

BENZYLTRIMETHYLAMMONIUM CHLORIDE IMMERSION EFFECT ON PHYSICAL PROPERTIES OF TiO₂ - Al₂O₃

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ABSTRACT

BENZYLTRIMETHYLAMMONIUM CHLORIDE IMMERSION EFFECT ON PHYSICAL PROPERTIES OF TiO₂-Al₂O₃. Mesoporous TiO₂ - Al₂O₃ powders have potential applications in catalysts or support catalysts. A novel method to control pore size of sol-gel by a cationic surfactant benzyltrimethylammonium chloride (BTAC) immersion was investigated. The gels of TiO₂ - Al₂O₃ in molar ratio of 0.2 of TiO₂ and 0.8 of Al₂O₃ were prepared by hydrolysis of aluminium *sec*-butoxide, Al(OC₄H₉^{sec})₃ and titanium isopropoxide Ti(OC₃H₇^{iso})₄ in an *n*-propanol solution with acid catalyst. The structures and porosities of the modified TiO₂ - Al₂O₃ was depended on the dimensions of surfactant, as long as the calcination was carried out at 500 °C to avoid aggregation process during removal of excess BTAC. If the calcinations were carried out at 800 °C no significant change of the pore volume of modified samples was remarkably not observed, even though formation of TiO₂ rutile has been taken place. It indicated that samples modification by initial immersion of gel into BTAC may avoid the sintering. These results suggest that during the calcinations TiO₂ was segregated from the Al₂O₃ particles to form nuclei of rutile and was crystallized prior to formation of α -Al₂O₃. Therefore, the formation of rutile TiO₂ induced the formation of α - Al₂O₃.

Key words : Mesoporous TiO₂ - Al₂O₃, sol-gel method, surfactant.

ABSTRAK

PENGARUH IMERSI BENZILTRIMETILKLORIDA PADA SIFAT-SIFAT FISIKA TiO₂-Al₂O₃. Serbuk TiO₂ - Al₂O₃ mesopori berpotensi untuk diaplikasikan pada katalis atau penyangga katalis. Metode baru untuk mengendalikan ukuran pori-pori dari sol-gel dengan cara merendam surfaktan kation *benzyltrimethylammonium chloride* (BTAC) telah diamati. Gel TiO₂ - Al₂O₃ dengan perbandingan mol 0,2 untuk TiO₂ dan 0,8 untuk Al₂O₃ telah dibuat dengan cara hidrolisis dari aluminium *sec*-butoksida, Al(OC₄H₉^{sec})₃ (ASB) dan titanium isopropoksida Ti(OC₃H₇^{iso})₄ dalam larutan *n*-propanol dengan katalis asam. Struktur dan porositas TiO₂ - Al₂O₃ termodifikasi bergantung pada dimensi surfaktan, proses agregasi dapat dihindari selama penghilangan BTAC pada suhu 500 °C. Perubahan volume pori-pori tidak signifikan setelah contoh termodifikasi dikalsinasi pada 800 °C, meskipun fasa rutil TiO₂ telah terbentuk. Dari hasil tersebut dapat diperkirakan bahwa selama kalsinasi partikel TiO₂ terpisah dari partikel Al₂O₃ membentuk inti atom rutil sebelum terbentuknya kristal α -Al₂O₃. Karena itu pembentukan fasa rutil TiO₂ akan mempercepat terbentuknya fasa α - Al₂O₃.

Kata kunci : TiO₂ - Al₂O₃, mesopori, metode sol-gel, surfaktan.

INTRODUCTION

New classes of nanostructure materials with well defined porosities have potential applications in catalysis, [1, 2] optical devices, [3] separation, [4] and microelectronics.[5] The properties of catalyst and support material are depending on their preparation procedure [6-11]. The high porosity and the high specific surface area of material prepared by sol-gel method make

it 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 preparing a support oxide catalyst from a homogenous solution containing both the metal precursor and the support precursor [6,10]. As a process to prepare highly porous materials, supercritical drying

is well known [14], but it requires high temperatures and pressures. Several methods to prepare porous materials at ambient pressure, such as solvent exchange and process using polymer additives [15] have been proposed. TiO_2 - Al_2O_3 that have been prepared by sol-gel method are the most homogeneous than that of TiO_2 - Al_2O_3 , which was prepared by coprecipitation and hydrogel kneading [12]. The addition of TiO_2 to the Al_2O_3 in molar ratio of 0.2 of TiO_2 and 0.8 of Al_2O_3 increased slightly the surface area, where as a decrease of that was taken place when more TiO_2 was added [13]. Many studies concerning the preparation of mesoporous or microporous materials have used the self assembled structure, such as surfactants or block copolymers as a template. Modified sol-gel method using surfactants are recently used in material science to fabricate porous materials and enhance their properties [8, 9]. The factors controlling the pore spacing include the type, length and concentration of surfactants [9], solvent, and reaction or processing conditions.

In this study, the effect of immersion a cationic surfactant benzyltrimethylammonium chloride (BTAC) on the physical properties of TiO_2 - Al_2O_3 prepares by sol-gel method was investigated.

EXPERIMENTAL

The gels of TiO_2 - Al_2O_3 in molar ratio of 0.2 of TiO_2 and 0.8 of 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 acidic *n*-propanol solution. The molar ratios used for the synthesis were $\text{H}_2\text{O}/\text{alkoxide} = 2$, $\text{HNO}_3/\text{alkoxide} = 0.06$ and $n\text{-propanol}/\text{alkoxide} = 12$. According to the given

formulation the appropriate amount of (ABS) was initially dissolved in *n*-propanol at 65°C with vigorous stirring for a complete dissolution, stirring was continued at 65°C for one hour. Once the (ABS) was dissolved and cooled at room temperature, the appropriate amount of TIP in *n*-propanol to produce the designed mixed oxide formulation was added and stirred for one hour. After that, a mixture of the remaining *n*-propanol, H_2O and HNO_3 was added dropwise under continuous stirring. The gel formed after the addition of the last drop. For the formation of xerogel, the wet gel was dried at 90 °C overnight. To form a modified gel materials, the wet gel was initially immersed into *n*-propanol solution containing benzyltrimethylammonium chloride (BTAC) at room temperature for 12 hours. The solution was then decanted and the gel was dried at 90 °C for 12 hours. Changes of the microstructure of the gels during heating were evaluated using thermal gravimetric and differential thermal analyses (TG-DTA) and N_2 adsorption. TG-DTA measurements were carried out in a Seiko (Exstar 6000) TG/DTA 6200 System under airflow of 300 mLmin⁻¹, with heating rate of 10 °C.min⁻¹. The specific surface area, pore size distribution, and pore volume of gels, before and after annealing, were estimated by the Barret-Joyner-Halenda (BJH) method using N_2 adsorption-desorption curves. Crystallization behaviors of the samples have been observed by X-ray diffractometer (Rigaku, RAD-C) after calcining at 500, 600, 750, 800, and 1000°C, respectively.

RESULTS AND DISCUSSION

The profiles of TG-DTA of dry gels are given in Figure 1 for xerogel and Figure 2 for modified-gel. For

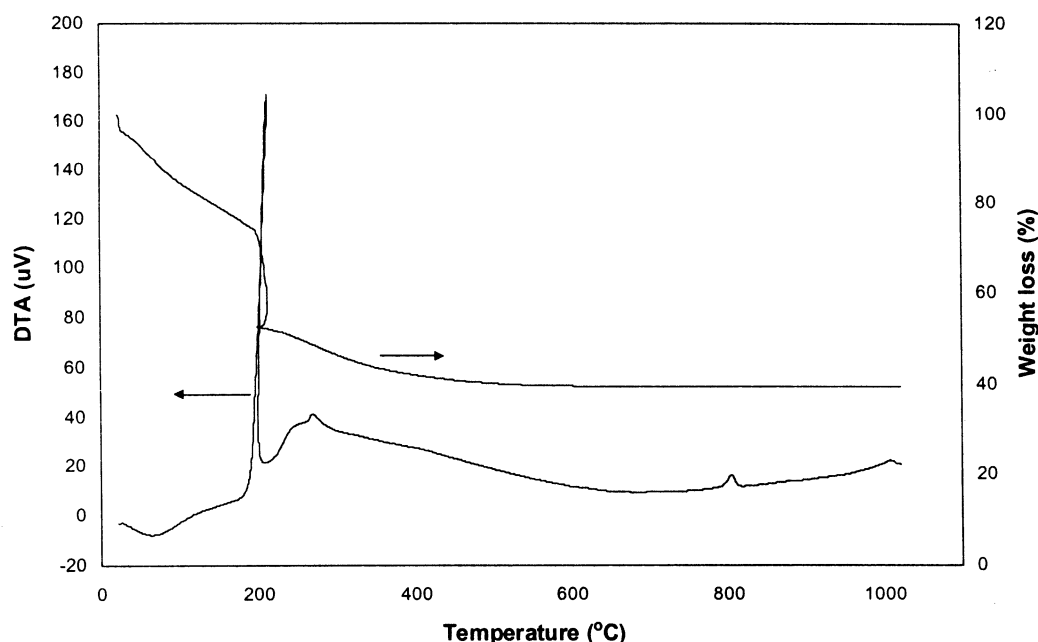


Figure 1. Profile TG-DTA of dry xerogel.

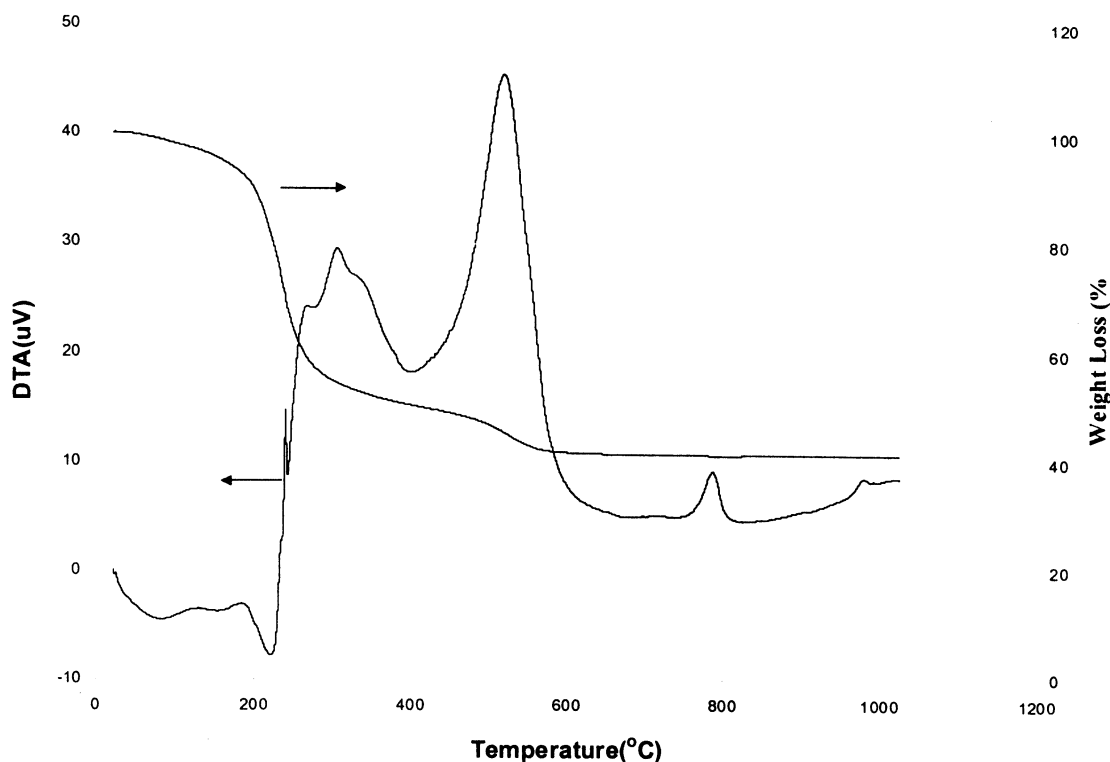


Figure 2. Profile TG-DTA of dry modified-gel.

the dried xerogel, weight loss around 55 % was mainly observed at around 200°C. Beyond 300°C the sample of xerogel lost practically no more weight. In the DTA curve, the dried xerogel showed endothermic peak around 100 °C and sharp exothermic peak around 200 °C accompanied by weight loss around 55%, and small exothermic peaks at around 250°C, 800, and 1000°C. For the dried modified gel Figure 2, weight loss around 55% was mainly observed below 600°C. Beyond 600°C the sample of modified gel lost practically no more weight. In the DTA curve, the dried modified gel showed endothermic peak around 100°C, big exothermic peak around 300°C, broad exothermic peak at around 500°C accompanied by weight loss around 55% and small exothermic peaks at around 800 and 1000°C.

Endothermic peaks appeared in almost same temperature region, namely at around 100 °C as the boiling point of water and *n*-propanol as hydrolyzing reagent and solvent, respectively. Sharp exothermic peaks, which generally came up from combustion of organic, appeared at higher temperature for modified gel namely at around 300°C than that of xerogel namely at around 200 - 250°C. Therefore, the weight loss at 200°C for xerogel and 300 °C for modified gel appeared to correspond to the combustion of the organic residues in the gel and the organic residues in the gel – surfactant frameworks. The broad exothermic peak at around 500°C, and followed with weight loss to correspond to the combustion of surfactant. For the xerogel and

modified gel, the small exothermic peaks at 800°C and at 1000°C derived from crystallization of samples.

Figure 3 shows the FT-IR spectra of TiO₂ - Al₂O₃ with and without modification by BTAC or CTAC after drying at 100 °C and calcining at 500 °C in the 4000–400 cm⁻¹ region. The broad spectra around 3400 cm⁻¹ for all samples indicated the OH group, whose origin is likely to be occluded water and surface ≡Ti-OH groups with H-bridging. The dried sample without modified surfactant indicate the presence of strong peak at 1636 cm⁻¹ for stretching of –OH and at 1377 cm⁻¹ for vibration of –C-H. The dried samples modified by surfactant showed the presence of strong peak at 2920 cm⁻¹ and 2851 cm⁻¹ for –C-H bonding, at 1636 cm⁻¹ for stretching of –OH, at 1473 cm⁻¹ for -OH bonding and at 1377 cm⁻¹ for –C-H vibration. After calcining of samples at 500 °C for 2h, the peaks at 2920 cm⁻¹, 2851 cm⁻¹, 1473 cm⁻¹ and at 1377 cm⁻¹ disappeared, but the peaks at 3400 cm⁻¹ for OH group and at 1635 cm⁻¹ for stretching of –OH still existed.

The temperatures to eliminate residual alcohol, that is physically adsorbed on the solid surface of dried xerogel and dried modified gel are different, which is higher for the later. It may cause by the strong interactions of surfactant with the dried modified gel. The surfactant, which located in the structure of the gel – surfactant frameworks was burned out at around 500°C as indicated, by disappearance of FT-IR spectra of surfactant after calcination at 500°C, which is representing about 39% of the total weight lost. The presence of Ti-O groups

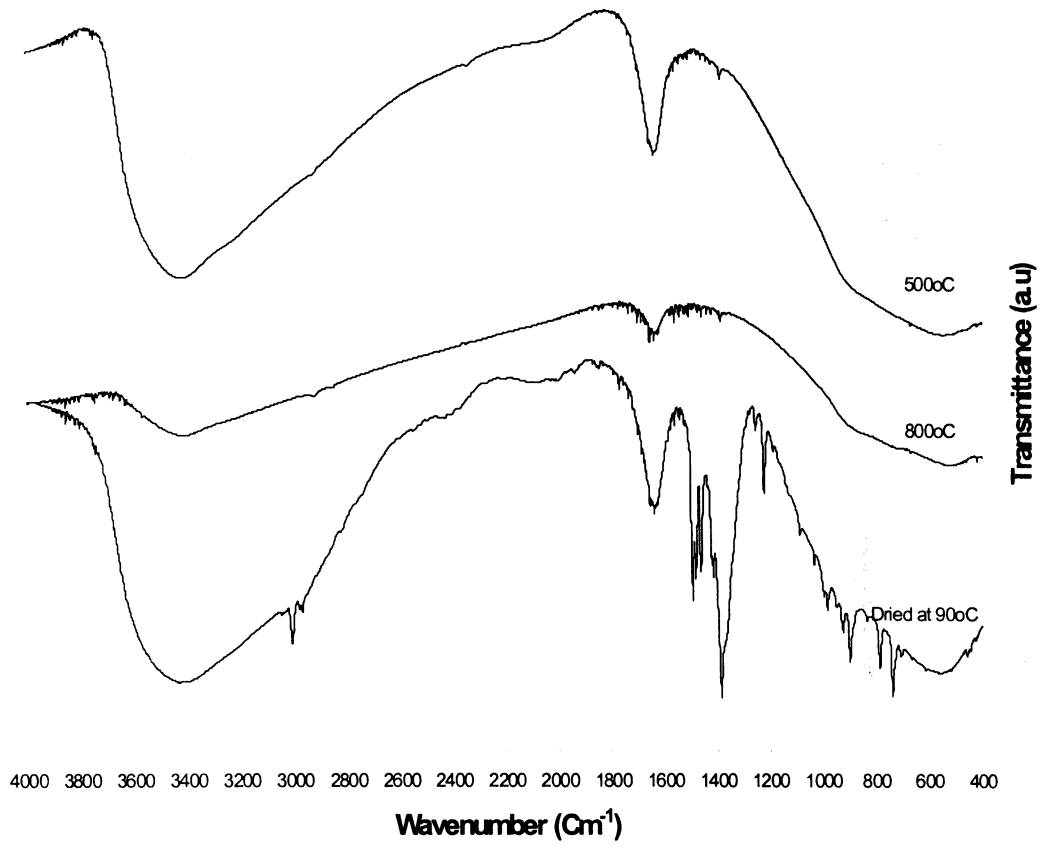


Figure 3. Infrared spectra of alumina-titania with BTAC modified

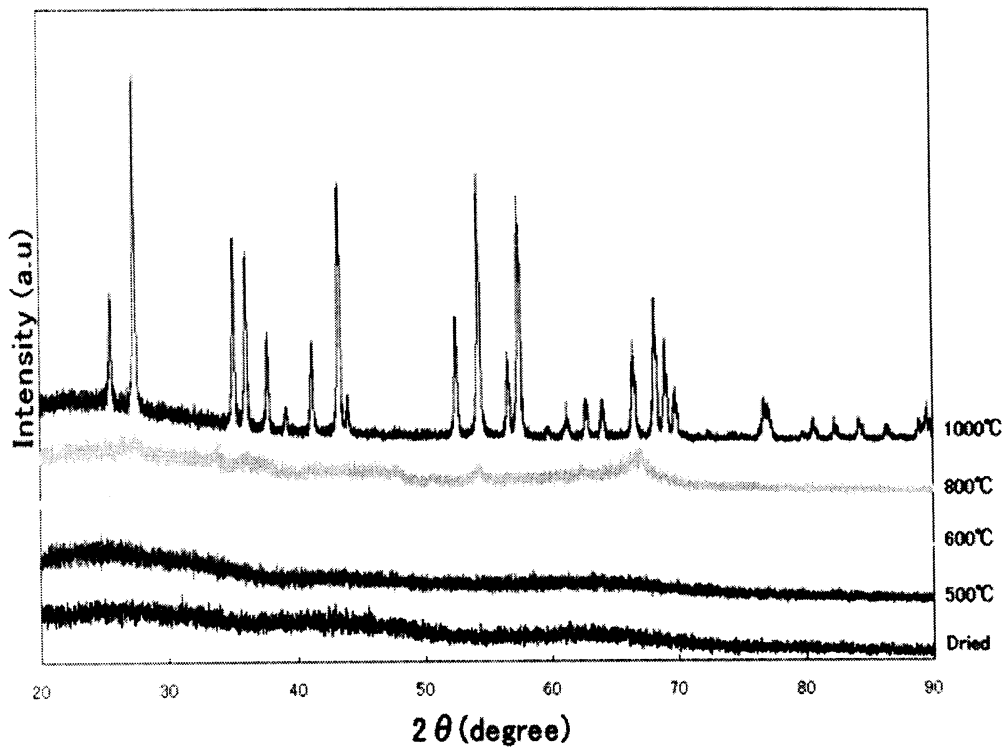


Figure 4. X-ray diffraction patterns of alumina/titania after calcining at various temperatures.

was indicated by the presence of the strong, but broad peak between 500 and 900 cm⁻¹. The sample calcined at 500 °C indicated the presence of strong peak at 1635 cm⁻¹, which also indicated that the -OH stretching mode originated from a high degree of surface hydroxylation.

A detailed study of the crystalline phases formed during the calcinations process is of a great importance, because the nature of the crystalline phase can affect the catalytic behavior of the support. The both samples of xerogel and modified gel after drying at 90 °C for overnight are amorphous, as detected in their corresponding diffraction patterns (Figure 4). After calcining up to 600 °C for 2 hours, the amorphous phases of both samples do not change. After calcining at 800 °C for 2 hours, the amorphous phases of both of the samples change to rutile phases. Finally, after calcining at 1000 °C for 2 hours, the rutile phases and α -alumina were observed. These results indicated that the anatase, θ and γ -alumina phases were not found on both samples of calcined xerogel and modified gel.

The DTA peaks of both samples of xerogel and modified gel detected at the 800 °C may be assigned to the direct crystallization of amorphous TiO₂ into rutile (Figure 4). No anatase TiO₂ was observed for both sample of xerogel and modified gel. The DTA peak at 1000 °C for both samples of xerogel and modified gel may be assigned to the direct crystallization of amorphous Al₂O₃ into α -Al₂O₃ (Figure 4). No θ and γ -Al₂O₃ were observed for both sample of xerogel and modified gel. These results suggest that during the calcination treatment, 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.

Figure 5 shows the effect of various BTAC concentration treatments on specific surface area of alumina-titania after calcining at 500 °C for 2 h, determined by the BET. Specific surface area of the alumina-titania

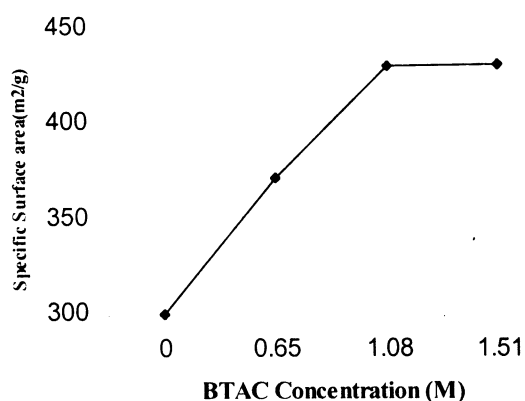


Figure 5. Effect of various BTAC concentration treatments on Specific Surface Area of alumina-titania after calcining at 500 °C.

increase with an increasing in concentration of BTAC. The specific surface area was increased up to 412 m²/g at 1.08 M BTAC treatment. The specific surface areas have not been changed further by treatment with a BTAC concentration more than 1.08 M, it indicated that surfactant of BTAC which introduced into the pores were completed.

Figure 6 and Figure 7 show the effect of BTAC treatment on specific surface area and pore volume of alumina-titania after calcining at various temperatures for 2 hours. The modified gel has large specific surface area and large cumulative pore volume than the xerogel without surfactant immersion. The specific surface area and cumulative pore volume decreased with increasing of calcined temperature.

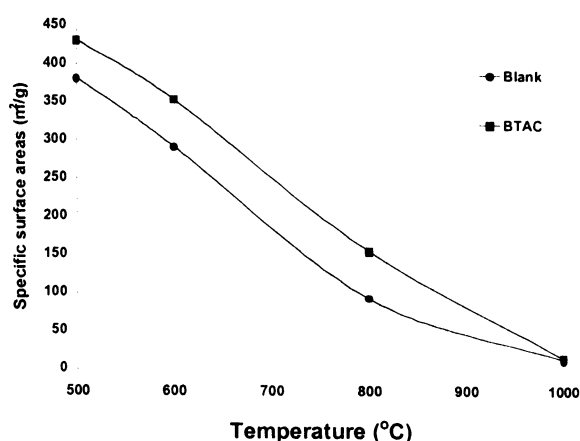


Figure 6. Cumulative pore volume of alumina-titania after calcination at different temperature.

The samples calcined at 500 °C showed high value of surface area. After calcining at 600 °C and 800 °C the specific surface areas of both samples decreased, but the specific surface areas of samples modifying by BTAC still higher than that of unmodified sample. After calcining

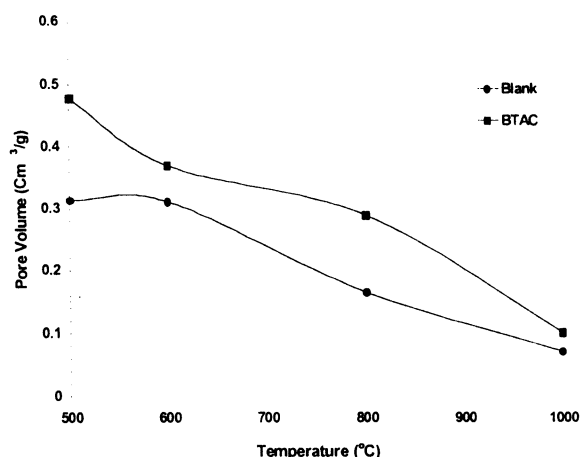


Figure 7. The effect of BTAC treatment on specific surface area.

at 600 °C the pore volume of both samples decreased, indicates that both surfactant of BTAC are completely disappeared. It is remarkable, that calcination at 800 °C did not change the pore volume of samples, and those are modified by BTAC as well, even though after calcining at that above temperature the TiO₂ rutile was formed. It indicates that the samples that were modified by surfactant could impede the sintering. After calcining at 1000 °C the specific surface area and cumulative pore volume of both samples were drastically decreasing. It does indicate that crystallization of the rutile Titania and α-alumina phases were occurred (Figure 4).

CONCLUSION

The preparation of TiO₂ - Al₂O₃ powders using surfactant immersion procedure provides a possibility to develop highly surface area and pore volume materials, by controlling the pore size, porosity, and network structure using immersion of gel into surfactant prior to drying and to calcination. The structures and porosities of the modified TiO₂ - Al₂O₃ was depended on the dimensions of surfactant, as long as the calcination was carried out at 500 °C to avoid aggregation process during removal of excess surfactant. If the calcinations were carried out at 800 °C no significant change of the pore volume of modified samples was remarkably not observed, even though formation of TiO₂ rutile has been taken place. It indicated that samples modification by initial immersion of gel into surfactant may avoid the sintering. These results suggest that during the calcinations TiO₂ was segregated from the Al₂O₃ particles to form nuclei of rutile and was crystallized prior to formation of α - Al₂O₃. Therefore, the formation of rutile TiO₂ induced the formation of α - Al₂O₃.

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REFERENCES

- [1]. A. CORMA, *Chem. Rev.* **97** (1997) 2373
- [2]. M. W. ELLSWORTH, D. L. GIN, *Plym. News* **24**, (1999) 331
- [3]. Q. HUO, D. ZHAO, J. FENG, K. WESTON, S. K. BURATTO, G. D. STUCKY, S. SCHACHT, F. SCHUTH, *Adv. Mater.*, **9** (1997) 974
- [4]. X. FENG, G. E. FRYXELL, L. Q. WANG, A. Y. KIM, J. LIU, K. M. KEMNER, *Science*, **276** (1997) 923
- [5]. P. J. BRUINNSMA, N. J. HESS, J. R. BONTA, J. LIU, S. BASKARAN, *Mater. Res. Soc. Symp. Proc.*, (1997) 443, 105

- [6]. J. RAMIREZ, L. RUIZ-RAMIREZ, L. CEDENO, V. HARLE, M. VRINAT and M. BREYSSE, *Appl. Catal. A*, **93** (1993) 163
- [7]. H. NAKABAYASHI, *Bull. Chem. Soc. Jpn.*, **65** (1992) 914
- [8]. H. HIRASHIMA, H. IMAI, V. BALEK, *J. Non-Crystalline Solids*, (2001) 285, 96.
- [9]. M. M. YUSUF, H. IMAI, H. HIRASHIMA. *J. Non-Crystalline Solids*, (2001) 285, 96.
- [10]. H. WOHLFROMM, P. PENA, J.S. MOYA and J. REQUENA, *J. Am. Ceram. Soc.*, **75** (1992) 3473
- [11]. B.N. DAS, *J. Mater. Sci. Lett.*, **11** (1992) 843
- [12]. M. TOBA, F. MIZUKAMI, S. NIWA, Y. KIYOZUMI, K. MAEDA, A. ANNILA and V. KOMPPA, *J. Mater. Chem.*, **4** (4) (1994) 585
- [13]. R. LINACERO, M.L. ROJAS-CERVANTES, J. DE D. LOPEZ-GONZALEZ, *J. Mater. Sci.*, **35** (2000) 3279
- [14]. S. TURSILOADI, D. SONDAR, N. RENALDI and H. HIRASHIMA., *Indonesian Journal of Materials Science*, **4** (2) (2003) 40
- [15]. Y. LIU, A. WANG, R. CLAUS, *J. Phys. Chem.*, **B 101**, (1997) 1385