

PREPARATION AND CHARACTERIZATION OF POROUS ALUMINA-TITANIA AEROGEL VIA CO₂ SUPERCRITICAL EXTRACTION

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ABSTRACT

Porous aerogel of titania-alumina were prepared by hydrolysis of metal alkoxides and supercritical extraction of the solvent. Monolithic wet-gel of 0.2TiO₂-0.8Al₂O₃, prepared by hydrolysis of metal alkoxides in alcoholic solutions, and the solvent in wet gel was supercritically extracted in CO₂ at 60°C and 24Mpa for 2h. Thermal evolutions of the microstructure of the gel were evaluated by differential thermal analysis (TG-DTA), N₂ adsorption, scanning electron microscopy and X-ray diffractometer. After calcination at 500°C, the specific surface area of the gel was more than 400m²g⁻¹. The average pore radius of aerogel, about 8nm, was about 50% of that for alumina aerogel, but about 4 times larger than that of the xerogel. The specific surface area of the aerogel was more than 200m²g⁻¹ after calcination at 800°C. The pore size and pore volume of aerogel hardly decreased after calcinations at 800°C, although those values of the xerogel remarkably decreased after calcination up to 800°C. The thermal stability of the microstructure of porous titania-alumina is improved by supercritical extraction.

Keywords: Oxides, Sol-gel chemistry, X-ray diffraction, Infrared pectroscopy

INTRODUCTION

One of the most important applications of the sol-gel method can be found in the field of catalysis. The properties of catalysts and support materials strongly depend on the preparation procedures [1-6]. The high porosity and the large specific surface area of materials prepared by the sol-gel method make them very attractive from catalytic point of view. The sol-gel method does not only allow a good control of the characteristics of the support, but also offers the possibility of preparation of oxide-supported metal catalysts from a homogenous solution containing both of the metal precursor and the support precursor. Porous material as aerogels have a variety of application: as thermal insulators, filters, membrane, catalyst, catalyst support etc [7-9]. Aerogel are porous materials produced via sol-gel processing and supercritical drying. Aerogel have a low density, very high surface area and high pore volume [7-9].

TiO₂ ceramics are attractive materials for catalyst and support. However, the relatively low surface area and the poor stability of the structure at high temperatures are disadvantages.

Therefore, much attention has been paid to the applications of mixed oxides containing TiO₂. Al₂O₃ ceramics are more stable and have a large surface area but Al₂O₃-supported catalyst has poor sulfidation activity. The mixed oxides of TiO₂ and Al₂O₃ seem to be a good alternative to overcome the problems of the poor sulfidation activity of the Al₂O₃-supported catalyst and the low surface area of the TiO₂-supported catalysts. The high acidity of mixed oxides of TiO₂ and Al₂O₃ is generally attributed to the excess of negative or positive charge caused by the formation of hetero metal-oxygen bonds, -Ti-O-Al-, at low content of TiO₂ [2]. The acid amount at a certain acid strength per unit surface area of any binary oxide is larger than the sum of the acid amount of the component oxides [2]. The acid strength may affect the catalytic activity. The mixed oxides of TiO₂ and Al₂O₃ have been reported to be promising alternative supports for hidrosulfurization (HDS) catalysts [3-6, 10], since these oxides improve the catalytic activity for sulfur removal and the resistance to abrasion.

TiO₂-Al₂O₃ catalysts prepared by the sol-gel method are more homogeneous than those prepared by the co-precipitation or the hydrogel

kneading [10]. The $\text{TiO}_2\text{-Al}_2\text{O}_3$ prepared by the sol-gel method has higher surface area than the sol-gel derived Al_2O_3 and TiO_2 , hence the mixed gel is interesting as a catalytic support [11]. With the addition of 20 mol% TiO_2 to Al_2O_3 , the surface area increased, and it decreased when more TiO_2 was added [11]. On the other hand, Weissman, et al. [12] reported that titania-zirconia mixed aerogel with high concentration of titania was unstable.

In this study we report the synthesis and morphological of porous sol-gel derived alumina-titania aerogel were prepared by CO_2 supercritical extraction and characterized. The alumina-titania xerogel dried under an atmospheric pressure was also prepared for comparison.

EXPERIMENTAL PROCEDURE

Monolithic wet-gels of 0.2 TiO_2 - 0.8 Al_2O_3 were prepared by hydrolysis of aluminium-sec-butoxide, $\text{Al}(\text{OC}_4\text{H}_9^{\text{sec}})_3$ (ASB), and titanium-isopropoxide, $\text{Ti}(\text{OC}_3\text{H}_7^{\text{iso}})_4$ (TIP), in an n-propanol solution with acid catalyst. The molar ratios used for the synthesis were $[\text{H}_2\text{O}]/[\text{alkoxide}] = 2$, $[\text{HNO}_3]/[\text{alkoxide}] = 0.06$ and $[\text{n-propanol}]/[\text{alkoxide}] = 12$. Aluminium-sec-butoxide was firstly dissolved in n-propanol at 65°C with vigorous stirring and continuously stirred at 65°C . Then, the solution was cooled and TIP was added at room temperature, and stirred for one hour. After that, a mixture of the remaining n-propanol, H_2O and HNO_3 was added drop-wise under continuous stirring. The solution gelled after the addition of the last drop. The wet gel was dried at 90°C for overnight (Xerogel), or dried by flowing supercritical carbon dioxide in a supercritical extraction system at 60°C and 24Mpa for 2h (Aerogel).

Changes in the microstructure of the gels during heating were evaluated by thermogravimetry and differential thermal analysis (TG-DTA, Seiko Exstar 6000 TG/DTA 6200) and N_2 adsorption. TG-DTA measurements were carried out under air flow of 300ml min^{-1} with a heating rate of $10^\circ\text{C.min}^{-1}$. The specific surface area, pore size distribution, and pore volume of the dried and calcined gels were estimated by the Barret-Joyner-Halenda (BJH) method using N_2 adsorption-desorption curves (Quantachrome, Autosorb). The microstructure of the gels was observed by a scanning electron microscope (FESEM, Hitachi, and S-4700). The crystallization behaviors of the gels were observed by an X-ray diffractometer (Rigaku, RAD-C) after calcination at temperatures in the range from 500 to 1000°C . The surface acidity was evaluated by TPD of benzene (TPD-TPR 2900, Micromeritics).

RESULTS

TG-DTA profiles of dried aerogel and xerogel are given in Figs. 1 and 2. For the xerogel (Fig. 1), a broad endothermic peak with gradual weight losses around 80°C , a strong exothermic peak with a sharp weight loss about 20% at 200°C , and broad exothermic peaks with a gradual weight loss in the temperature range from 220°C to 600°C were observed. Beyond 600°C , the xerogel practically lost no more weight. Also small exothermic peaks about at 800°C and 1000°C without weight changes were observed. An endothermic peak with a weight loss at 80°C and a broad exothermic peak at 400°C with shoulders at 190 and 250°C , accompanied with weight losses, were observed for the aerogel (Fig. 2). Beyond 500°C , the aerogel practically lost no more weight. The small exothermic peaks about at 800 and 1000°C were also observed.

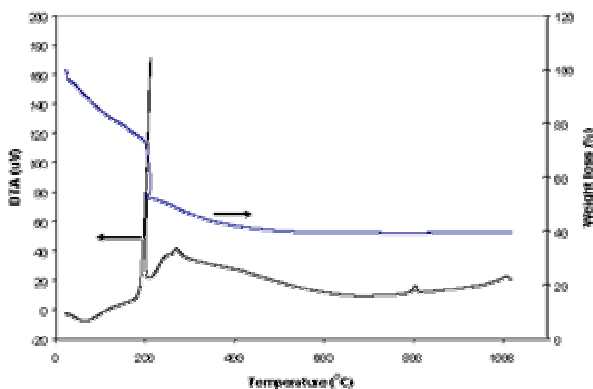


Fig. 1 TG-DTA pattern for the alumina-titania xerogel

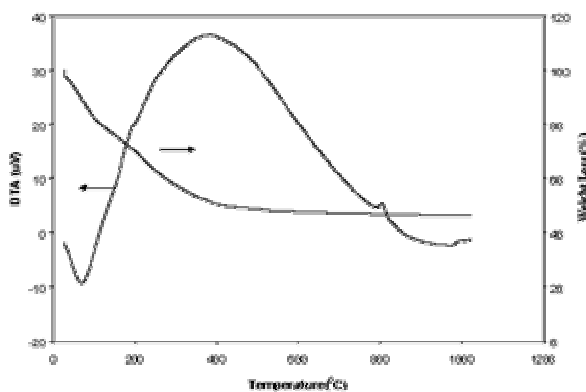


Fig. 2 TG-DTA pattern for the alumina-titania aerogel

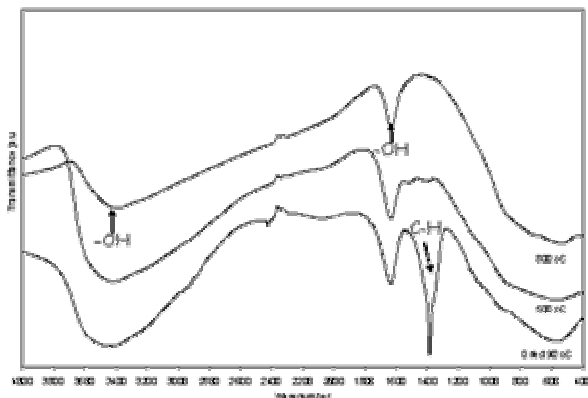


Fig. 3 IR spectra of an alumina-titania xerogel at different temperature

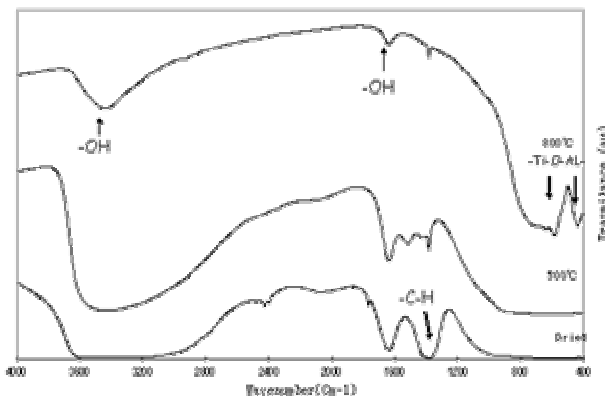


Fig. 4 IR spectra of the alumina-titania aerogel at different temperature

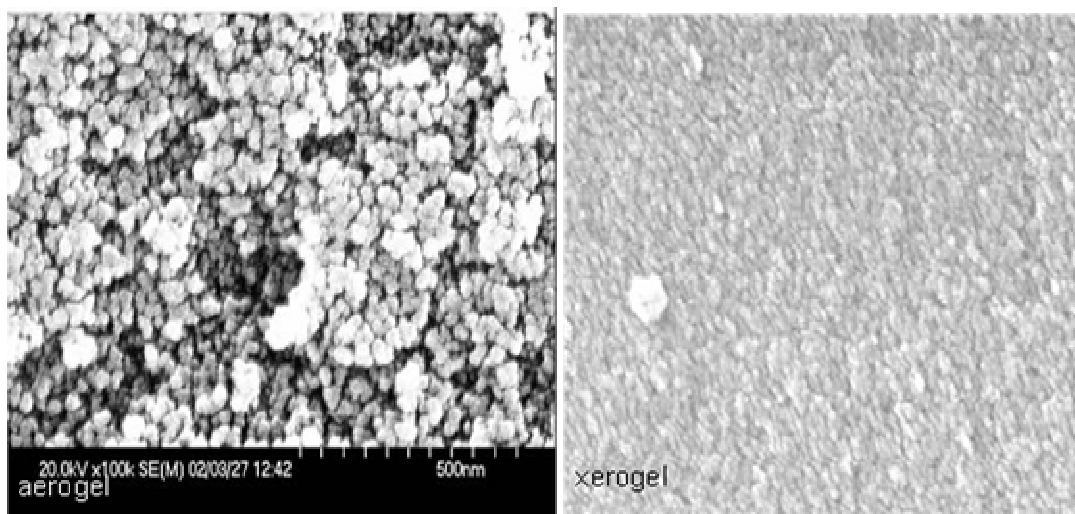


Fig. 5 SEM images of xerogel and aerogel after calcination at 500 °C.

Fig. 3 and Fig. 4 show the FT-IR spectra of the xerogel and aerogel after drying at 90°C, calcined at 500°C, and at 800°C in the range from 4000 cm^{-1} to 400 cm^{-1} . The broad absorption band around 3400 cm^{-1} for both samples indicates the OH group, whose origin is likely to be showed water and surface \equiv Ti-OH groups with H-bridging. After calcination at 800°C, the peaks at 3400 cm^{-1} and at 1636 cm^{-1} ascribed to OH group still existed and strong peaks at 583 and at 439 cm^{-1} , attributed to hetero metal-oxygen bonds of -Ti-O-Al-, were found.

After calcinations at 500 °C for 2h, the shape of the grain surface of alumina – titania xerogel is globular and grain diameter size is around 20nm by FESEM (Fig.5). The TiO₂ - Al₂O₃ aerogel are porous and their grain size is around 30 nm, is larger than that of the TiO₂ - Al₂O₃ xerogel. The shape of the grain and grain diameter size of alumina – titania did not change significantly after calcination up to 600 °C for 2 h (Fig.6). After

calcination at 800 °C for 2h, the grain size of aerogel a bit increases to be around 50 nm. After calcinations at 1000 °C for 2h, the size of grains were drastically increased, namely the shape of the grain surface of alumina – titania is cylindrical with length and diameter are around 200nm and 75nm, respectively (Fig.6). It is due to the grains of TiO₂ - Al₂O₃ were sintered.

A detailed study of the crystalline phases formed during the calcination process is of a great importance, because the nature of the crystalline phase can affect the catalytic behavior of the support. The both of the as-dried samples are amorphous (Fig.7). After calcination up to 750°C for 2h, the amorphous phases of both samples do not change. After calcination at 800°C for 2h, the diffraction peaks of rutile were found for both of the samples. Finally, after calcination at 1000°C for 2h, the rutile phase and α -alumina were observed. The diffraction peaks of anatase, θ - and γ -alumina phases were not found for both of it.

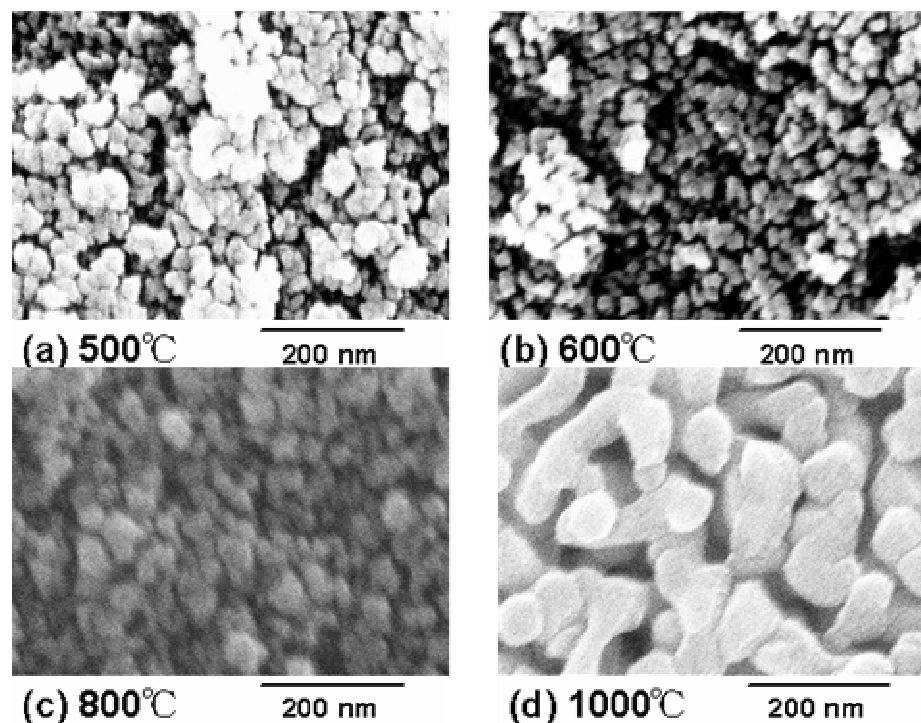


Fig. 6 SEM images of aerogel at different calcination temperatures

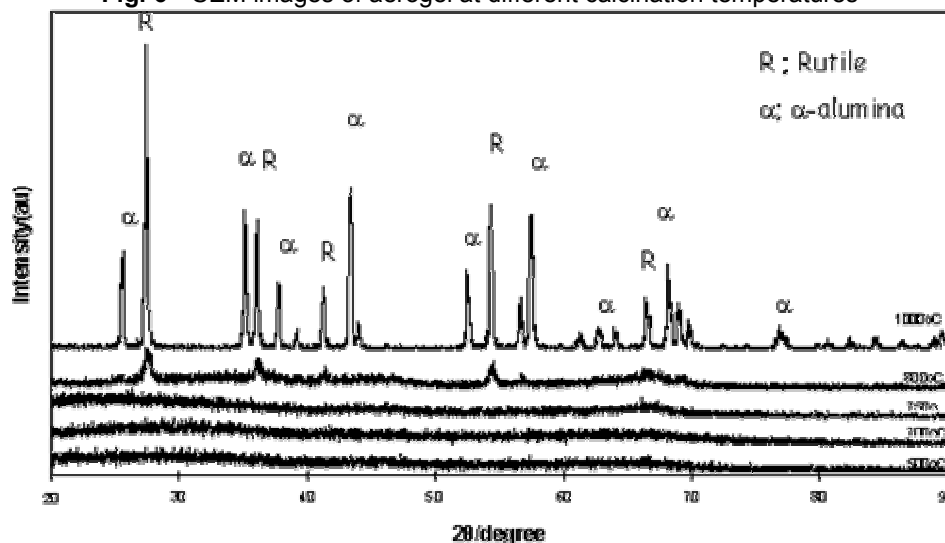


Fig. 7 XRD patterns of alumina-titania at different temperatures

Fig. 8 shows the effect of the supercritical extraction on specific surface area of the gels after calcination at various temperatures for 2h. The aerogel has larger specific surface area than the xerogel. The specific surface area decreased with increasing calcination temperature, but the surface area of the aerogel was more than 50% larger than that of the xerogel after calcinations at 800°C.

Fig. 9 shows the cumulative pore volume of the gels. The cumulative pore volume of the aerogel is larger than that of the xerogel. The pore volume of the aerogel decreases after calcination at 600°C for 2h, and does not change after calcination up to 800°C for 2h. In contrast, the pore volume of xerogel decreases about 50% after calcination at 800°C. After calcination at 1000°C for 2h, the pore volume of both samples is drastically decreased.

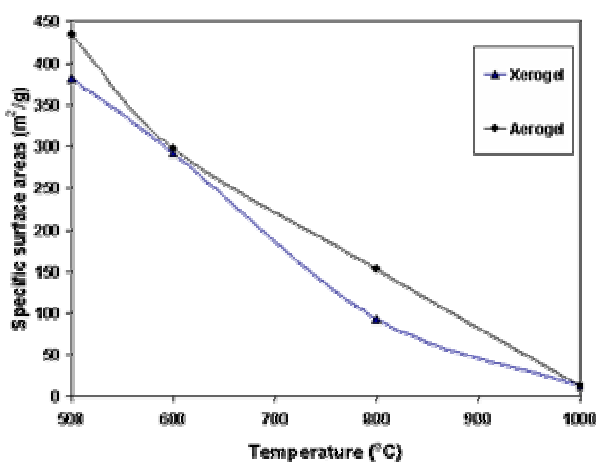


Fig. 8 Specific surface area of alumina-titania after calcination at different temperature

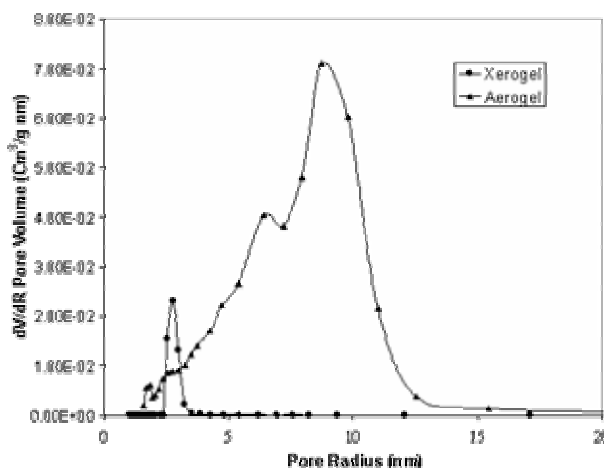


Fig. 10 Pore size distribution of titania-alumina after calcination at 800 °C

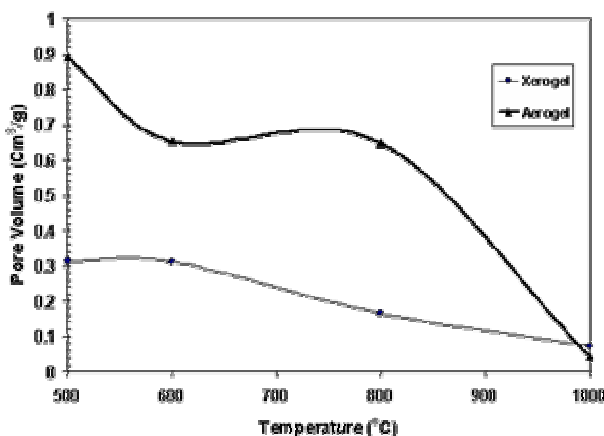


Fig. 9 Cumulative pore volume of alumina-titania after calcination at different temperature

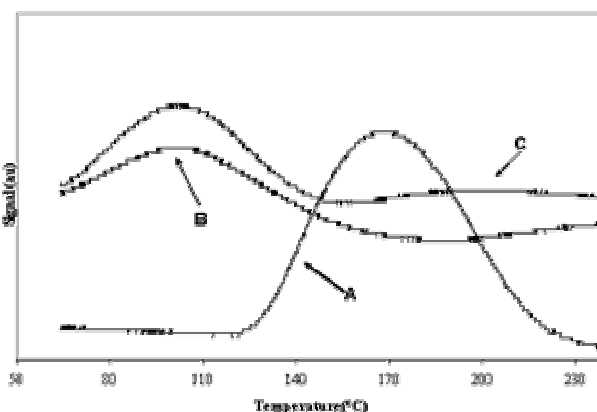


Fig. 11 C₆H₆-TPD curves of the calcined aerogel at 500 °C (A) TiO₂-Al₂O₃, (B) TiO₂ and (C) Al₂O₃

Figure 10 shows the effect of the supercritical extraction on the pore size distribution of alumina-titania gels after calcination at 800°C for 2h. The pore radius and pore volume of aerogel are bigger than the pore radius and pore volume of xerogel.

Measurement of acidity by temperature programmed desorption of benzene should also render information on the acid properties of the samples under study. Fig. 11 shown the effect of TiO₂ addition on Al₂O₃ in benzene desorption curves. The samples of alumina and titania after calcination at 500°C show the clear presence of peaks around at 105 °C, the peaks is mainly due to physisorbed C₆H₆, while the peak around at 170 °C of alumina -titania assigned to the presence of acidic centers. The effect of TiO₂ addition on Al₂O₃ in acidity comes stronger than that of alumina or titania.

DISCUSSION

The residual organics in the as-dried gels can be eliminated by heating up to 600°C. Endothermic peaks appeared around 80°C for all of the dried gels may be attributed to evaporation of water and n-propanol. Large exothermic peaks accompanied with weight losses at temperatures higher than 200°C may correspond to the combustion of the organic residues in the gels. The small exothermic peaks at 800°C and at 1000°C are attributed to the crystallization.

The broad exothermic peak of the xerogel and the aerogel around 400°C (Figs. 1 and 2) has almost the same height of peaks. Exothermic peaks at temperatures lower than 400°C are hardly found for the aerogel. It may be caused by the solvent (alcohol) that hardly remained in the aerogel. The solvent may be removed by the supercritical

extraction. The exothermic peak at 400°C is combustion of residual alkoxy group.

The presences of Ti-O and Al-O group were indicated by the presence of the strong, but broad peak between 400 and 900cm⁻¹. The dried samples indicated the presence of strong peak at 1636cm⁻¹, which also indicated that the -OH stretching mode originated from a high degree of surface hydroxylation. After calcination of sample at 800°C for 2h, the peaks at 3400cm⁻¹ for OH group and at 1636cm⁻¹ for stretching of -OH still existed and strong peaks at 583 and at 439cm⁻¹ for hetero metal-oxygen bonds of -Ti-O-Al-, were found. The mixed oxides of TiO₂ and Al₂O₃ has high acidity (Fig. 11) due to the formation of hetero metal-oxygen bonds, -Ti-O-Al-.

The small exothermic of peaks of both samples of xerogel and aerogel detected at the 800°C (Figs. 1 and 2) may be assigned to the direct crystallization of amorphous TiO₂ into rutile (Fig. 7). No anatase TiO₂ was observed for both samples of xerogel and aerogel. The DTA peak at 1000°C for both samples of xerogel and aerogel may be assigned to the direct crystallization of amorphous Al₂O₃ into α-Al₂O₃ (Fig. 7). No θ- and γ- Al₂O₃ were observed for both samples of xerogel and aerogel. Probably, diffraction peaks of anatase were not found because of the low TiO₂ content (0.2TiO₂), small amount of anatase, and small crystall size of anatase. Perhaps with the same reason, the intermediate phases of alumina (γ-, θ-, η-, etc) were not found. These results suggest that during the calcination, TiO₂ was segregated from the Al₂O₃ particles and formed nuclei of rutile, which then crystallized prior to formation of α-Al₂O₃. Therefore, the formation of rutile TiO₂ induces the formation of α-Al₂O₃.

The shape of the grain and its diameter size of alumina – titania a bit change after calcination up to 800 °C for 2 h (Fig.6), due to after calcining at that above temperature, the TiO₂ rutile was formed. After calcinations at 1000 °C for 2h, the size of grains were drastically increased, namely the shape of the grain's surface of alumina – titania is cylindrical with length and diameter are around 200nm and 75nm, respectively (Fig.6). It is due to the grains of TiO₂ - Al₂O₃ were sintered.

Specific surface area of the alumina-titania decreased with increasing temperature calcination (Fig.8). Although the preparation conditions have not been optimized for the highest surface area, the calcined alumina-titania aerogel at 500 °C has a surface area bigger than the xerogel, did not radically change the texture characteristics of the calcined alumina-titania aerogel. These results suggest that the alumina-titania aerogel obtained

from translucent bulk gels has the inherent rigid porous network structure of the polymeric gels. In the case of the xerogel, the increase of the surface area and pore volume, after calcination up to 500 °C, was a result of the removal of organic residues from microspores, rendering the surface accepted for the physical adsorption on nitrogen at 77K. It is remarkable, that calcination at 800°C did not change the pore volume of aerogel (Fig.9), even though after calcining at that above temperature, the TiO₂ rutile was formed (Fig.7). It indicated that the aerogels obtained from translucent gels had the rigid porous framework with better thermal stability; the pore volume of the alumina-titania aerogel did not change much as the sample was heated. It is also noted from Fig. 10 that the alumina-titania xerogel was exclusively microporous and had relatively poor thermal stability. After calcining at 1000°C the specific surface area and cumulative pore volume of both samples were drastically decreased. It does indicate that crystallization of the rutile titania and α-alumina phases were occurred (Fig.7). The thermal stability of porous ceramics may depend on the pore sizes. When pore sizes are very small, the gel can easily sinter and can be easily densified to result in smaller surface area. The supercritically dried aerogels with large pores are known to be more stable than the xerogels [13].

CONCLUSION

The porous TiO₂ - Al₂O₃ powders have been prepared by supercritical extraction using CO₂ method. We have obtained the following conclusion:

1. The porous powders with high porosity and large surface area can be obtained by supercritical extraction.
2. The thermal stability of the microstructure of porous titania-alumina is improved by supercritical extraction.
3. The mixed oxides of TiO₂ and Al₂O₃ at 0.2 mol content of TiO₂ has high acidity due to the formation of hetero metal - oxygen bonds, -Ti-O-Al-.

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