

Synthesis of Tailored Porosity Materials Using the Sol-Gel Method

Z. Ecsedi

"Politehnica" University of Timisoara, Faculty of Industrial Chemistry and Environmental Engineering,
P-ta Victoriei No.2, 300006 Timisoara, Romania, E-mail: zoltan.ecsedi@chim.upt.ro

Abstract: This paper summarizes the study about producing ceramic materials with tailored nanoporous structure, as thin films, nonsupported membranes and as bulk gel. The ceramic materials were prepared by the sol-gel method using alkoxide precursors especially based on hydrolysis and condensation reaction of the aluminium triisopropylate. The optimal processing, drying and firing conditions for obtaining tailored porosity materials have been established. The influence of different way of nitric acid addition on the sol-gel process, the thermal behaviour of materials and also the effect of different polyvinyl alcohol (PVA) contents at different calcination temperatures on the characteristics of the prepared materials were investigated.

Keywords: Al₂O₃, sol-gel process, ceramic film, mesoporous alumina, polyvinyl alcohol template

1. Introduction

As consequence of the rapid development of high technology industries, in the last years the production of homogeneous and nanoscale ordered structure materials with accurate shapes and dimensions become a priority for research and industry. The current preoccupations in the field of sol-gel synthesis implementation in technology are multiple because of its advantages in the production of materials with tailored properties [1].

The main advantages of the sol-gel synthesis are the possibilities to obtain well shaped materials with designed texture and composition at low processing temperatures. The designed texture achieved by tailoring the gel porosity allows the synthesis of materials with high specific surface area and ordered pores used for production of membranes, insulators, sensors and antireflective coatings [1-6]. The most important application of the sol-gel process is the production of ceramic membranes, films and coatings due to its advantages like thermal stability, chemical stability and the possibility to be cleaned and sterilized at high temperature. Comparative with the production of membranes and films using conventional synthesis methods, the sol-gel process requires just a few and cheap equipments and allows the control of synthesis conditions which leads to the production of a wide range of porous materials, with small pores ($d < 0.4$ nm) and high specific surface area ($S_{\text{BET}} > 250$ m²/g), or dense ceramic products [1,2,5,6].

The textural properties of sol-gel derived ceramic materials can be improved with the addition of different type of porosity control additives. The most used porosity control technique is the addition of some organic polymer solutions especially polyvinyl alcohol (PVA) to the colloidal precursor solution because this lead to the

achievement of a very good homogeneity of the resulted condensation product and PVA gel [1,3,4].

2. Experimental

Alumina colloidal precursor solution was synthesized by sol-gel method, using aluminium triisopropylate (Al(OⁱC₃H₇)₃) (Merck), isopropanol (Chimopar), distilled water, nitric acid (Riedel-de Haën) and different types of alcohols and PVA - polyvinyl alcohol (Moviol 10-98). For the sol preparation, different recipes were tested, using an experimental installation built with a glass flask, having attached water cooled refrigerator, mixer and thermometer.

The synthesis temperature was kept constant at 80 °C using a thermostated oil bath. The turbulent state of the reaction liquid was achieved using a blade mixer adjusted to 500 rpm. Nitric acid (HNO₃ 65 %) was used as peptization agent to yield a stable sol. Different proportion of polyvinyl alcohol water solution was added into the sol. A highly condensed product is achieved after the slowly evaporation of the alcohol and water in open air, at the temperatures up to 90 °C, until increasing of viscosity is observed. When the sol achieves the desired viscosity, it was deposited as a thin film into Petri dishes and as bulk gel in capsules where gelation takes place. The formed product has been dried 24 hours in normal conditions at room temperature, followed by 4 hours at 90 °C in a drying stove, than annealed at different temperatures in the range of 500-1000 °C.

The thermal behavior of the samples during heating was studied by thermal analyses using „Mettler STAR SW 9” derivatograph. The pore size distribution, pore volume (BJH method), average pore size and surface area (BET method) were determined by nitrogen adsorption and desorption porosimetry (Quantachrome instruments “NOVA 2200”).

3. Results and discussion

3.1. The influence of HNO₃ addition to the stability of sols and rheology of gels

The nitric acid behaves as peptization agent, catalyst, and pH regulator. The acid dissolves a part of the aluminium hydroxide precipitate and provides acid pH inducing acid-catalyzed hydrolysis and condensation mechanisms by nucleophilic substitution. At low amount of acid, above 6-7 pH range, the condensation reactions are slowly and at higher amount than 3 moles acid to 1 mol hydroxide, the aluminium hydroxide is being transformed into Al(NO₃)₃. According to the tested recipes, transparent and stable sols are achieved using 0.5-1 moles of acid to one mole of hydroxide in the pH range 3.5-4.5.

Three different way of nitric acid addition to the sol-gel process were tested:

- addition to the hydrolysis water;
- addition to the colloidal precursor solution;
- 7 steps addition to the colloidal precursor solution.

When the hydrolysis of aluminium triisopropylate, (previously diluted with isopropanol) takes place with distilled water, without catalyst, opaque unstable aluminium hydroxide colloidal solution with pH = 8-8.5 is obtained. After evaporation and drying, poorly condensed aluminium hydroxide gel and amorphous AlO(OH) type oxide hydroxide are obtained.

a) When the sol is prepared adding 1 mole nitric acid in 200 mole distilled water for 1 mole of aluminium triisopropylate, (previously diluted with isopropanol) the hydrolysis take place initially at pH = 2.5-3.0 and after the aluminium hydroxide formation the pH is increasing to 4.0-4.5. After evaporation, a stable slightly opaque sol are obtained, which due to the condensation processes is transformed ($t_{\text{gelation}} = 24$ hours) in gel with pH = 4-4.5. Thermal analysis (Fig.1.) prevails endothermic dehydration process in the range of 50-150°C, followed by exothermic combustion of the organic compounds in range of 150-250°C. When the temperature is increasing in range of 250-500°C the degradation of gel and formation of boehmite takes place.

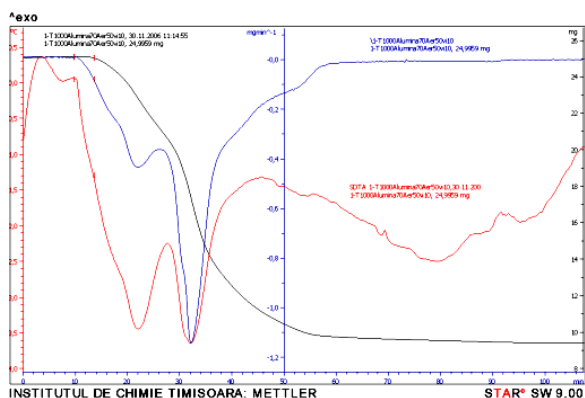


Figure 1. Thermal analysis of dried gel prepared with the nitric acid addition to the hydrolysis water.

The total loss of weight was 62.54% up to 500°C; at higher temperature the polymorphic transformations of boehmite take place without any further weight loss. The polymorphic transformations of boehmite are:
boehmit \rightarrow γ -Al₂O₃ \rightarrow δ -Al₂O₃ \rightarrow θ -Al₂O₃ \rightarrow α -Al₂O₃.

b) When the sol is prepared adding 1 mole nitric acid into the colloidal solution, prepared with 200 mole distilled water/mole of aluminium triisopropylate, (previously diluted with isopropanol), the hydrolysis take place initially at neutral pH, than due to the aluminium hydroxide formation, the pH is increasing up to 7-7.5 and after the nitric acid addition the pH is decreasing to 2.5-3, followed by a slowly increase of the pH due to the hydrolysis process up to 4-4.5. After evaporation, a transparent and stable sol is obtained which, due to the condensation processes is transformed ($t_{\text{gelation}} = 12-15$ minutes) in gel with pH = 4-4.5. Thermal analysis (Fig.2.) prevails endothermic dehydration process in the range of 50-170°C, followed by exothermic combustion of the organic compounds in range of 170-200°C. When the temperatures is increasing in range of 250-500°C the degradation of gel and formation of boehmite takes place. The total loss of weight was 58.20% up to 500°C; at higher temperature the polymorphic transformations of boehmite take place without any further weight loss.

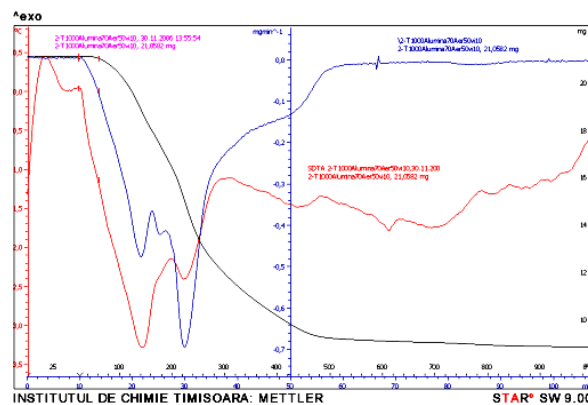


Figure 2. Thermal analysis of dried gel prepared with the nitric acid addition to the colloidal precursor solution.

c) When the sol is prepared adding 1 mole nitric acid in 7 steps into the colloidal solution, prepared with 200 mole distilled water/mole of aluminium triisopropylate, (previously diluted with isopropanol), the hydrolysis takes place initially at neutral pH than due to the aluminium hydroxide formation and the nitric acid addition (step by step) the hydrolysis process takes place at almost constant pH around to 3-3.5 in the first 70 minutes until the whole acid is added, after that the pH is increasing due to the hydrolysis process up to 4-4.5. After evaporation, a transparent and stable sol is obtained which, due to the condensation processes is transformed ($t_{\text{gelation}} = 2-4$ minutes) in gel with pH = 4-4.5. Thermal analysis (Fig.3.) prevails endothermic dehydration process in the range of 50-150°C, followed by exothermic combustion of the organic compounds in range of 150-220°C. When the temperature is increasing in range of 220-500°C the degradation of gel

and formation of boehmite takes place. The total loss of weight was 57.47% up to 500 °C; at higher temperature the polymorphic transformations of boehmite take place without any further weight loss.

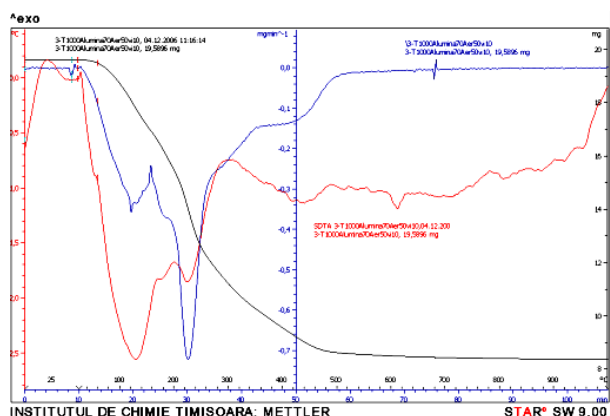


Figure 3. Thermal analysis of dried gel prepared with the 7 steps nitric acid addition to the colloidal precursor solution.

The obtained experimental results according to the thermal analyses of the dried gels, (prepared and dried in same conditions) prepared by different way of nitric acid addition prove that, the way of nitric acid addition and the pH of the solution have a considerable effect on the hydrolysis and condensation processes of aluminium triisopropylate precursor. The best results were obtained for the step by step addition of the acid when the gelation times (t_{gelatin}) are shorter and the rheological properties of the obtained gel are suitable for production of porous materials especially as thin films.

3.2. The effect of the polyvinyl alcohol addition

The addition of polyvinyl alcohol (PVA) to the sol was made when the increasing of viscosity, resulting through the progress of condensation processes, was observed. The gelation point is achieved through condensation (at which no flow is observed in a 45° sloped vessel) during evaporations, at temperatures up to 90 °C, in the presence of PVA. Higher evaporation temperatures have as result the degradation of PVA, which changes its color into dark brown.

The addition of polyvinyl alcohol has multiple effects on the films producing processes: at the drying processes, the addition of PVA decreases the cracking tendency, conferring porosity and elasticity to the film; during the structure consolidation heat treatment, the decomposing of PVA leaves empty spaces in the film structure, providing the increase of porosity.

Using PVA, crack-free Al_2O_3 films were obtained, with different thickness in the range of 20-40 μm . By contrast, macro- and microcracks were present in the reference sample prepared without the addition of PVA. The continuity of the film and the lack of the micro-cracks were examined using optical microscopy (Fig.4) on the film prepared with and without PVA.

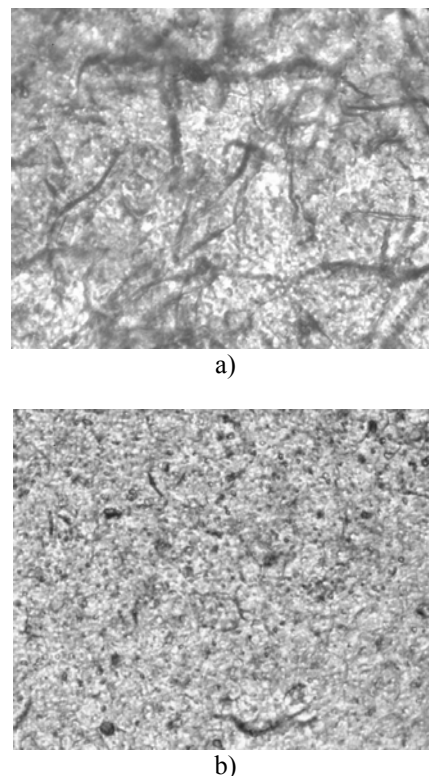


Figure 4. Optical microscopy images (400x) of Al_2O_3 ceramic films obtained at 500 °C without APV (a), respectively with APV addition (b).

It is suggested that the PVA template could be present in the form of oligomers or polymers and play a significant role in the mesoporosity formation.

Using different PVA contents at different Al_2O_3 /PVA weight ratio in the range of 2,5/1,25-2,5/3,75; mesoporous films with adjustable texture are obtained. The mesoporous structure of the obtained alumina films has been confirmed by nitrogen adsorption-desorption. The samples present type IV isotherm (definition by IUPAC), which is characteristic for mesoporous materials. The physisorption measurements reveal a pore size distribution in the range of 3.2-9.4 nm for the films annealed at 800 °C, respectively 11.4-22.8 nm at 1000 °C. The experimental results are presented in table 1.

TABLE 1. Characteristics of the mesoporous alumina films.

PVA content [g] / temperature [°C]	D_p (Adsorption) [Å]	D_p (Desorption) [Å]	S_{BET} m^2/g	V_p cm^3/g
3,75/1000	170,9647	114,6627	46,39	0,2001
1,845/1000	169,7018 – 228,4839	139,8664	51,34	0,2233
1,25/1000	167,1104 – 229,3743	140,4838	33,76	0,1803
3,75/800	65,8943	53,8228	168,1	0,2772
1,845/800	94,2389	66,1437	164,5	0,3287
1,25/800	32,6757 – 72,2790	35,0685 – 74,5373	135,1	0,2322

4. Conclusions

Step by step addition of HNO₃ leads to shorter gelling times. The nitric acid behaves as peptization agent, catalyst, and pH regulator. The acid dissolves a part of the aluminium hydroxide precipitate and provides acid pH inducing acid-catalyzed hydrolysis and condensation mechanisms.

The obtained results prove the possibility of producing mesoporous crack-free Al₂O₃ ceramic films, with average pore dimensions in the range of 3.2-22.9 nm and specific surface area 33.7-168.1 m²/g at temperature in range of 800-1000°C. The specific surface area and pore sizes can be tailored by the use of different amount of PVA and annealing the films at different temperatures.

The obtained bulk alumina aerogel exhibit a foamy texture which after annealing at 1000°C is transformed in highly porous Al₂O₃ with 0,06-0,08 g/cm³ bulk density.

ACKNOWLEDGEMENTS

Some of these results were attained with the financial support of Scientific Authority MATNANTEC, contract CEEX No.51/2006.

REFERENCES

1. Lazău I., Păcurariu C., Ecsedi Z., Ianoș R., Metode neconvenționale utilizate în sinteza compușilor oxidici, Ed. Politehnica, Timișoara, **2006**.
2. Brinker C.J., Scherer G.W. – The Physics and Chemistry of Sol-Gel Processing, Academic Press, New York, **1989**.
3. Ecsedi Z., Toth A., Gagea L. – Alumina Films Prepared by Sol-Gel Method with Applications in Separation Processes, Proc. Romanian International Conference on Chemistry and Chemical Engineering, Bucharest, vol. 1, (S.08), Ed. Printech, **2005**, pp.248-255.
4. Ecsedi Z., Lazău I., Păcurariu C. – Alumina Films with Induced Porosity Prepared by Sol-Gel Method, Proceedings "The Sixth Students' Meeting-SM-2005, School of Ceramics" Dec. 1-2, Novi Sad, Serbia and Montenegro, **2005**, pp.49-52.
5. Dislich H., Pettit R.B., Ashley C.S., Reed S.T., Brinker C.J. – Sol-gel technology for thin films, fibers, preforms, electronics and specialty shapes, Edited by Klein L.C., Noyes Publications, New Jersey, **1988**.
6. Wachtman J.B., Haber R.A. – Ceramic films and coatings, Noyes Publications, New Jersey, **1993**.