Novel Method for Synthesizing Zirconium Oxide Thin Membrane on/into Polymer Membranes

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Polymer supported zirconium oxide thin layer was prepared by means of a simple sol-gel method using inorganic salt and methanol. This simplified method was effective for reducing steps of sol-gel procedure and was applicable to many kinds of polymer substrate not only hydrophilic but hydrophobic. This method was also applicable to porous membrane as substrate, and was effectively applied to fill the pore with zirconium oxide.

Due to their some useful functions,[1-5] zirconium oxide based materials have been examined for various applications. However, it is difficult to obtain fine structure or thin membrane of high performance zirconium oxide, because of their brittleness. Therefore, in some cases, its incident performance has hardly been exerted. To overcome these problems, especially to obtain thin layer of zirconium oxide, polymer film has been used as substrate. Until recently many attempts have been carried out to get zirconium oxide thin layer on polymer film, for examples chemical vapor deposition (CVD), sputtering and sol-gel methods,[6] however each method has some disadvantages. For CVD and sputtering, expensive equipment is required and substrate film size or shape is limited. For sol-gel method, the expensive precursor is needed and the process is very complicated. Recently new method for preparing zirconium oxide thin layer from aqueous solution was reported.[7] This method requires no expensive equipment, and by this method, substrate size was not limited. However, this method is limited to the hydrophilic polymer. In particular, it seems difficult to fill porous polymer membrane with aqueous solution because of the large surface tension of water. In order to overcome these problems, we have used organic solvents to prepare the hybrid material. This method does not require any expensive equipment, precursors and complicated processes. In particular this process does not need pH adjustment of the solution. In this report, we will show a manufacturing method of hybrid material and characterizations.

Polymer supported zirconium oxide thin layer was prepared from methanol solution of zirconium sulfate. Polyimide, polyamide, poly(ethylene terephthalate) and polypropylene films were used as substrate. After the dissolving zirconium sulfate into methanol at room temperature, polymer substrate was soaked into solution. Then this solution was held at constant temperature. White layer was formed on the substrate during this treatment. In the case of 15 mmol dm^{-3} solution, 308 K was good for this reaction. This white layer was not broken easily and fixed to substrate tightly. When temperature was lower than 300 K, the white layer was not formed, and when higher than 313 K, it was difficult to control the layer thickness because of high reaction rate. The substrate was taken out from the solution and dried at room temperature. After that the white layer turned into clear layer.

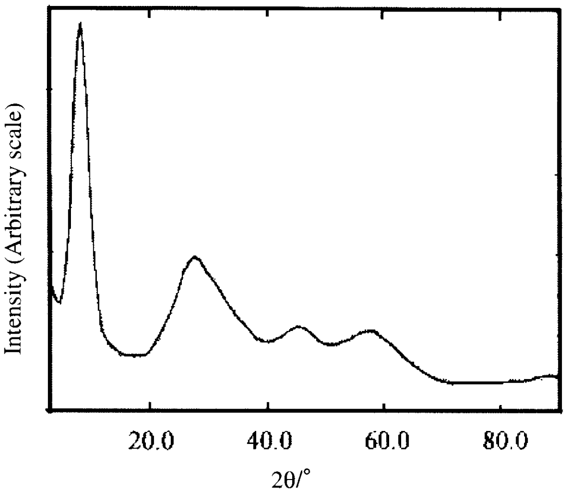

Figure 1. X-Ray diffraction pattern of zirconium oxide thin layer.

X-Ray diffraction analysis of the film is shown in Figure 1. As this material was very thin, it was difficult to observe strong X-ray diffraction peak directly. Therefore, sample was collected by striping from substrate for the X-ray analysis. The result of X-ray analysis indicates that this layer had low crystallinity. Moreover, it shows a diffraction peak at very low diffraction angle. The peak at such a lower region is present in some sulfuric ion included zirconium compounds,[8] and it is suggested that this thin layer also contained sulfate ion. It was cleared by Fourier transform infrared spectroscopy analysis.[9] TG-MS analysis showed that the layer's weight was about 20% diminish at 473 K because of desorbed water. X-Ray fluorescence and elementary analysis for the layer gave wt% of Zr, 42.11; S, 5.76; C, 0.2; H, 2.56; O, 50. From these results, it is considered that the thin layer was zirconium oxide with containing sulfate ion. Field emission scanning electron microscopy was used to observe the surface of polyimide film supported zirconium

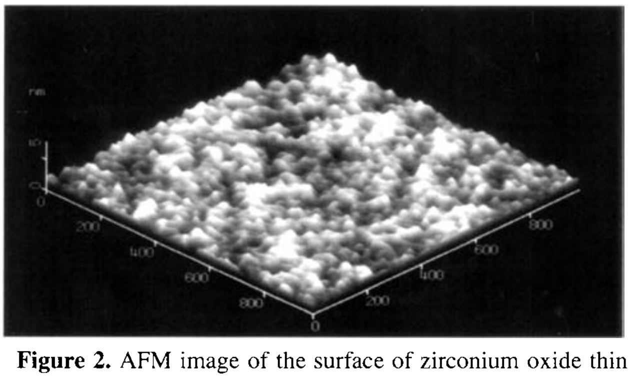

Figure 2. AFM image of the surface of zirconium oxide thin layer.

oxide thin layer. The micrograph did not show any structure on the surface, only showed that this layer had very flat surface. In order to get some information about surface of that, atomic force microscopy (AFM) was used. Figure 2 shows AFM image of zirconium oxide thin layer. It is made clear that the layer was gathering of nano-size particles. The average roughness of polyimide film surface was 4.02 nm. However, average roughness of zirconium oxide surface was 0.35 nm. This means that nano-size particles filled large undulation and formed a very flat surface. Figure 3 shows transmission electron microscopy (TEM) image of the cross-section of that. The thickness of zirconium oxide thin layer was about 2 μm and shows that it adhered to polyimide film very tightly. Even when the film was bended, the thin layer did not peel off from the substrate.

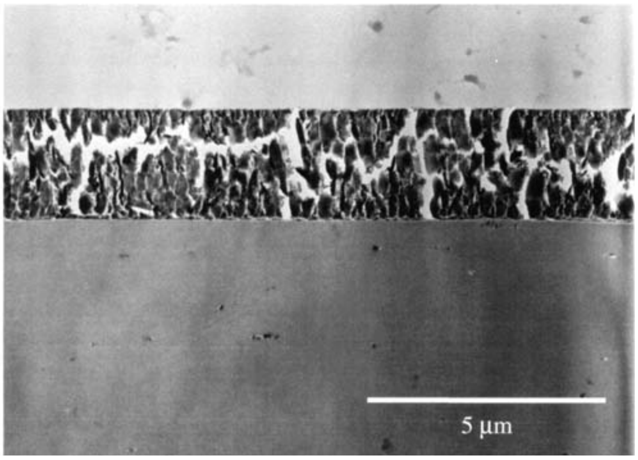

Figure 3. Cross-sectional TEM image of zirconium oxide thin layer supported on polyimide film.

Porous polypropylene membrane was also used as substrate. Polypropylene is hydrophobic polymer, so it is difficult to introduce inorganic materials into their micro pores without giving hydrophilic character. Figure 4 shows the cross-section of TEM image of the supported material. Average pore size of polypropylene porous membrane was 0.1 μm. The upper right image shows the center of supported material. In spite of that the pore is very small, zirconium oxide was filled as far as center of membrane without hydrophilic treatment.

Gel formation process was considered by varied water concentration. Water concentration was changed between 1% and less than 50 ppm. When water concentration was 1%, reaction rate was very high. Therefore, gel grew independently and could not adhere to substrate tightly. With the decrease of water concentration, reaction rate deceased. When water concentration was less than 50 ppm, reaction hardly occurred. This result suggests that ligand exchange by water induces gel formation. In this method, gel formation rate is so slow, because water concentration is lower than usual sol-gel method. Therefore, it is considered that fine particles are generated on the substrate.

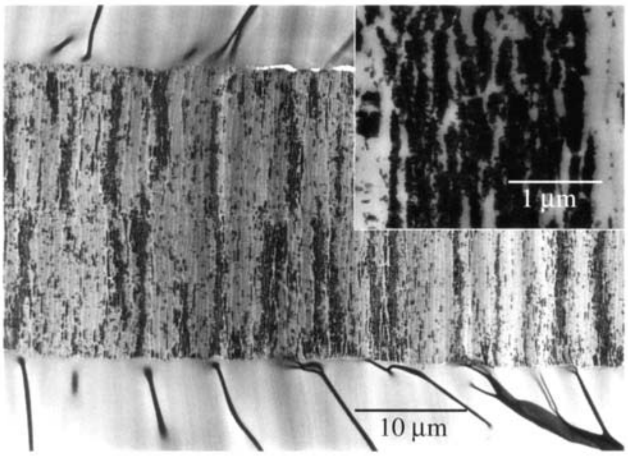

Figure 4. Cross-sectional TEM image of the porous polypropylene supported material. The center part is shown in inset.

In conclusion, this method is simple process for preparing hybrid materials and does not require any expensive equipment. Moreover, it does not limit a variety and size of substrates. In addition, because the zirconium oxide thin layer contained sulfate ion, some catalytic activities are expected.

References and Notes

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9 IR spectra gave typical absorbance for sulfate ion: 1114.67, 1008.60, 620.97 cm^{-1}.