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Pore surface fractal analysis of PEG and La(III)-doped mesoporous alumina obtained by the sol–gel method

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Abstract: Active porous alumina was prepared *via* a sol–gel method and subjected to thermal treatment in the temperature range 500–1200 °C. The addition of lanthanum effectively inhibited the surface area loss of the aluminas. Fractal analysis from nitrogen adsorption isotherm was used to study the pore surface roughness of alumina samples with different chemical compositions (PEG, PEG and lanthanum) and calcinations conditions in terms of the surface fractal dimension, *d*. The Mahnke and Mögel (MM) model was used to determine the value of *d* of La(III)-doped alumina. Following the MM model, the *d* value of the activated aluminas increased as the calcination temperature increased from 500 to 700 °C but decreased after calcination at 1000, 1100 and 1200 °C. The addition of polyethylene glycol (PEG 5600) to the boehmite sol reduced the surface fractal of the activated alumina due to the heterogeneous distribution of the pores. With increasing La(III) concentration from 0.015 to 0.045 mol La(III)/mol Al(III), the *d* value of La-modified alumina samples decreased, indicating a smoother surface. The obtained PEG+La-doped boehmite sol can be used as a precursor dispersion for the deposition of mesoporous alumina coatings on stainless steel foil, by the spray pyrolysis method.

Keywords: mesoporous alumina; porous structure; surface fractal dimension; sol–gel.

INTRODUCTION

Porous materials are of scientific and technological interest because of their potential applications in separation processes, catalysts, chromatography, low dielectric constant fillers, microelectronics, electro-optics and other emerging nanotechnologies. Active aluminas are prepared mainly by hydrothermal or thermal

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transformations of aluminum hydroxides or alumogel. They are widely used as catalyst supports, because their high specific surface areas, surface properties and crystalline structures are important in the field of various catalysis.^{1,2} Since the temperature of the catalyst can rise to over 1000 °C in a modern engine, thermal stabilization of the catalysts is important. The additive of lanthanum species greatly improves the thermal stability by inhibiting the sintering and phase transformation of alumina.^{3,4} In the sol–gel process, calcination plays an important role in determining the performance of the resultant xerogels. During calcination, organic groups are removed and densification of the gel textures might also occur above a certain temperature. The evolution of the gel structure during calcination might also be influenced by the calcination procedures and thermal history.^{5,6} The preparation routes also influence the surface area and pore structure at the operation temperatures.⁷ In addition, changes in the phase composition and the degree of alumina dehydration also cause changes of the internal pore structure of the alumina. Therefore, in order to better understand a particular physical process occurring within a porous medium, it is necessary to have detailed knowledge of the internal geometry and topology of the internal pore network. However, the surface area and pore size distribution alone do not meet all requirements to describe the characteristics of the pore structure of alumina. Another parameter to characterize the pore structure is surface fractal analysis, which is characterized by the fractal dimension. Gas adsorption is a method that is frequently used to determine the surface fractal dimension of porous media. Several different theories have been developed to analyze gas adsorption data to obtain the surface fractal dimension, which is an important parameter reflecting the roughness of the pore surface.^{8–11} The standard BET equation generally overpredicts the amount adsorbed above the BET region. On a fractal surface, the amount adsorbed on each subsequent layer above the first decreases according to a power law. This principle has been used to derive versions of the BET model for adsorption on a fractal surface, *e.g.*, that derived by Mahnke and Mögel.¹²

In this work, the surface fractal dimensions of activated alumina samples were calculated using the Mahnke and Mögel method (MM). The MM equation provides a relationship between the surface fractal dimension and nitrogen adsorption, that is to say, the pore surface roughness can be probed by nitrogen molecules. The surface fractal dimension by Mahnke and Mögel method yields the following equation:

$$\log \frac{Vp}{p_0} = \log V_m + \log \frac{Cp}{1 - \frac{p}{p_0}(1+C)} - \alpha \log \left(1 - \frac{p}{p_0}\right) \quad (1)$$

where V_p is the volume of adsorbed gas at equilibrium pressure (p), p_0 is the saturation pressure, V_m is the volume of a monolayer and C is the BET constant.

This logarithmic version of the Mahnke and Mögel Equation (1) enables the estimation of the optimal values (with respect to mean square error) of α , C and V_m for the measured isotherms using the simplex optimization method.¹³ The values of the volume of a monolayer, V_m , and the BET constant, C , can be obtained from the BET model and the surface fractal dimension, d , can be calculated from the relation $\alpha = 3 - d$.

In the present work, an effort was made to investigate the influence of poly(ethylene glycol) (PEG), pure or combined with La(III), added to the boehmite sol, and of the calcination temperature on the structure (pore size distribution) and the surface fractal dimension of active porous alumina prepared by the sol-gel method. The surface fractal dimension was used to characterize the pore structure of the active porous alumina. These properties are crucial for the implementation of doped boehmite sol as a precursor solution for the synthesis of γ -alumina coatings on stainless steel foil, by the spray pyrolysis method, which can be used in three-way catalytic processes.

EXPERIMENTAL

Active porous alumina was prepared by the sol-gel method using aluminum alkoxide as a precursor. To prepare boehmite sols, aluminum isopropoxide was hydrolyzed in excess amount of water (100:1 H₂O:Al(III), mol) at 80 °C, followed by peptization with the appropriate amount of HNO₃ (0.07:1 H⁺:Al(III), mol) to form a stable colloidal sol.¹⁴ The sol was kept at about 90 °C for about 72 h under reflux conditions, during which time most of the formed alcohol evaporated. The freshly prepared boehmite sol and polyethylene glycol (PEG, MW 5600, molecule radius: 2.3 nm) or variable concentration of lanthanum nitrate solution combined with PEG, were mixed together and then vigorously stirred in order to obtain homogeneous PEG-doped and La(III)-doped boehmite sols. The doped boehmite sols were then gelled at 40 °C. The gels were heated from room temperature at a rate of 2 °C/min and calcined in air at different temperatures (500–1200 °C) for 5 h to obtain activated alumina samples. The experimental parameters and the variables are given in Table I.

TABLE I. Experimental parameters and variables

Experimental parameters	Variables
Calcinations temperature, °C	500, 700, 1000, 1100 and 1200
Concentration organic additive	1g PEG / 100 ml boehmite sol
Amount of lanthanum, mol La(III)/mol Al(III)	1.5, 3, and 4.5

Nitrogen adsorption was performed at -196 °C and a relative pressure interval between 0.05 and 0.98 in a high vacuum volumetric apparatus.¹⁵ Before each measurement, the sample was degassed at 250 °C under vacuum for time sufficient (4 h < t < 10 h) to obtain vacuum stability. The adsorbed amount of nitrogen was measured by volume at standard temperature and pressure. The specific surface areas S_{BET} and C were calculated by the BET method from

the nitrogen adsorption isotherms, using data up to $p/p_0 = 0.03$; the pore size distribution was computed from the desorption branch of the isotherms.¹⁶⁻¹⁸

RESULT AND DISCUSSION

Effect of the calcination temperature

The complete N_2 adsorption–desorption isotherms of alumina samples obtained for the pure and PEG-doped boehmite sols at calcinations temperatures 500–1200 °C are shown in Figs 1a–1e.

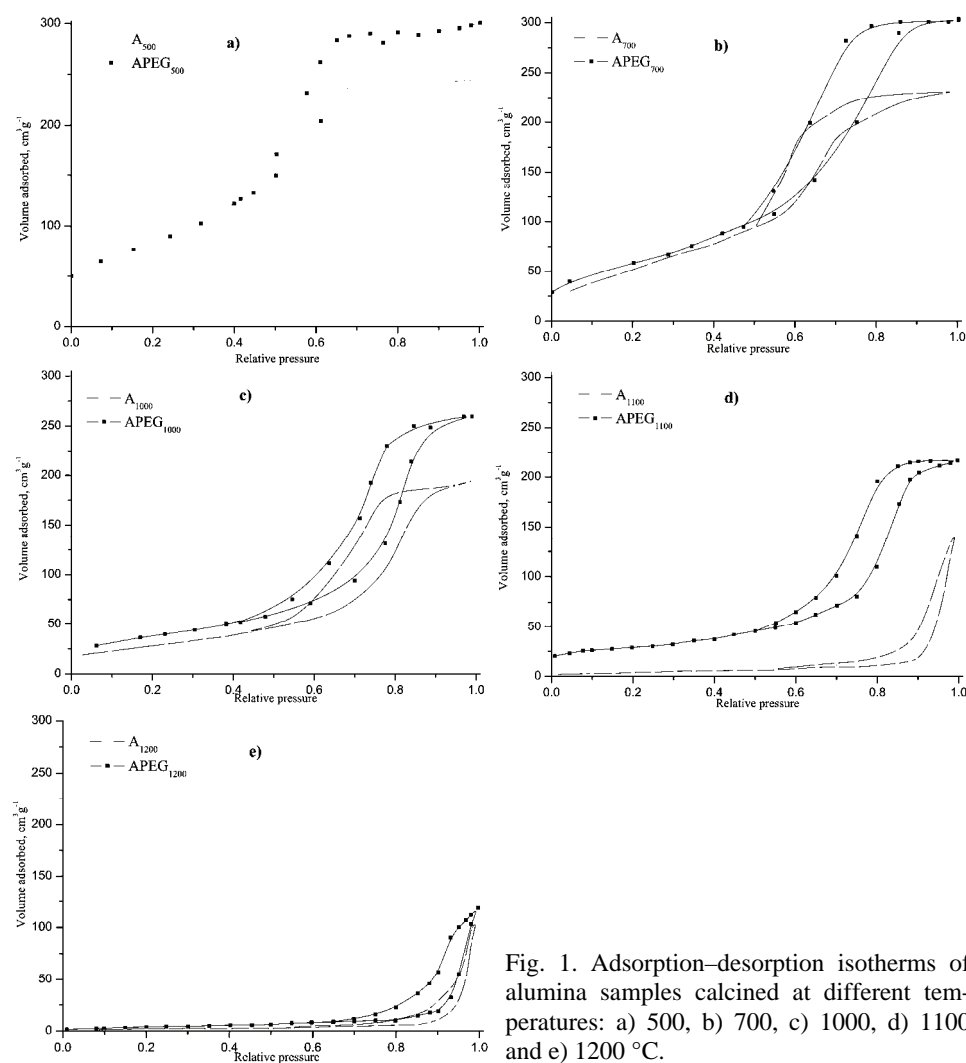


Fig. 1. Adsorption–desorption isotherms of alumina samples calcined at different temperatures: a) 500, b) 700, c) 1000, d) 1100 and e) 1200 °C.

All isotherms at low relative pressures were reversible, but exhibited a hysteresis loop at higher relative pressures. Such a type of adsorption isotherm indicates that the multilayer adsorption of nitrogen onto the sample surface was connected with capillary condensation in the mesopores. The alumina samples calcined at 500 and 700 °C (Figs. 1a and 1b) are characterized by a type IV isotherm with a hysteresis loop of the H2 type.¹⁸ The slope of the desorption branch for the alumina samples obtained from the PEG-doped boehmite sol indicated a broader pore size distribution than in the non-doped alumina sample. However, the adsorption isotherms for the alumina samples calcined at a temperature of 1100 °C (Fig. 1d) are characterized as type II isotherms. A type II isotherm is encountered when adsorption occurs onto a low porosity material or on material with pore diameters mostly mesoporous. They also showed hysteresis on the desorption isotherm curve with a smaller desorption step. The most prominent changes of the adsorption–desorption isotherms were obtained from the non-doped boehmite sol, indicating the biggest changes of its porous structure after sintering at 1100 °C.

The cumulative pore volumes and the pore size distributions were computed from the desorption branch of the isotherms.

The pore size distribution profiles of the alumina samples obtained from pure and PEG-doped boehmite sols at calcination temperatures of 500–1200 °C are present in Fig. 2. With increasing calcination temperature, the mean pore size increased but the total pore volume decreased. The decrease in pore volume can be associated with $\approx 50\%$ volume shrinkage at 1200 °C, which essentially eliminates all porosity.¹⁹ The larger pore volume in alumina samples obtained from the boehmite sol doped with the large molecular weight PEG (molecule radius: 2.3 nm) was affected by the specific surface action of PEG molecules as alumina gel network modifiers, which after calcinations at 500 °C are burnt out, leaving some micro-cavities in the gel. Increasing the treatment temperature within the range from 500 to 700 °C did not cause any significant cumulative pore volume changes, but it caused a slight increase of the predominant pore diameter.

The specific surface areas, S_{BET} , were calculated by the BET method from nitrogen adsorption isotherms, using data up to $p/p_0 = 0.3$. The effects of the treatment temperature on the specific surface area for non-doped and PEG-doped alumina samples are given in Table II.

The specific surface area decreased approximately linearly with increasing treatment temperature up to *cca* 1000 °C. Thermal treatment of the non-doped alumina sample at 1100 and 1200 °C caused a considerable decrease of its specific surface area to a value of 20 and 10 m² g⁻¹, respectively. The alumina obtained from the PEG-doped boehmite sol retained a surface area of 65 m² g⁻¹ after thermal treatment at 1100 °C for 5 h, but treatment at 1200 °C reduced its surface area to 15 m² g⁻¹.

The changes in the porous structure were accompanied by phase transformation of the γ - Al_2O_3 . At higher temperatures (1100 °C), the formation of larger pores due to the collapse of the pores with shrinkage of the material structure resulted in a large increase in the crystallite size and a decrease of the surface area and pore volume. This means that the rapid collapse of the fine mesoporous structure started as conversion to the stable α - Al_2O_3 phase, which is at a temperature of 1100 °C. The transformation into the α - Al_2O_3 occurred at calcination temperatures higher than 1000 °C.^{19,20}

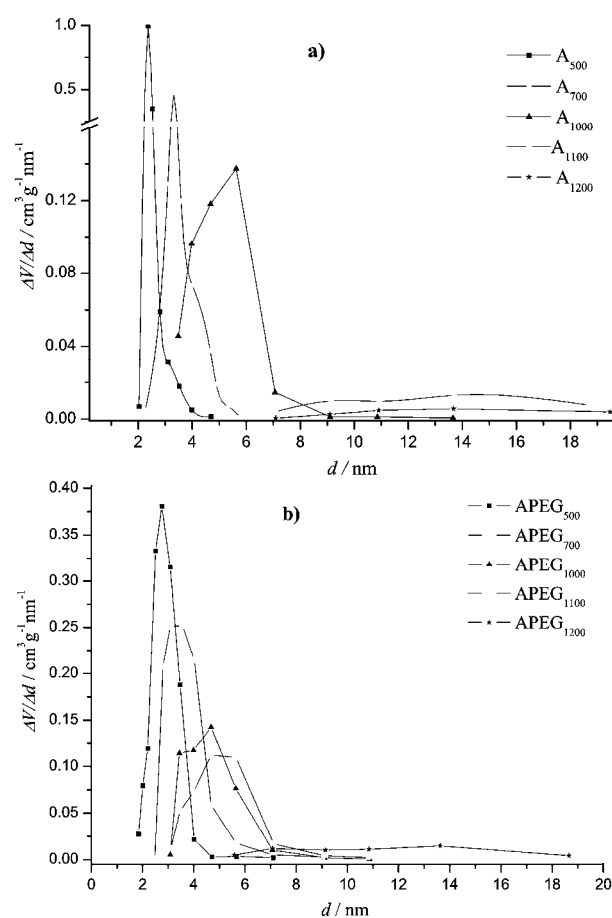


Fig. 2. Pore size distribution of (a) pure alumina and (b) PEG-doped alumina samples calcined at different temperatures.

The surface fractal dimensions, d , of the non-doped and PEG-doped alumina samples are also given in Table II. The experimental data fitted the model well with r^2 values greater than 0.99 for each fit, and the d values of the alumina samples were calculated from the nitrogen adsorption data, using the Mahnke and Mögel method. It was shown that the d values display very similar trends for

both alumina samples. For the non-doped alumina samples, increasing the calcination temperature from 500 to 700 °C resulted in an increase in the surface fractal dimension from 2.082 to 2.122. This is due to the pore formation mechanism in the aluminas, which caused higher surface roughness and more irregular surfaces. However, at 1000 °C, the surface fractal dimension of the non-doped alumina samples decreased to 2.048, which implies that larger pores were formed due to the collapse of the pores, which led to a decrease in the porosity. A similar trend was observed for the PEG doped aluminas.

TABLE II. Specific surface area and surface fractal dimension, d , of the non-doped and PEG-doped alumina samples

Sample	Calcinations temperature, °C	Specific surface area $\text{m}^2 \text{g}^{-1}$	Surface fractal dimension
Alumina	500	290	2.082
	700	230	2.122
	1000	102	2.048
	1100	20	2.387
	1200	10	2.323
PEG-doped alumina	500	295	2.040
	700	241	2.047
	1000	136	2.013
	1100	65	2.116
	1200	15	2.311

The sintering process at 1100 °C for the non-doped alumina and at 1200 °C for the PEG-doped alumina induced a restructuring phenomenon, which resulted in an increase of the mass fractal dimension of the alumina clusters; hence, there was a sharp increase of the surface fractal dimension in the alumina samples. The increasing in pore surface fractal dimension can also be associated with the appearance of new pores due to solubilization of the alumina constituents and to crystallization of the $\alpha\text{-Al}_2\text{O}_3$ phase inside the pores, which contributed to the irregularities of the alumina surface. According to the present analysis, the surface fractal dimensions of alumina were rather stable during calcination (until the appearance of the α -alumina phase).

Effect of amount of La(III)-added

The effect of different amounts of La(III) added to the PEG-doped boehmite sol on the surface areas and the pore volumes of the alumina samples calcined at 1000 °C temperature was studied. The complete N_2 adsorption-desorption isotherms of PEG-La(III)-doped alumina samples at calcined at a temperature of 1000 °C are shown in Fig. 3a.

The isotherms of all alumina samples exhibited type IV isotherms with a hysteresis loop of the H2 type. This means that all samples were porous and con-

tained mostly mesopore area. The pore size distributions of the PEG–La(III)-doped aluminas with different amount of doped lanthanum are shown in Fig. 3b. The pore size distribution profiles became narrower, the average pore size gradually decreased and the pore volume slightly increased with increasing amount of lanthanum. These results show that with increasing amount of lanthanum, the homogeneity of the distribution of the pores increased due to surface screening effects. This effect also leads to smoothening of the pore surface of the La(III)-modified aluminas. The value of surface fractal dimensions of PEG-aluminas doped with 0.015, 0.03 and 0.045 mol La(III)/mol Al(III) were 2.170, 2.137 and 2.133, respectively. It can be seen that, the surface fractal dimensions decreased with increasing amount of lanthanum added to the sol. This indicates that the pore surface of alumina became smoother and less irregular as the content of lanthanum particles increased. The smoothening of pore surface roughness was due to the blocking of the alumina pores by lanthanum particles.

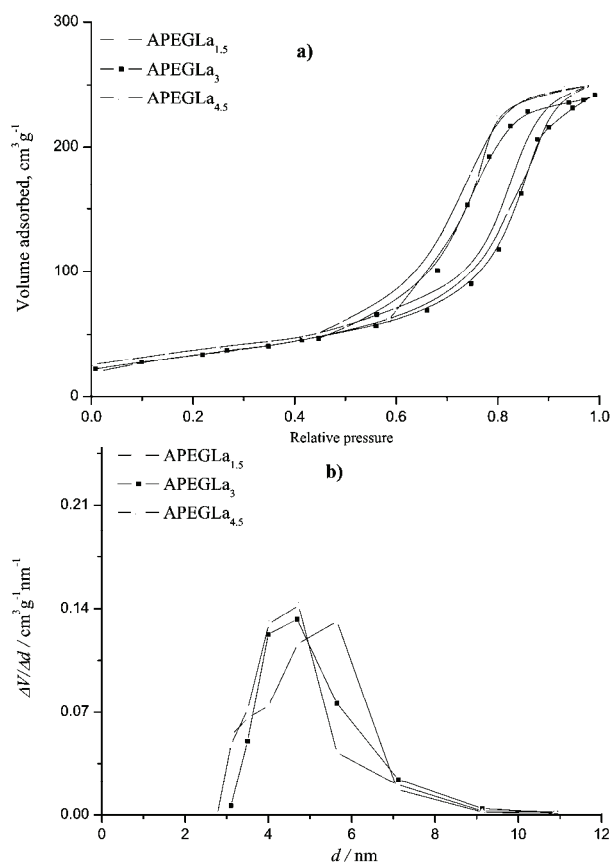


Fig. 3. Adsorption–desorption isotherms (a) and pore size distributions (b) of alumina samples doped with different amounts of lanthanum.

Synergism between poly(ethylene glycol) and La(III)-ion added in the aluminas

The influences of the calcination temperature on the specific surface area and surface fractal dimension for PEG–La(III)-doped aluminas with 0.03 mol La(III)/mol Al(III) are presented in Table III.

TABLE III. Specific surface area and surface fractal dimension for PEG–La(III)-doped aluminas (0.03 mol La(III)/mol Al(III))

Temperature, °C	Specific surface area, m ² g ⁻¹	Surface fractal dimension
500	235	2.068
700	207	2.084
1000	155	2.137
1100	115	2.178
1200	65	2.192

Increasing the calcination temperature from 500 to 1200 °C decreased the surface area and the pore volume of the alumina samples. The addition of La(III) to the boehmite sol inhibited the decrease of the surface area of the produced aluminas during its calcination at high temperatures. Increasing the temperature, especially in the range from 1000 to 1200 °C, decreased the surface area of the La(III)-doped aluminas less than the undoped ones (Table III). In accordance with this, the thermal treatment of La(III)-doped alumina samples at temperatures from 500 to 1200 °C caused a considerable increase in their surface fractal dimension from 2.068 to 2.192. These results were consistent with the deductions from the adsorption isotherms and the pore size distribution analysis. The surface fractal dimension as well as the pore connectivity did not change significantly during thermal treatment until the formation of crystalline α -Al₂O₃ commenced.

Hence, the addition of lanthanum to the boehmite sol in an atomic ratio of 0.03 La(III)/Al(III) can raise the temperature of the phase transformation to α -Al₂O₃ to above 1200 °C. If the most likely nucleation and growth mechanism for the phase transformation to α -Al₂O₃ is assumed, the obtained results indicates that the presence of La(III)-ions on the surface of the alumina crystallites reduce the nucleation of α -Al₂O₃, thus raising the phase transformation temperature.

CONCLUSIONS

Porous, high surface area, active alumina samples, pure and doped with PEG or PEG+La(III) ions, were obtained by the sol–gel process. The influence of calcination temperature, organic additive and different amounts of lanthanum on the mesoporous structure and surface fractal dimension was investigated using the Mahnke and Mögel model. The calcination temperature induces a change of pore surface roughness of the porous materials. The surface fractal dimension of pure and PEG-doped alumina samples increased slightly on increasing the calcination temperature from 500 to 700 °C and then decreased at 1000 °C for the pure alu-

mina, *i.e.*, 1100 °C for the PEG-doped alumina. This phenomenon can be explained by the deformation mechanism of the pore size. When the calcinations temperature increases, the average pore size increases and the pore volume decrease due to volume shrinkage, which eliminates some of the smaller pores.

The addition of La(III) to the boehmite sol inhibits the surface area loss of the produced aluminas during its calcination at high temperatures. Thermal treatment of La(III)-doped alumina samples at a temperature from 500 to 1200 °C caused a considerable increase in the surface fractal dimension of the samples from 2.068 to 2.192. The surface fractal dimension as well as the pore connectivity did not change significantly during the thermal treatment until the formation of crystalline α -Al₂O₃.

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ИЗВОД

ФРАКТАЛНА АНАЛИЗА ПОВРШИНЕ МЕЗОПОРОЗНОГ АЛУМИНИЈУМ(III)-ОКСИДА СА ДОДАТКОМ PEG И La(III) ДОБИЈЕНОГ СОЛ-ГЕЛ ПОСТУПКОМ

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Активни порозни алуминијум-оксид добијен сол-гел методом је термички обрађен на повишеним температурама у интервалу од 500 до 1200 °C. Испитиван је утицај температуре термичке обраде и додатка полиетилен гликола (PEG) и La(III) јона на специфичну површину, запремину пора и пречник пора, као и фракталну димензију површине активiranог алуминијум-оксида. На основу података из адсорпционо–десорпционих изотерми азота одређен је тип пора и израчунате су вредности основних параметара текстуалних својстава узорака. Пораст температуре термичке обраде проузроковао је смањење специфичне површине са 280 на 65 m² g⁻¹, запремине пора са 0,45 на 0,27 cm³ g⁻¹, пораст преовлађујућег пречника пора од 3 до 6 nm и пораст фракталне димензије површине од 2,068 до 2,192. Добијени бемитни сол са додатком PEG и La(III) јона може се искористити као прекурсорска дисперзија при спреј-пиролитичкој методи синтезе алуминијум оксидних превлака на носачу од нерђајућег челика.

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