the lanthanum concentration, no crystalline La–Al mixed oxide was observed for these samples even when they were prepared without P123. When the samples were fired at 1200 °C the formation of $\text{LaAl}_{11}\text{O}_{18}$ was detected when La coverage exceeded 4.5 La atom/nm² for the xerogels prepared without P123, and 2.5 La atom/nm² for the materials prepared with P123. It is worth noticing that the formation of $\text{LaAl}_{11}\text{O}_{18}$ was always associated with a decrease of surface area and pore volume. This suggests that, beyond a limit temperature, the lanthanum atoms blocking the active sites can migrate to form

a more stable mixed oxide, leaving the active site unprotected and available for the sintering process. Therefore increasing the lanthanum concentration beyond the amount required to block all the active sites will create less stable La–Al species, which can act as nucleation sites for the mixed oxides.

Of course, with the addition of a large amount of lanthanum, the full coverage of alumina with a continuous layer of mixed oxide could provide an effective thermal stabilization but at the cost of a significant decrease of the surface area (because the specific surface area of the mixed oxides is low) and the loss of surface properties of alumina.

5. Conclusion

In summary, this work shows that addition of Pluronic[®] P123 and lanthanum nitrate in a boehmite hydrosol is a very convenient method to obtain, after drying and calcination, transition alumina xerogels which can retain large surface area and porosity at high temperature (<1200 °C).

The improvement of the porosity and the thermal stability of these materials can be explained by the synergy of two effects:

- i) the inhibition of the sintering process through the formation of thermally stable species between reactive surface sites (strong Lewis acid sites) and lanthanum atoms.
- ii) the adsorption of copolymer onto fiber-like boehmite nanoparticles, preventing their compact rearrangement during the drying and maintaining a large porosity after calcination.

This study shows that the detection of La–Al mixed oxides ($\text{LaAl}_{11}\text{O}_{18}$ and LaAlO_3) is always associated with a decrease of

surface area and pore volume. This indicates that, beyond a limit temperature, the lanthanum atoms blocking the active sites can migrate to form mixed oxides more stable at high temperature. Then the active site can be involved in the sintering process. This has two consequences:

i) whatever the initial transition alumina, long-term stabilization of its textural properties by lanthanum only depends on the stability of the La–Al species on the active sites. It seems only effective below 1200 °C.

ii) optimum lanthanum amount, required to achieve the best thermal stabilization, depends on the specific surface area of the initial γ -alumina.

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