

Influence of the Sol-Gel Processing Method on the Structure and the Porous Texture of Nondoped Aluminas

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Alumina supports for high-temperature catalysts were synthesized by different sol-gel methods, including one xerogel dried by simple evaporation and two aerogels dried by supercritical drying in CO₂ or in alcohol. The influence of the gel synthesis technique and the additives used for gelation on the porous structure of alumina and its evolution during heat treatment at 400, 900, and 1200°C was analyzed by X-ray diffraction and by the BET nitrogen adsorption method. Complexation with acetic acid at the gel step followed by supercritical drying at low temperature (35°C) caused a retardation of α -alumina formation with a significant residual specific surface area after heating for 5 h at 1200°C in air, namely 70 m²/g. © 1997

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1. INTRODUCTION

Clean combustion catalytic processes require that catalysts are thermostable up to 1000–1200°C. These catalysts are at least binary composites: an active component such as Pd, Pt (or an oxide) is supported by a refractory oxide which develops as large a surface area as possible under the reaction conditions. Alumina (or alumina based) supports have been described frequently in the literature (1–6). However, relatively few data concerning their thermal behavior are available as a function of their mode of preparation and in relation to their porous texture and crystalline structure as a function of the temperature of heat treatment up to 1200°C. To meet the heat stability requirements, alumina is usually doped by a rare earth element such as Y, as described recently by Ponthieu *et al.* (7). In this study based in part on results already published by Vicarini *et al.* (8) for aerogels, we added the performance of xerogel and studied again the sol-gel method of preparing alumina gels. Indeed, the sol-gel technique appears to be quite promising for the synthesis of materials resistant to high-temperature calcination treatments (9). The present study is an attempt to synthesize alumina supports with a high specific area at high temperature; it addresses the influence of the chemical (sol-gel) and

physical (drying) processing technique on the pore texture and on crystalline structure transformations in alumina (9).

2. METHODS

Alumina was synthesized by sol-gel according to a large number of methods leading to the formation of xerogels or aerogels (10). The analysis of the porous texture of three of these gels is reported in the present paper, and their synthesis conditions are summarized in Table 1.

Sample XBa70/25 designates a xerogel, made by dissolving aluminum sec-butoxide (Al-sb) in isobutanol and adding ethyl acetoacetate (etac) for complexation. Water, close to stoichiometry for hydrolysis, and a small quantity of ammonia were added. Gelation took place in a thermal bath at $\approx 70^\circ\text{C}$ and drying was accomplished by evaporation at $\approx 25^\circ\text{C}$.

Two aerogels are compared to this xerogel. They were also made from Al-sb hydrolyzed in a series of solvents including isobutanol (sample ABc25/35) and water (sample AWn85M/260). The additive was nitric acid (label n) or acetic acid (label c). The hydrolysis temperature was 25°C in the organic solvent and $\approx 85^\circ\text{C}$ in excess water, respectively. In sample AWn85M/260, hydrolyzed in excess water, the solvent was exchanged for methanol by excess dissolution in this alcohol by evaporation just before gelation. These two aerogels were dried by the supercritical method in CO₂ (sample with end label/35) or in methanol at $T \approx 260^\circ\text{C}$ (samples with end label/260). It is interesting that the first method of aerogel preparation (ABc25/35) is much shorter (2 days) than the second one (AWn85M/260: several weeks).

The nature of the phases in all samples was analyzed by powder X-ray diffraction, right after drying, with a Siemens D500 diffractometer using CuK α radiation, followed by a heat treatment in air at 900°C for 5 h (heating and cooling rates $\approx 5^\circ\text{C}/\text{min}$ in an air flow $\approx 6\text{ L/h}$) and then a heat treatment at 1200°C for 5 h (heating and cooling rates $\approx 2^\circ\text{C}/\text{min}$ between 900 and 1200°C).

The pore textures of all samples, before and after heat treatment at 900 and 1200°C, were analyzed by adsorption

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TABLE 1
Synthesis Conditions of Gels

Sample reference	Precursors (composition)	Hydrolysis (gelation) conditions	Characteristics before drying
XBa70/25	Isobutanol/etac/Al-sb/H ₂ O/NH ₄ OH (1 M) (20 ml/4 ml/9.50 g/1.9 ml/a few drops)	25°C (thermal bath 70°C)	Clear liquid + a small amount of white precipitate
ABc25/35	Isobutanol/etac/Al-sb/H ₂ O/acetic acid (41 ml/8 ml/8.7 g/1.9 ml/1.2 ml)	25°C (room temperature)	Transparent liquid becoming opaque
AWn85M/260	Al-sb/HNO ₃ /H ₂ O (200 ml) (1/0.21/67 molar ratio)	85°C (evaporation to 150 ml at 90°C, then addition of 300 ml methanol and evaporation at 35°C)	Bluish sol, transforming to a thixotropic gel

of nitrogen according to the BET method. All samples were previously desorbed at 400°C under vacuum (10^{-5} torr) for at least 4 h before recording their BET isotherms.

3. RESULTS

The X-ray diffraction patterns of the three gel samples are reported in Fig. 1. The crystallographic structure of the gels just after drying depended mainly on the hydrolysis and drying conditions. Aerogel ABc25/35, hydrolyzed in 2-butanol, was amorphous. On the contrary, aerogel AWn85M/260, hydrolyzed in excess water at 85°C and dried at 260°C in supercritical methanol, was composed of well-crystallized boehmite. The X-ray diffraction pattern of xerogel XBa70/25 also consisted of boehmite but it was more poorly crystallized (larger peaks).

After a heat treatment at 900°C most X-ray patterns, such as for aerogel AWn85M/260 and for xerogel XBa70/25 (Fig. 1), could be indexed as δ - or γ -Al₂O₃. However, one noteworthy exception was for aerogel ABc25/35, made with acetic acid as the additive, where κ '-Al₂O₃ crystallized.

After another heat treatment at 1200°C, the formation of well-crystallized α -alumina was expected. It was indeed the only observable phase in most aerogels not reported here and in xerogel XBa70/25 (Fig. 1). However, sample ABc25/35 had transformed to a mixture of κ '- and α -Al₂O₃ after firing for 5 h at 1200°C, while sample AWn85M/260 had transformed to a mixture of θ - and α -Al₂O₃ (Fig. 1).

The nitrogen adsorption-desorption isotherms of gels after desorption at 400°C are reported in Fig. 2. For all samples, the specific surface area was high, well above 100 m²/g as can be seen Fig. 3. The isotherms were of type IV with a marked hysteresis for aerogel AWn85M/260; this sample was mesoporous with a radius narrowly centered in a range of \approx 11 nm. The isotherm of aerogel ABc25/35, made with acetic acid, showed no significant hysteresis, and the pore distribution was very broad and composed of micro- and mesopores. The isotherm of xerogel XBa70/25 was of type I with virtually no hysteresis. Its specific surface area, though determined by the BET method, was essentially

due to the micropores. Pajonk *et al.* (12, 13) showed that for microporous aluminas their BET and "t" specific surfaces were very close to each other, in the range of experimental error. The same holds true for other microporous oxides, such as microporous ZrO₂ and Y₂O₃ as reported recently by Lecloux *et al.* (14). In terms of the total pore volume, since this differs from the total gas volume adsorbed under standard conditions, aerogels ABc25/35 and AWn85M/260 had a significantly lower pore volume than all the other aerogels, not reported in the present paper. However, the pore volume was much higher than in xerogel XBa70/25.

All samples had a significant specific surface area after a heat treatment at 900°C (Fig. 4). However, it is noteworthy that aerogels ABc25/35 and AWn85M/260 had the two lowest specific surface areas of the three samples at this temperature. The adsorption isotherm of aerogel AWn85M/260 was intermediate between types II and IV with respect to its shape (Fig. 5) and pore volume. This aerogel was mesoporous with a radius narrowly centered at \approx 10 nm. Aerogel ABc25/35 was also mesoporous, but with a broader size distribution and a slightly higher maximum size distribution. The xerogel XBa70/25 still had a type I isotherm but with slight hysteresis. Its pore size was narrowly centered at \approx 2 nm, near the limit micropores and mesopores.

The adsorption isotherms of the previous xerogel, heat treated at 1200°C, shifted to type II (Fig. 3), which essentially corresponded to a non-porous material with a very low specific surface area (\approx 1 m²/g). The residual pores were mesopores. Under these conditions, the two aerogels also displayed type II isotherms (Fig. 5). However, the sample made with acetic acid (ABc25/35) as well as sample AWn85M/260 stood out with the highest specific surface areas, \approx 70 and \approx 33 m²/g, respectively. All other aerogels not reported here had much lower specific surface areas.

4. DISCUSSION

The present study showed for the first time that low-temperature synthesis and the drying of alumina by the

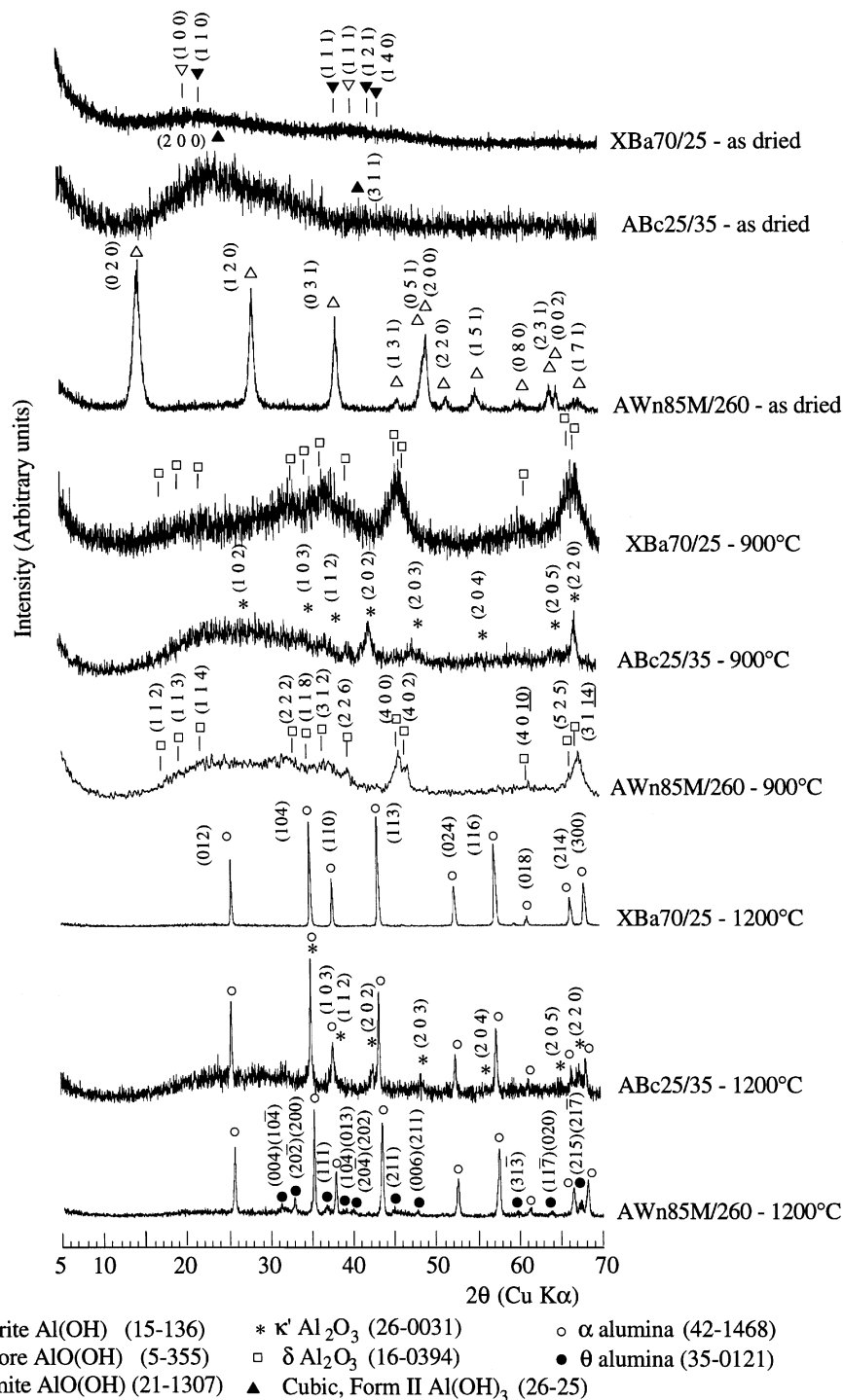


FIG. 1. Powder X-ray diffraction patterns (CuK α , Ni filtered) of the gels just after drying and after heat treatments at 900 and 1200°C.

sol-gel process can have an important effect on residual porosity, even after a heat treatment at 1200°C. The values of the specific surface areas, obtained after 5 h at 1200°C, ranged from ≈ 1 m²/g in alumina derived from xerogel to ≈ 70 m²/g in alumina derived from aerogel made with acetic acid as the additive. These results are in line with those of

Simon *et al.* (15) for xerogels and with those of Pajonk (16) for aerogels.

It would be interesting to deduce general rules for this procedure which could be used as guides for obtaining a significant specific surface area at 1200°C. However, such rules cannot be deduced from the value of the specific

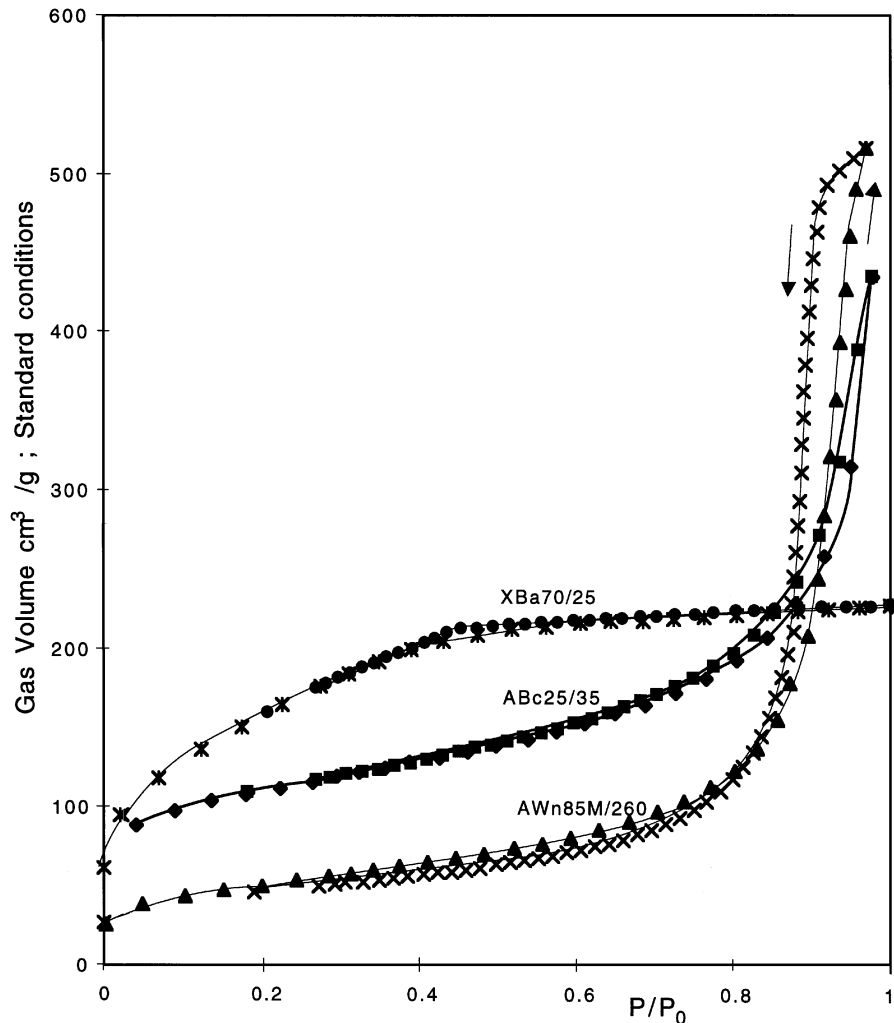


FIG. 2. Nitrogen adsorption-desorption isotherms of gels after desorption at 400°C.

surface area just after drying. Indeed, in Fig. 3, the two samples with the highest specific surface areas at 1200°C had the lowest specific surface areas just after drying. However, a more extended study (10) with a greater number of xerogels and aerogels showed that such a trend did not exist, because the samples with the highest specific surface areas at 1200°C were in the middle of the range for all gels just after drying. This means that the pores responsible for a significant specific surface area at 1200°C were masked by a larger contribution from micropores and small mesopores which characterized the gels just after drying.

However, when looking back the data on the two samples with the highest specific surface areas at 1200°C, i.e., samples ABc25/35 and AWn85M/260, it also seemed that these two samples showed a singular pore texture and phase transformation behavior from the beginning.

First, these two samples were the only ones which did not transform to pure α -alumina at 1200°C. Sample ABc25/35

was a mixture of κ' -alumina and α -alumina, while sample AWn85M/260 was a mixture of θ -alumina and α -alumina. Hence, the high specific surface areas were achieved simultaneously with a retardation in the phase transformation from transition alumina to α -alumina. Similar results were achieved by other researchers but with inorganic additives for instance by doping alumina with Yttrium (Ponthieu *et al.* (7)), or with Ba (Machida *et al.* (17)). In the latter case, the material investigated was the Ba-hexaaluminate BaAl_2O_9 composed of mixture of two crystalline phases, one of them being of the β -alumina type. In the present study, the retardation of sintering was achieved by modifying the initial pore network instead of incorporating additives into the final material. This is consistent with the general theories on sintering according to which the initial pore texture can have an effect similar to that of additives on the sintering behavior (18).

Second, the high specific surface areas of the aerogels ABc25/35 and AWn85M/260 at 1200°C correlated well with

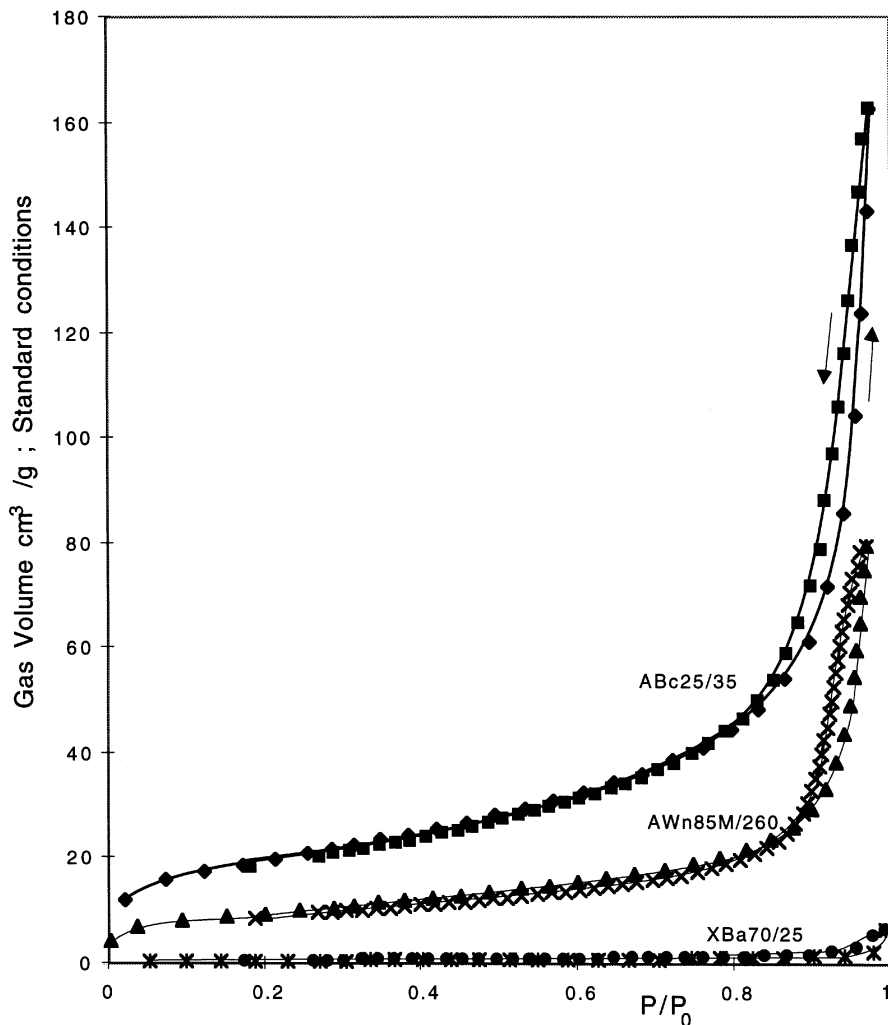


FIG. 3. Nitrogen adsorption-desorption isotherms of gel-derived alumina after heat treatments at 1200°C.

their specific areas after the heat treatments at 900°C. Figure 3 shows that these two aerogels had the lowest specific surface areas, also true for a larger number of alumina aerogels and xerogels not described in this paper.

Apart from this similar high-temperature behavior, the initial pore textures of aerogels ABC25/35 and AWn85M/260 were different. Sample ABC25/35 was a white powder with a much higher specific surface area ($\approx 369 \text{ m}^2/\text{g}$) than sample AWn85M/260 ($\approx 178 \text{ m}^2/\text{g}$). The white color characteristic of both samples, indicated that they were composed of aggregates and pores with a size similar or bigger than the visible light wavelengths.

The synthesis techniques necessary to make alumina with a significant specific surface area at 1200°C must still be defined. In ABC25/35, acetic acid was used as a complexing agent. Recent studies showed that carboxylic acids, such as acetic acid, markedly reduce the reactivity of alkoxides toward hydrolysis by forming acetoalkoxides (19, 20). In the case of aluminum-sec-butoxide added with acetic acid,

Rezgui *et al.* (21) obtained a material with a structure dependent on the molar ratio $r = [\text{acetic acid}]/[\text{Al-sec butoxide}]$. When $r < 2$, these authors obtained a material with a low surface area after drying at 300°C. In the present study, the condition $r < 2$ was met. However, a stoichiometric portion of water was also added for hydrolysis as well as some etec as a primary organic complexing agent before the acetic acid. Our sample was also subject to supercritical drying in liquid CO_2 , at $\approx 35^\circ\text{C}$, which explains the significant high initial specific surface area ($369 \text{ m}^2/\text{g}$), higher than for all the gels made by Rezgui *et al.* However, sample ABC25/35 also had the lowest specific surface area of all samples after treatment at 900°C ($84 \text{ m}^2/\text{g}$). Hence, our result was consistent with the results of Rezgui *et al.* They showed the great importance of organic additives for modifying the pore texture.

A new remarkable result was that the low specific surface area in ABC25/35, recorded at 900°C only slightly decreased at 1200°C, in relation to a noticeable stability of the

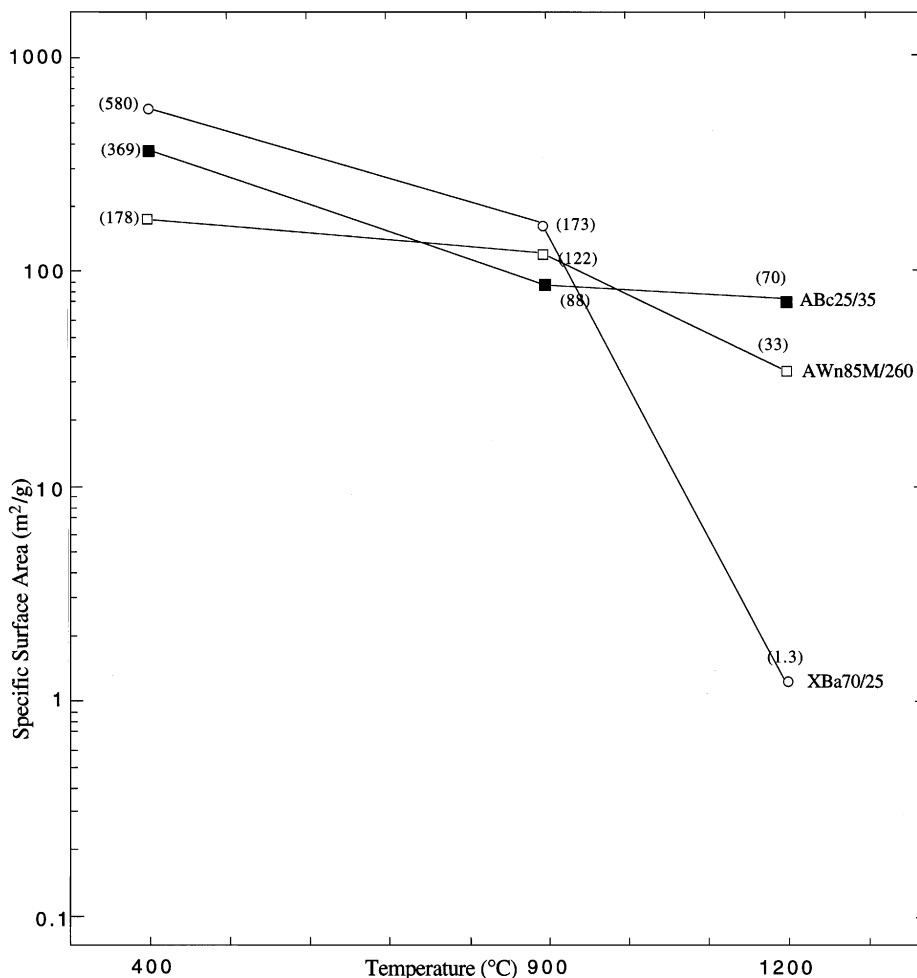


FIG. 4. Specific surface areas, as a function of temperature, of the alumina discussed in the present study.

κ' -alumina phase. A possible explanation is that the fast decrease in specific area at 900°C favored the nucleation of κ' -alumina grains, while growth remained very slow. Hence, crystals bigger than in the initial poorly crystallized gels, but still in the nonometer range, were formed. At 1200°C, the size and aggregation texture of these nanocrystals possibly retarded the occurrence of densification.

The above view is consistent with the result obtained with sample AWn85M/260. This sample was originally hydrolyzed in excess water, according to a method detailed by Yoldas (11). This technique is known to produce very poorly crystallized boehmite, which can be considered as being boehmite nuclei. However, in the present study, this sol was also diluted in excess methanol before gelation, while drying was done at high temperature (260°C). It can be argued that, under such conditions, the initial boehmite nuclei could grow fairly well, to form well-crystallized boehmite nanocrystals, as shown in Fig. 1. As for sample ABc25/35, it is possible that the aggregation mode of the nanocrystals was such that further sintering at 1200°C was hindered,

thus maintaining a residual specific surface area as high as 33 m²/g.

5. CONCLUSION

The present study showed that low-temperature wet-chemistry conditions can have an important effect on the residual pore texture and specific area of nondoped alumina at high temperature (1200°C). Favoring the germination of a crystalline phase at low temperature, where growth was slow, seemed to induce the development of a finely grained crystalline texture which maintained a significant residual porosity at 1200°C and a high specific surface area, 70 and 33 m²/g, respectively, for the two alumina aerogel samples made by different methods. One method for achieving this aim was to add organic acids, such as acetic acid, and dry the resulting gel by the supercritical CO₂ technique. A second method was to dry by the supercritical method at 260°C, in quasi-hydrothermal conditions, a sol where boehmite nuclei were formed at lower temperature in excess water. The

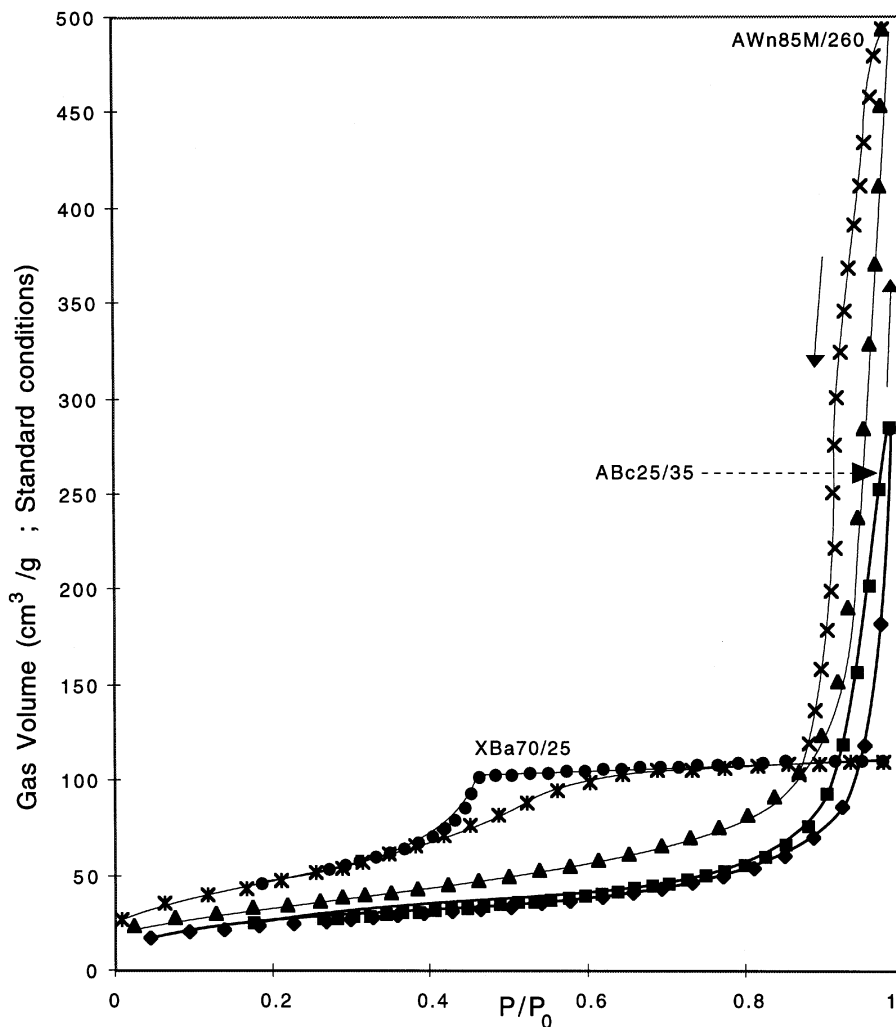


FIG. 5. Nitrogen adsorption-desorption isotherms of gel-derived alumina after heat treatments at 900°C.

latter required a much longer time for synthesis to occur than the former.

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