비알콕사이드계 솔-젤 공정을 이용한 고표면적 알루미나 에어로젤의 합성

Minh Tuan Nguyen, 박태진, 서동진
한국과학기술연구원 청정기술연구센터

Synthesis of high-surface-area alumina aerogels by non-alkoxide sol-gel process

Minh Tuan Nguyen, Tae-Jin Park and Dong Jin Suh
Clean Technology Research Center, Korean Institute of Science and Technology, P.O. Box 131,
Cheongryang, Seoul 136-791, Korea

1. Introduction

Aerogels show promise in catalytic applications due to their morphological and chemical properties [1,2]. Alumina, one of the most widely used catalyst supports was prepared in the form of aerogel by non-alkoxide sol-gel process from aluminum chloride in ethanol solution and then the supercritical removal of the solvent. Transparent monolithic alumina gels were obtained from precursors of aluminum chloride hexahydrate, ethanol, water and propylene oxide at room temperature. The highly mesoporous alumina aerogel prepared by the subsequent carbon dioxide supercritical drying had a surface area in excess of 700 m^2/g. The surface area decreased with heat treatment but remained at relatively high value of over 200 m^2/g after calcined at 1000^0C. This method has been extended to the preparation of nikel-alumina aerogel catalysts.

2. Experimental procedure

Aluminum chloride hexahydrate *(Junsei Chemical)* was first dissolved in pure ethanol *(99%, Merck)* and distilled water. After mixing for 1 hour at room temperature, nitric acid *(99%, Aldrich)* was added for the pH adjustment. Propylene oxide, as a gelation promoter in the sol-gel synthesis [3], was added to the solution mixed for 1 hour after the previous addition. Gel formation usually occurred within 5 minutes. The procedure for the preparation of alumina aerogels is illustrated in Figure 1 and is summarized in Table 1 the sol-gel parameters that are optimal for obtaining high surface-area aerogel.

The wet gel was aged for 72 hours and then dried by flowing supercritical carbon dioxide in a supercritical extraction system at 333 K and 24 MPa, standard supercritical drying conditions of our laboratory.

Table 1. Sol-gel parameters used to prepared the alumina alcogels

Reagent	Aluminum chloride hexahydrate	Ethanol	Water	Propylene oxide	Nitric Acid
Mole ratio	1	25	3	5	0.076

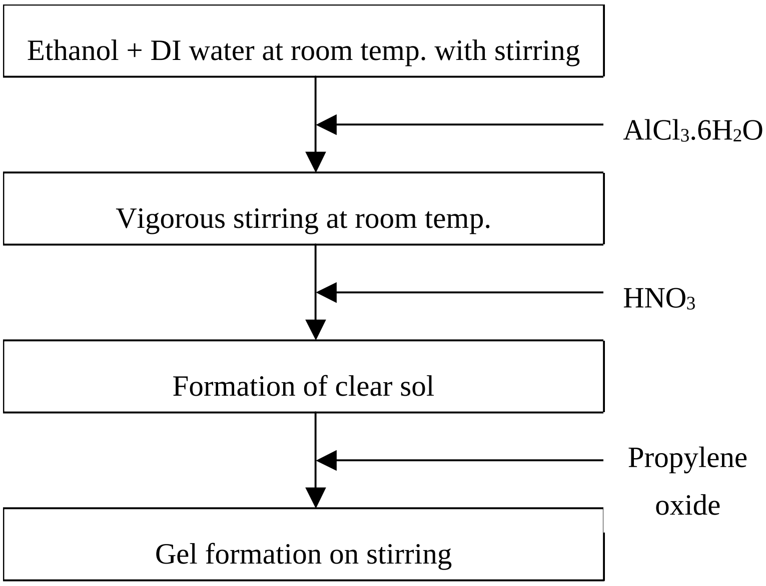

Figure 1. Non-alkoxide sol-gel process for alumina aerogel synthesis.

The product aerogel was heated in a tube furnace in flowing helium at 573 K for 2 hours and then in oxygen at 773 K for 2 hours according to our standard calcination procedure.

An alumina xerogel, for comparison, was prepared by drying the wet gel prepared under the same sol-gel conditions at room temperature for 48 hours and in a vacuum oven at 353 K for 24 hours.

BET surface areas, pore volumes and pore size distributions were measured by nitrogen adsorption – desorption at 77 K using a Micromeritics ASAP 2000 instrument. The mesopore size distributions were calculated applying the Barrett-Joyner-Halenda method to the desorption branch of the isotherm. Prior to the measurement, all samples were outgassed at 383 K overnight.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) investigations were performed using a heating rate of 5^0C / min under nitrogen and air flowing.

3. Results

The alumina gel prepared from the composition in Table 1 exhibited dimensional changes by syneresis phenomena resulted in the exudation of fluid onto the surface and shrinkage in gel structure. However, these phenomena completed after 72-hour aging and the amount of exudate does not exceed 65% of total solvent. After analyzing the amount of alumina precursor in exudates, we could affirm that metal component lost by syneresis phenomena was negligible (<1%).

Table 2. Textural properties of the alumina aerogel and xerogel samples before and after heat treatment at different temperature [S_{BET}, surface area *(m^2/g)*; V_P, total pore volume *(cc/g)*; D_P, average pore diameter *(nm)*]

Heat treatment (K)	**Alumina *Aerogel***			**Alumina *Xerogel***		
	S_{BET}	V_P	D_P	S_{BET}	V_P	D_P
383 – vacuum - overnight	795	4.2	21.6	325	0.31	3.8
573 – He – 2 hrs	755	4.1	21.8	416	0.41	4.0
773 – O_2 – 2 hrs	723	3.5	22.4	359	0.48	5.4
1073 – O_2 – 2 hrs	514	2.9	22.7	211	0.43	8.2
1173– O_2 – 2 hrs	390	2.2	22.8	169	0.39	9.2
1273 – O_2 – 2 hrs	247	1.2	19.1	119	0.32	10.8

Table 2 summarizes the surface areas, pore volumes and average pore sizes of our alumina aerogel and xerogel samples. In general, aerogel samples after calcination at 773 K have surface areas of above 700 m^2/g, which are greater than those of commercial samples and even alumina aerogels prepared by the fast sol-gel synthetic route using alkoxide [4]. All of aerogel samples treated at different temperatures maintained mesoporosity in the range of 19 – 23 nm and the corresponding pore size distribution curves became smaller. The pore volume and average pore diameter of the xerogel sample are significantly smaller than those of the aerogel samples. However, both aerogel and xerogel samples maintained relatively high surface area of over 200 m^2/g and over 100 m^2 /g, respectively, even after additional heat treatment at 1273 K.

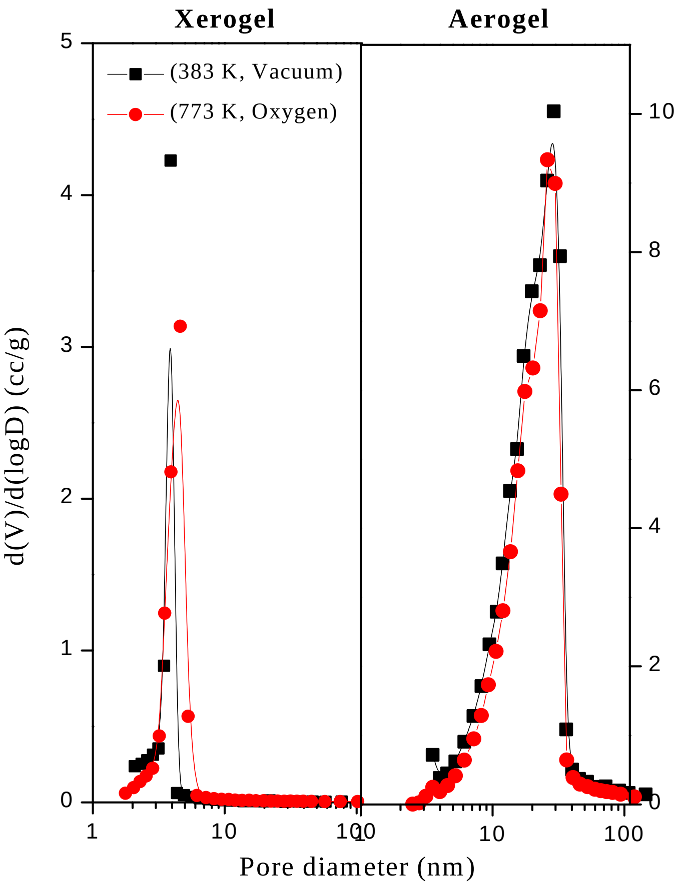

Figure 2. Pore size distributions of the alumina xerogel and aerogel samples before and after calcination at 773 K for 2h.

4. Discussion

The different textural characteristics between aerogel and xerogel samples are most likely due to the different processing conditions each was subjected to. The evaporation of the ethanol from the xerogel sample exerted substantial capillary forces on the gel's pore structure, which resulted in shrinkage of the pores, relative to the aerogel sample.

Additional heat treatment up to 1273 K did not radically change the textural characteristics of the calcined alumina aerogel. These results suggest that our alumina aerogel has the inherently rigid porous network structure of the polymeric gels. In the case of the xerogel, the increase of the surface area and pore volume, after calcinations at 723 K, was a result of the removal of organic residues from micro-mesopores, rendering the surface accessible for the physical adsorption of nitrogen at 77 K. However, the surface area and pore volume of the calcined xerogel decreased after heat treatment at 773 K. This is probably due to the exothermic phase transformation process evidenced by X-ray diffraction (XRD) and thermal analysis.

Thermal analysis performed in air flowing at a heating rate of 5^0C /min showed exothermic peak within 150-200^{0}C for both xerogel and aerogel and could be attributed to the decomposition of residual organics. On the basis of XRD shown in Figure 3, the calcined alumina xerogel and aerogel samples remained amourphous up to 500^{0}C and 800^{0}C, respectively, and contained a more ordered transition alumina phase, likely γ-alumina, after further heat treatments. However, the XRD peaks of the aerogel were not only broader and weaker but also were growing slowly than those of the xerogel, indicating the relatively retarded phase transformation for the aerogel.

The pronounced mesoporosity and high surface area of alumina aerogel prepared by non-alkoxide sol-gel process combined with its thermal stability, renders it a promising catalyst support for use in various reactions. The further improvement for higher surface area – thermal stability of alumina aerogels and their catalytic applications are currently being investigated in our laboratory.

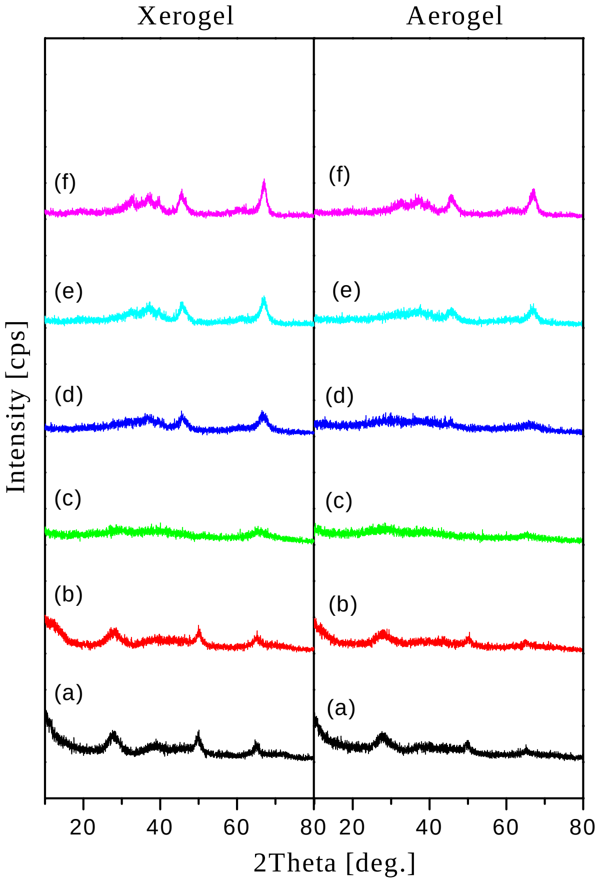

Figure 3. X-ray diffraction patterns of alumina xerogel and aerogel samples before and after heat treatment at different temperatures: (a) as prepared; (b) 573 K; (c) 773 K; (d) 1073 K; (e) 1173 K; (f) 1273 K.

References

[1] M.Schneider and A.Baiker, Catal. Rev. Sci. Eng., 31 (1995) 515.

[2] G. M. Pajonk, Catal. Today, 35 (1997) 319.

[3] A. E. Gash, T. M. Tillotson, J. H. Satcher Jr., L. W. Hrubesh and R. L. Simpson, J. Non-Cryst. Solids, 285 (2001) 22.

[4] D. J. Suh, T.-J. Park, J.-H. Kim, and K.-L. Kim, Chem. Mater., 9 (1997) 903.