

Fabrication and structural characterization of pure TiO₂ aerogel and Au nano-particles-embedded TiO₂ aerogel

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We have firstly fabricated pure titania aerogel from the prepared wet gel by super-critical drying process (9.11 [MPa], and 373[K]) using liquid CO₂ as super-critical drying medium. The obtained aerogels were further heat treated at 673-773[K] for 2hr to complete the growth of titania crystallites. The measured specific-surface-area of it was 110.4[m²/g] by BET method. Only anatase titania phase was identified by XRD. TEM and SAED revealed that the net work structure composed of the anatase titania polycrystalline with 35 [nm] in the averaged diameter.

Additionally we prepared titania aerogel embedded by the dispersed Au nano-particles with about 3.7 [nm] in diameter. The good catalyst performance for the ground sample was confirmed by chemical reaction of oxidation of CO at temperature lower than room temperature.

Key word: Anatase titania, Aerogel, Au particles, Sol-gel method, Catalyst

1. Introduction

Among transition metal oxides, TiO₂ (titania) is n-type semiconductor with wide band gap, and have considerably attracted as catalyst and catalyst-container applications[1-4], which are due to redox and acid properties, photo-catalytic characteristic and high thermal durability [5, 6] of titania. Moreover, the designated oxide embedded by dispersed nano-sized noble metal such as Au, Pt, Rh and Pd is known as a promising catalyst to decompose automobile emission gases[7].

The characteristic features of transition-metal oxide aerogel, processed by super-critical drying from the wet gel composed of transition-metal oxide polymer through sol-gel reaction, are three dimensional fractal network structure, large porosity, large surface area, and low density [8, 9].

Hence, we desire to fabricate titania aerogel and/or titania aerogel embedded by nano-sized Au particulates which has large surface area to improve great potentiality for the applications to catalyst and/or catalyst-container as well as sensor.

The purpose of this study is to find the optimal processes for fabrication of the designated materials. Particularly, the molar ratio of the chemical precursors in sol for wet gel, the polymerization process in titania wet gel through sol-gel reaction, the preparation of the solution with nano-sized Au particulates, the mixing process of the designated solution into titania wet gel, the super critical drying process and the followed post-annealing treatment are identified to be important. Moreover, the

feasibility study on catalyst was carried out for the ground sample of titania aerogel embedded by the dispersed nano Au particles through the simple CO oxidation reaction as the function of temperature.

2. Experiment

2-1 Preparation of titania aerogel

Firstly, by following the sol-gel method reported by Dagan and Tomkiewick at room temperature and in air [10, 11], titanium tetra iso-propoxide (TTIP: Ti(PrOH)₄) and ethanol (EtOH) were mixed in the first vessel, and ethanol, water and nitric acid were mixed in the second vessel. Then two solutions were mixed and stirred in another vessel for the preparation of titania wet gel. After the repeated experiments, the optimum molar ratio of TTIP, EtOH, water and nitric acid were about 1:20:2.5:0.08. The wet gel was aged in air at 293[K] for 20 days to complete gelation in the sealed vessel. Thirdly, to remove residual nitric acid and water in wet gel, wet gel itself was rinsed in iso-propanol solution at least three times. Finally, the wet gel was processed by super-critical drying process under 9.11[MPa] and 373[K] for 2hr for the formation of titania aerogel. The prepared aerogel samples were further heated up to 773[K] by the step of 100[K] temperature increment for 2hr to improve the crystallization of titania. For the comparison, one sample (hereafter denoted as sample Ti-7) was heated up to 500[K] in the super critical drying process instead of the post annealing treatment.

X-ray diffractometry (XRD) (RINT-2000, CuK α radiation) with a normal θ -2 θ scan was used for the

identification of crystallization. The microstructure and the phase formation were analyzed by transmission electron microscopy (TEM) (Philips Tecnai 20, 200[KeV]) with point to point resolution of 2.3[Å] and selected area electron diffractometry (SAED). For TEM observation, the samples were ground into particulates and a small amount of it was dispersed onto the carbon-film-coated Cu micro-grid.

2-2 Preparation of Au embedded titania aerogel

Commercially available Au ultra fine particles 3.0[mg] in weight with average diameter of 3.7[nm] (ULVAC perfect gold) was dispersed in 50[ml] toluene, and then the prepared titania wet gel was soaked into the solution for about 24 hr for the complete absorption of Au particles. The details of the preparation method are cited in the reference by Tai et al [12, 13]. Finally the prepared wet gel turned to the titania aerogel embedded by the dispersed Au particles by the previously described process.

2-3 Evaluation of catalytic performance of Au embedded titania aerogel

The catalytic performance of Au embedded titania aerogel was evaluated by the measurement of the conversion ratio of the oxidized reaction from CO to CO₂ gas. The ground sample of 100[mg] was contained in the testing glass tube. The used inlet gas was mixed by air and CO with 1% volume fraction. The gas flow rate was 33[ml/min]. The residual CO gas content in the outlet was quantitatively analyzed.

3. Results and discussion

3.1 XRD

Fig.1 shows XRD results for the titania aerogel samples annealed at various temperature indicated in the figure caption.

The samples annealed lower than 573[K] (samples Ti-1, Ti-2 and Ti-3) are amorphous.

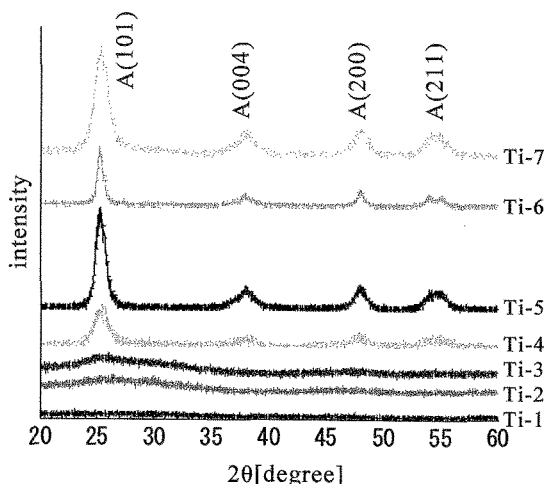


Fig. 1, XRD of titania aerogel annealed at various temperature [K]. Ti-1(without annealing), Ti-2 (373), Ti-3(473), Ti-4(573), Ti-5(673), Ti-6(773) and Ti-7(without annealing, but heated at 500[K] in the super critical driving process)

The peaks observed in sample Ti-4, Ti-5, Ti-6 and Ti-7 are identified with anatase (A)-titania peaks indexed as (101), (004), (200) and (211) after JCPDS [14]. The peak intensity increases upon increasing of the temperature from 573 up to 773[K]. The annealing temperature ranging from 673 to 773[K] is regarded to be optimal for obtaining the high quality crystallized A-titania aerogel because of the observed strong intensities and narrow full-width at half-maximum (FWHM) of four peaks. Sample Ti-7 processed by the super critical drying at about 500[K] also shows the well growth of A-titania phase, and this suggests the possibility of a simpler one-step fabrication process in comparison with the commonly used two-step process (super critical drying plus post anneal-treated) for the crystallization of A-titania.

3.2 TEM images and SAED patterns

The low magnified TEM images of Ti-6 and Ti-7, and SAED ring pattern of Ti-6 are given in Fig.2a, 2b, and 2c respectively. The ring pattern of Ti-7 is quite similar to Fig.2c. The ring pattern reveals the secondary particulates of aerogel are polycrystalline A-titania. The averaged diameter of the secondary particulates of Ti-6 in Fig.2a is about 35nm and that of Ti-7 in Fig.2b being about 20nm. HRTEM of sample Ti-6 is also given in Fig.3 and A-titania aerogel is confirmed to be composed by the crystallites with 20-50nm in diameter. The d-spacing of A-titania (101) lattice plane is clearly observed in a hexagonal faceted crystal.

Fig. 4a shows the low magnified TEM image of the titania aerogel embedded by the dispersed Au nano-particles. The histogram of the size for the embedded Au particles is also given in Fi.4b.

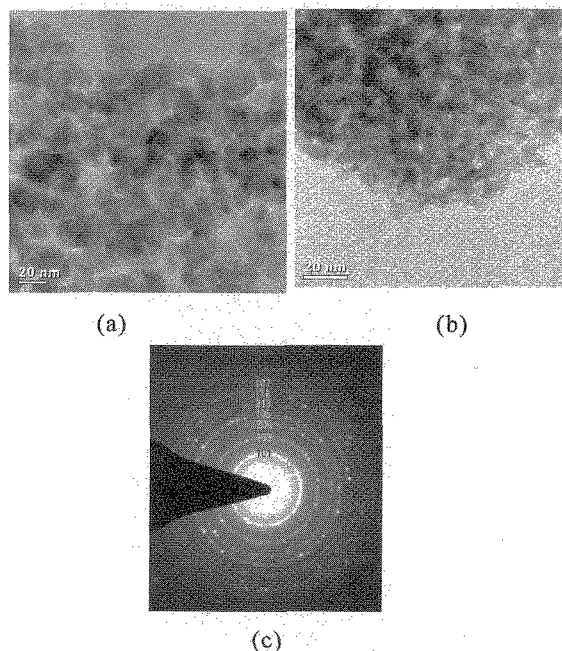


Fig. 2, Low magnified TEM image of Ti-6(a), and Ti-7, (b) and SAED of Ti-6 (c). The indexed rings from the inner ring are: (101), (103), (200), (105), (213), (116), and (107) of anatase titania phase respectively.

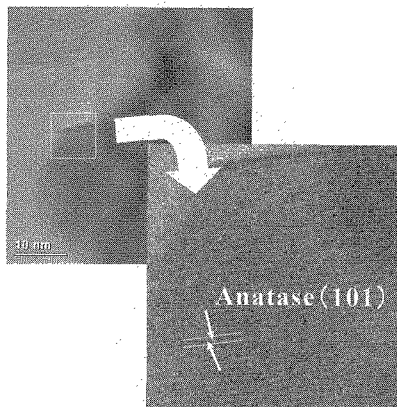
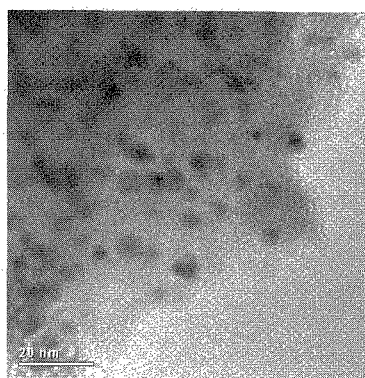
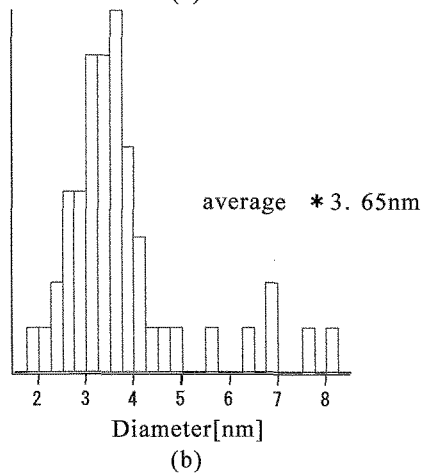


Fig. 3. HRTEM image of sample Ti-6. The enlarged part shows lattice image of A-titania (101).



(a)



(b)

Fig. 4. (a) Low magnified TEM image of A-titania aerogel embedded by Au particles and (b) the histogram of the diameter of the dispersed Au particles.

The average size of them is about 3.7[nm] which is approximately the same with that of the as-received Au.

3.3 Catalytic performance of Au embedded A-titania aerogel

The temperature dependent catalytic performance of the ground sample of Au embedded A-titania aerogel is given in Fig.5. For the comparison, the result obtained for Au embedded silica aerogel by Tai et al [12] is shown. The high catalytic reaction even at temperature lower than room temperature is confirmed. The result is quite similar to that by Pietron et al [7] and this high performance is due to the firm solid contact between Au particles and titania aerogel net-work as suggested by Haruta and Date [15,16].

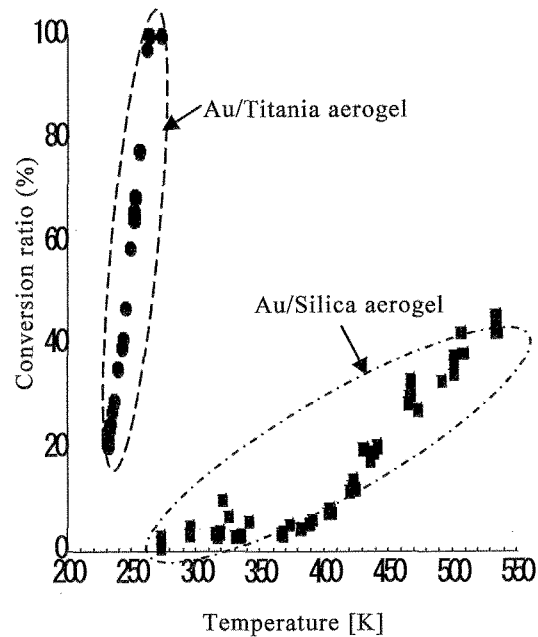


Fig. 5. Temperature dependent catalytic performance of Au embedded A-titania aerogel.

4. Conclusion

We have successfully fabricated A-titania aerogel and Au embedded A-titania aerogel by applied sol-gel process, super-critical drying process, and the post annealing treatment. The diameter of the secondary A-titania crystallites of aerogel is ranging from 20 to 50[nm]. The particle diameter of the embedded Au is not changed from the as-received even after the post annealing process.

Highly efficient catalyst performance of Au embedded titania aerogel is confirmed even at temperature lower than room temperature by oxidized reaction of CO.

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