

Preparation of Polymer Metal Composite Film as a Precursor of Metal Doped Carbon Membrane via Supercritical Impregnation

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Preparation of noble metal (Pt, Pd) particle-dispersed polyimide film as a precursor of metal doped carbon molecular sieve membrane was performed using impregnation of acetylacetonato complex dissolved in supercritical CO₂. Pt and Pd nanoparticles were successfully formed inside of the polyimide films. The impregnation temperature and varieties of polyimide films were strongly affects the dispersion of the metal particles.

INTRODUCTION

Metal/Polymer composites by impregnation of organometallic compounds dissolved in supercritical CO₂ (scCO₂) followed by their reduction /decomposition have been reported [1-8]. ScCO₂ have many advantages as impregnating media into polymers as the following reasons: (1) High diffusivity into polymers is expected since its low viscosity and swelling effect on many polymers, (2) solubility of solute is easily controlled and rapid decrease of the pressure is effective to make small clusters into polymers, and (3) this method does not use organic solvents and the process can be performed under dry condition. Preparation of Platinum (Pt) nanoparticles in poly(4-methylpentene) and Poly(tetrafluoroethylene) [1-3], Silver (Ag) nanoparticles on the surface of polyimide film [4-6], Ag nanoparticles in poly(ethylether ketone) [7] and poly(styleneme-divinylbenzene) [8] had been performed.

We applied this method to fabrication of carbon membrane for hydrogen separation. Currently high-temperature-proof hydrogen separation membrane is attracting significant attention because hydrogen energy systems and fuel cell are going to be developed. Carbon molecular sieve (CMS) membrane is known as good gas separation membrane with high resistibility to high temperature [9]. The gas separation property of CMS membrane can be controlled by doping metal particles having affinity to the objective gas [10]. Therefore hydrogen separation performance of CMS is expected to be improved by noble metals having affinity to hydrogen.

CMS membrane is generally prepared by pyrolysis of polymer precursors, such as polyimide membranes. In this work, we investigated the preparation of noble-metal particle dispersed polyimide films as a precursor of the CMS membrane. Considering toxicity and costs, we challenged the use of acetylacetonato complex, which have lower solubility than of metal complex used in previous study [1-8]. Effects of impregnation temperature and of variety of the polyimide film were studied in order to obtain composite film with high dispersion of noble metal nanoparticles.

EXPERIMENTAL

Polyimide film derived from pyromellitic dianhydride – 4,4'-oxydianiline (PMDA-ODA)(Fig. 1) was used for this work. Both conventional film (Kapton film, Toray Co. Ltd.)(KP) and synthesized film(SY) derived from casting of poly(amide acid) solution followed by thermal imidization *in vacuo* were used for comparison. Thickness of these films were 25 μ m and the size is 50 mm in diameter. Platinum (II) acetylacetonate (Pt(II)(acac)₂, Aldrich, 99.99%) and Palladium (II) acetylacetonate (Pd(II)(acac)₂, Aldrich, 98%) were selected as impregnating reagents. Solubility of these reagents to scCO₂ was measured prior to the impregnation experiments. The solubility of Pt(II)(acac)₂ was 2.6x 10⁻⁵ (mol/CO₂ mol) and that of Pd(II)(acac)₂ was 2.2x10⁻⁵ (mol/CO₂ mol) at 423 K and 19.6 MPa. They were almost independent of the temperature from 313 to 423 K.

Batch type high pressure vessel (50 cm³) was used for impregnation. KP or SY film and acetylacetonate were sealed in the vessel without contacting each other. The amount the reagent was calculated to be ten times much as the solubility to scCO₂ in the vessel. The vessel was pressurized by introduction of CO₂ followed by heating. The impregnation was performed at 313-473 K for 3-24 hours. The Pressure was 19.6 MPa for all runs. After the impregnation, the pressure decreased rapidly by releasing CO₂. The precipitated acetylacetonato complex on the film surface was washed out by methanol.

These composite films should be calcinated to carbon membrane under inert gas condition. In the present work, however, thermal decomposition of the acetylacetonato complex in air at 573K for 12 hours was performed to evaluate metal content and dispersion. Metal content was measured by X-ray fluorescence analysis. Dispersion of the metal particles was evaluated using transmittance electron microscopy (TEM, using JEOL 2000FXII with the voltage of 200 KV).

RESULTS AND DISCUSSION

Pt and Pd metal-dispersed polyimide film were successfully prepared even though acetylacetonato complex has low solubility to scCO₂. Fig. 2 shows effect of the impregnation time and temperature on Pt or Pd loading of the composite film, with the photograph of the samples. The color of the film changed to grayish with the increase of the metal content. As shown in Fig. 2(a) and (c), Pt and Pd content was controlled by the impregnation time. Significant increase of Pt content will depend on the decomposition of polyimide catalyzed by Pt particles during thermal treatment. Fig.2(b) and (d) shows that metal content strongly depends on the temperature. Since we had confirmed that the solubility of the Pt(II)(acac)₂ or Pd(II)(acac)₂ were independent of the temperature, the increase of the metal content should be ascribable to polyimide films, probably to thermal relaxation of polymer network..

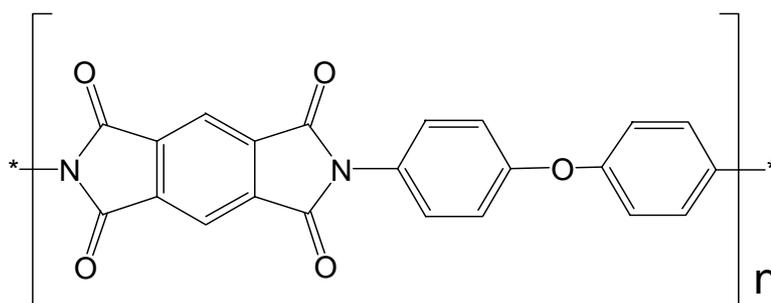


Fig. 1 Chemical Structure of Polyimide film (PMDA-ODA) in this work.

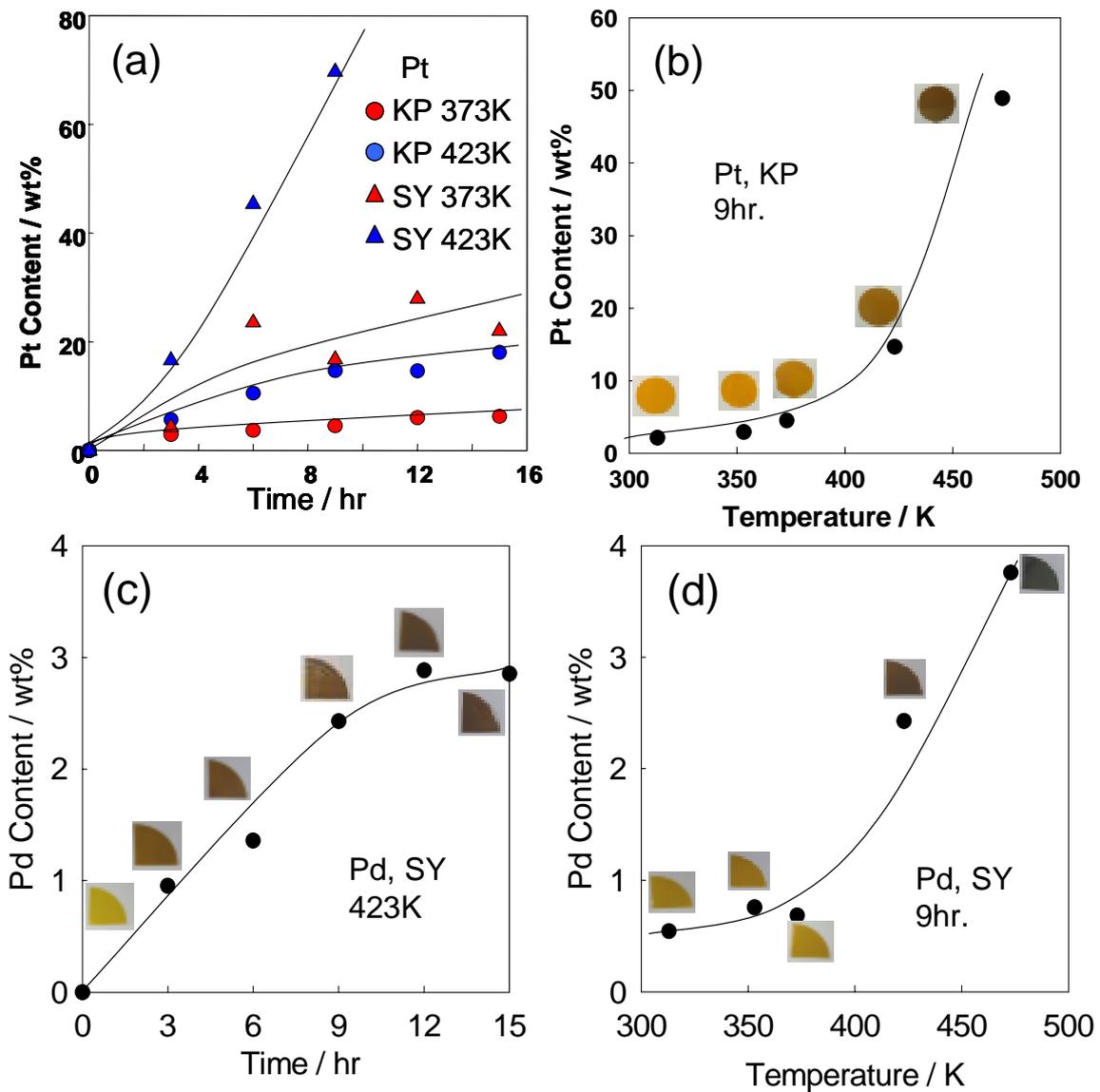


Fig. 2 Effect of impregnation time and temperature on metal content of the composite films with sample photos. (a) Pt content of both KP and SY film at 373 and 423 K, (b) Pt content of KP film treated for 9hrs, (c) Pd content of SY film prepared at 423K, (d) Pd content of SY film treated for 9hrs.

Fig. 3 shows TEM photographs of the Pt doped KP films. A small number of the aggregated Pt particles were observed in the case of 353 K. The dispersion of Pt aggregates was better than that at 353 K. At 473 K, Pt particles were not observed inside of the films and aggregated particles were found on the surface of the film. In the temperature, partial decomposition of Pt(II)(acac)_2 would be occurred and the Pt(II)(acac)_2 would not be impregnated inside of the film.

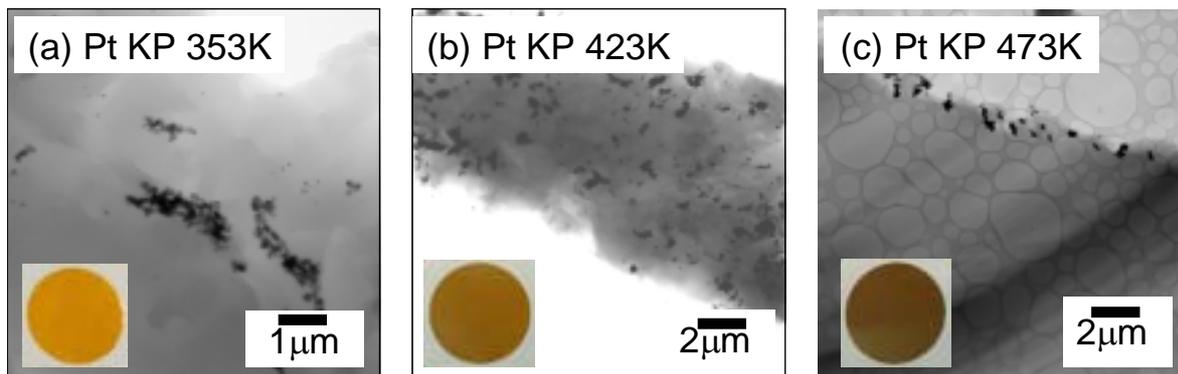


Fig. 3 TEM Images of Pt doped KP film prepared at (a) 353 K, (b) 423 K and (c) 473K, respectively. Impregnation was performed at 19.6 MPa for 9 hrs.

Fig. 4 shows TEM photographs of Pt-doped KP and SY film under the same impregnation condition. Smaller Pt particles have a smaller size and more homogeneous dispersion were observed in SY film than KP film. Both films did not have glass-transition and melting point, and they did not show significant swelling in the $scCO_2$ within our experimental conditions. The difference between KP and SY film would be caused by the distribution of molecular weight and arrangement of the polymer network. SY film would contain lower molecular weight of polymers and would have more flexible structure of the polymer network. Details are under investigation. The average Pt particle size was 12.6 nm ($n=150$) in **Fig 4(b)**.

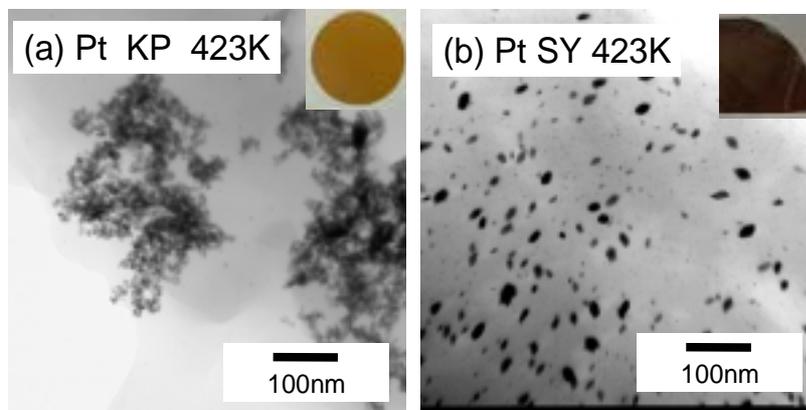


Fig. 4 TEM photographs of Pt-doped KP and SY films under the same impregnation condition (19.6 MPa, 423K, 9hr).

Pd particles in the polyimide film show higher dispersion than that of Pt particles. **Fig. 5** shows TEM photographs of Pd-doped SY polyimide films. Fine Pd particles were observed even at 373 K and they were quite homogeneously dispersed at 423K. The average particle size in **Fig.5(b)** was 4.6 nm ($n=150$) in diameter. Aggregated Pd particles were also observed on the surface. At higher temperatures, large surface Pd particles were observed frequently and the density of fine particles decreased. This would be caused by the decomposition of $Pd(II)(acac)_2$. Similar particle dispersion was also observed in the case of KP film, even though the aggregation of the particles was higher than that of SY.

Both Pt(II)(acac)₂ and Pd(II)(acac)₂ have similar solubility to scCO₂. The reason why Pd particles were highly dispersed could be related to lower decomposing temperature (> 453 K in air [11]) than Pt(II)(acac)₂ (its melting point is 523 K) and to chemical interactions with carboxyl structures of polyimide. The possible interaction was mentioned in the study Pd/block copolymer composite derived from Pd(II)(acac)₂ [12]. Interaction between carbonate in polyimide and Pd(II)(acac)₂ could resist the growth and the aggregation of the Pd particles.

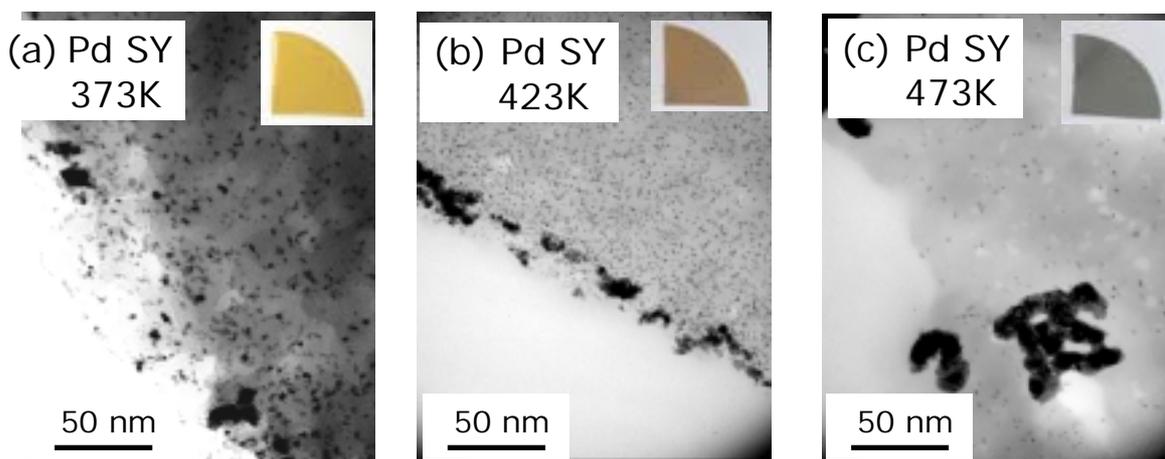


Fig. 5 TEM photographs of Pd-doped SY films prepared at (a) 373 K, (b) 423 K and (c) 473 K. Impregnation Pressure and time were 19.6 MPa and 9hrs., respectively.

CONCLUSIONS

Pt- and Pd- nanoparticle doped polyimide films as a precursor of CMS were successfully prepared by supercritical impregnation. Pt(II)(acac)₂ and Pd(II)(acac)₂, which have lower solubility than the complex used in previous reports, are confirmed to be used for preparation. Preparation of CMS from the composite films and evaluation of gas permeation properties are under investigation.

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