Preparation of a Platinum and Palladium/Polyimide Nanocomposite Film as a Precursor of Metal-Doped Carbon Molecular Sieve Membrane via Supercritical Impregnation

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The synthesis of a Pt- and Pd-nanoparticle-dispersed polyimide film as a precursor for the preparation of a metal-doped carbon molecular sieve (CMS) membrane for hydrogen separation has been performed. Impregnation of Pt(II) acetylacetonate and Pd(II) acetylacetonate dissolved in supercritical CO_2 yielded Pt and Pd nanoparticles (diameters 12 and 5 nm, respectively) that were highly dispersed inside polyimide films under optimized conditions. The impregnation temperature and varieties of polyimide films strongly influenced the dispersion of the metal particles. The Pd-doped CMS membrane was successfully prepared from the polyimide and Pd(II) acetylacetonate composite. It showed good hydrogen separation performance.

Introduction

Hydrogen separation systems working at high temperatures have recently been attracting considerable attention in the fields of hydrogen energy systems and fuel cells. A high-temperature-proof hydrogen separation membrane will be a crucial material, since it will open the way to low-energy-consuming separation systems. The carbon molecular sieve (CMS) membrane is known as a good gas separation membrane with considerable resistibility to high temperatures.[1] The gas separation properties of CMS membranes can be controlled by doping metal particles having varying affinities to the gas in question.[2] Therefore, the hydrogen separation selectivity of a CMS is expected to be improved by inclusion of noble metals showing an affinity toward hydrogen.

CMS membrane is generally prepared by pyrolysis of polymer precursors, such as polyimide films. Doping of noble-metal precursor into the carbon membrane or polymer precursors followed by decomposition of the precursor or mixing conventional noble-metal particles into the polymers are the conceivable methods. However, both the homogeneous dispersion of the metal particles and the doping of significant amounts of the metals in the interior of the membrane are difficult by these methods.

In our novel approach, we applied the impregnation of organometallic compounds dissolved in supercritical CO_2 ($scCO_2$) followed by their decomposition. $ScCO_2$ has many advantages as an impregnating medium for polymers for the following reasons: (1) A high diffusivity of the impregnating substances into the polymers is expected due to the low viscosity of $scCO_2$ and its swelling effect on many polymers. (2) The solubility of solutes is easily controlled by pressure, allowing control of nucleation/precipitation of solute into polymers. (3) Impregnation can be performed under dry conditions without using organic solvents. Preparation of platinum nanoparticles in poly(4-methyl-1-pentene) and poly(tetrafluoroethylene),[3−5] silver nanoparticles on the surface of polyimide film,[6−7] and silver nanoparticles in poly(etherether ketone)[8] and poly(styrene-divinylbenzene)[9] have already been performed.

In this work, we investigated the preparation of novel metal-nanoparticle-dispersed polyimide films as precursors of the CMS membrane. Platinum and palladium were selected as doping metals owing to their high affinity toward hydrogen. Organometallic compounds, such as dimethyl(cyclooctadiene)platinum [Pt(II)(COD)-Me_2] as precursors of platinum particles[3] and 1,5-cyclooctadiensilver(I)-1,1,1,5,5,5-hexafluoroacetylacet-

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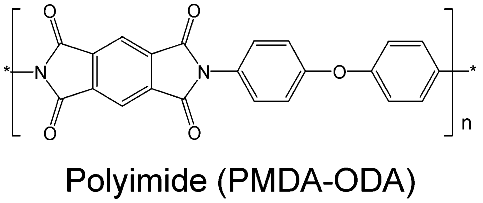

Figure 1. Chemical structure of the polyimide studied in this work.

onate[(Ag(I)(COD)(HFA)][6,7] with high solubility in $scCO_2$ and good sublimation properties, have all been used for the $scCO_2$ impregnation. These compounds, however, have relatively high toxicity and present handling difficulties due to their thermal and chemical instability.

In this work we resolved to create a more environmentally sustainable method by using acetylacetonato complexes, which are conventional, have low toxicity, and are inexpensive organometallic compounds, even though low solubilities in $scCO_2$ were anticipated. The solubilities of platinum(II) acetylacetonate [$Pt(II)(acac)_2$] and palladium(II) acetylacetonate [$Pd(II)(acac)_2$] in $scCO_2$ were investigated prior to preparation of the composite membrane. The effects of impregnation temperature and of the variety of the polyimide film were studied in order to obtain a composite film with high dispersion of noble-metal nanoparticles. The preparation of noble-metal-impregnated CMS and evaluation of their gas permeability were also studied.

Experimental Section

$Pt(II)(acac)_2$ (Aldrich, 99.99%) and $Pd(II)(acac)_2$ (Aldrich, 98%), without further purification, were used as the noble-metal sources. The solubility of these reagents in $scCO_2$ at 10−30 MPa and 313−473 K was measured using a flow type $scCO_2$ extraction system and gravimetry of extracted samples.[10] The UV−vis spectra of extracted samples dissolved in tetrahydrofuran were measured to confirm the stability of the acetylacetonate. For the determination of the melting and decomposing points of these chelates, differential scanning calorimetry (DSC) (Seiko Instruments, MAS-5800) analyses were performed under a nitrogen atmosphere. The observed melting point of $Pt(II)(acac)_2$ was 523 K, identical to the published value,[11] and its decomposing point was ca. 537K. $Pd(II)(acac)_2$, whose thermal property is not authorized, did not show a clear melting point. An endothermic DSC peak was noted at 523 K and decomposition was observed at almost the same temperature.

The polyimide film [pyromellitic dianhydride−4,4′-oxydianiline (PMDA−ODA)] (Figure 1) used in this work had been confirmed to be a good CMS membrane. Both conventional Kapton polyimide film 100H (Toray-Dupont Inc.) (KP) and a film synthesized by us (SY) were used for comparison. The SY film was derived from casting of poly(amide acid) dissolved in *N*,*N*-dimethylacetamide followed by thermal imidization at 473 K in vacuo. These films were 25 μm thick and 50 mm in diameter. Using a windowed high-pressure vessel, both films were confirmed to be stable in $scCO_2$ under our experimental conditions. Significant swelling, melting, or bubbling were not observed.

A batch-type high-pressure vessel (50 cm^3) was used for impregnation. Three sheets of KP or SY film and the acetylacetonate were sealed in the vessel without contacting each other. The amount of acetylacetonate was calculated from the solubility in $scCO_2$ to be 10 times the saturating amount in the vessel. The vessel was pressurized by introduction of CO_2 followed by heating. The impregnation was performed at 313−473 K for 3−24 h. The pressure was 19.6 MPa for all impregnation runs. After the impregnation, the pressure decreased rapidly by releasing CO_2. The acetylacetonate that precipitated on the film was washed with methanol, in which acetylacetonate is only slightly soluble.

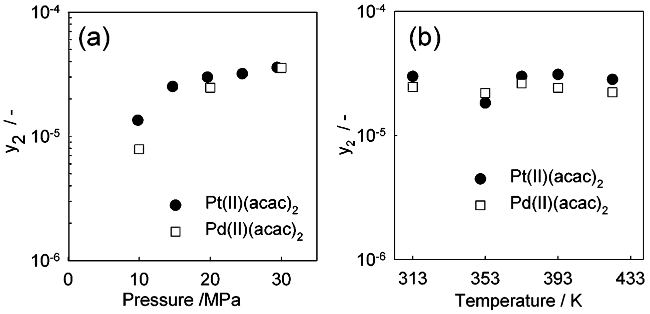

Figure 2. (a) Effect of pressure on the solubility of $Pd(II)(acac)_2$ and $Pt(II)(acac)_2$ in $scCO_2$ at 313K. (b) Effect of temperature on the solubility of $Pd(II)(acac)_2$ and $Pt(II)(acac)_2$ in $scCO_2$ at 19.6 MPa.

Pt and Pd particles were prepared by thermal decomposition of the acetylacetonate in air. The composite films were heat-treated in air at 573 K for 12 h to decompose the acetylacetonato complex. The metal content was measured by X-ray fluorescence analysis. The dispersion of the metal particles was evaluated using transmittance electron microscopy (TEM) (JEOL 2000FXII, 200 kV) with an energy-dispersive X-ray spectroscopy analyzer (EDS).

The CMS membrane was fabricated by pyrolysis of metal-impregnated polyimide films between graphite blocks at mainly 873−1273 K for 2 h with a heating rate of 10 K/min under a vacuum of 10^{-5} Torr.[12] All the membranes were allowed to cool to room temperature under each atmosphere. The gas permeability was measured at 373 K with a high-vacuum time-lag method[13,14] under a pressure difference of 0.1 MPa. Permeability values were calculated using the following equation

$$P = \frac{\mathrm{d}p}{\mathrm{d}t}\left(\frac{VT_0L}{p_0Tp_f\cdot A_m}\right) \qquad (1)$$

where P is the permeability expressed in Barrer [1 Barrer = 1×10^{-10} [$cm^3(STP)\cdot cm$]/[$cm^2\cdot s\cdot cmHg$], $\mathrm{d}p/\mathrm{d}t$ is the rate of the pressure increase at steady state, V is the volume, L is the membrane thickness, p_f is the feed pressure, T is the measurement temperature, A_m is the membrane area, and p_0 and T_0 are the standard pressure and temperature, respectively.

Results and Discussion

Solubility of $Pt(II)(acac)_2$ and $Pd(II)(acac)_2$. Figure 2a shows the experimental mole fraction solubility (y_2) of $Pt(II)(acac)_2$ and $Pd(II)(acac)_2$ in $scCO_2$ at 313 K. The solubilities of $Pt(II)(acac)_2$ and $Pd(II)(acac)_2$ were on the order of 10^{-5}, which is similar to that of the other acetylacetonates of bivalent metals.[15] Since the solubility was close to its limit at 20 MPa, the impregnating pressure was fixed at this value in the following experiments.

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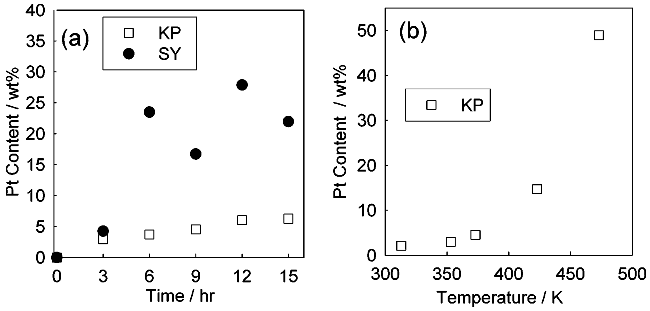

Figure 3. (a) Effect of impregnation time on Pt content of SY and KP film prepared at 373 K, 19.6 MPa. (b) Effect of the temperature on Pt content of composite KP film prepared at 19.6 MPa for 9 h.

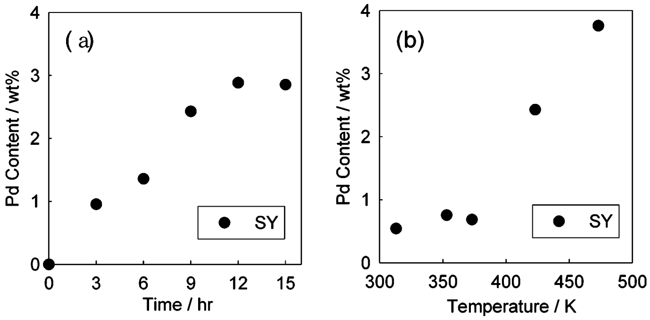

Figure 4. (a) Effect of impregnation time on Pd content of SY film prepared at 373 K, 19.6 MPa. (b) Effect of the temperature on Pd content of composite SY film prepared at 19.6 MPa for 9 h.

Figure 2b shows the effect of temperature on the solubility of Pt(II)(acac)$_2$ and Pd(II)(acac)$_2$. Both acetylacetonates were confirmed to be stable to at least 423K in scCO$_2$. The solubility of Pt(II)(acac)$_2$ and Pd(II)(acac)$_2$ was almost constant from 313 to 423 K. Extracts of samples of both acetylacetonates prepared at 473 K contained dark black powders insoluble in THF, suggesting decomposition of these chelates.

Noble-Metal Content in the Polyimide Film. Pt and Pd metal-dispersed polyimide films were successfully prepared. Figure 3 shows the effect of the impregnation time and temperature on the Pt loading of the composite film and Figure 4 shows that on the Pd loading. As shown in Figures 3a and 4a, the Pt and Pd contents were strongly dependent on impregnation time. The color of the film took on a brownish hue on increasing the metal content. The significant increase of Pt content with wobble observed in the SY film (Figure 3a) arises from the decomposition of polyimide film catalyzed by Pt particles during thermal treatment. KP film was more stable than SY film. A significant increase of the Pt content was also observed after long treatment time (Figure 3b). Decomposition of the polyimide film was not observed on Pd-impregnated samples.

Both Figures 3b and 4b indicate that the metal content strongly depends on the impregnating temperature. Since the solubility of the Pt(II)(acac)$_2$ and Pd(II)(acac)$_2$ were independent of the temperature, the increase of the metal content can be ascribed to the thermal alteration of the polyimide films.

Effect of Temperature on Particle Dispersion. Figure 5 shows TEM photographs of Pt-doped KP films prepared at different impregnation temperatures. All the particles shown in the micrographs were confirmed to contain Pt by EDS analysis. A small number of aggregated Pt particles were observed in specimens prepared at 353 K (Figure 5a). The dispersion of Pt aggregates was improved with an increase of the temperature, and the best dispersion was observed at 423 K (Figure 5b). At the higher temperature, 473 K, Pt particles were not observed inside the films, and aggregated particles were found on the surface of the polyimide (Figure 5c).

Similar results were obtained during Pd impregnation. Figure 6 shows TEM photographs of Pd-doped SY polyimide films prepared in the temperature range from 373 to 473 K. Pd particles in the polyimide film are more highly dispersed than Pt particles. The particle dispersion was quite good even in the inside of the film for the samples prepared at 373 K (Figure 6a) and 423 K (Figure 6b). The Pd particle size of samples prepared at 423 K was smaller than those prepared at 373 K, and the average particle diameter ($n = 150$) was 4.6 nm

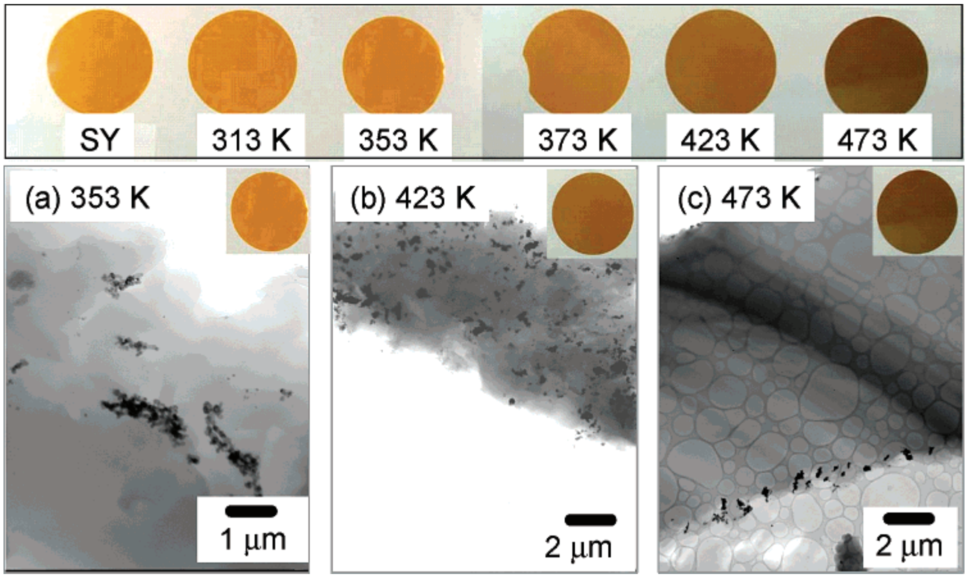

Figure 5. TEM Photographs of Pt-doped SY films prepared at (a) 353K, (b) 423K, and (c) 473 K. The impregnating pressure and time were 19.6 MPa and 9 h, respectively.

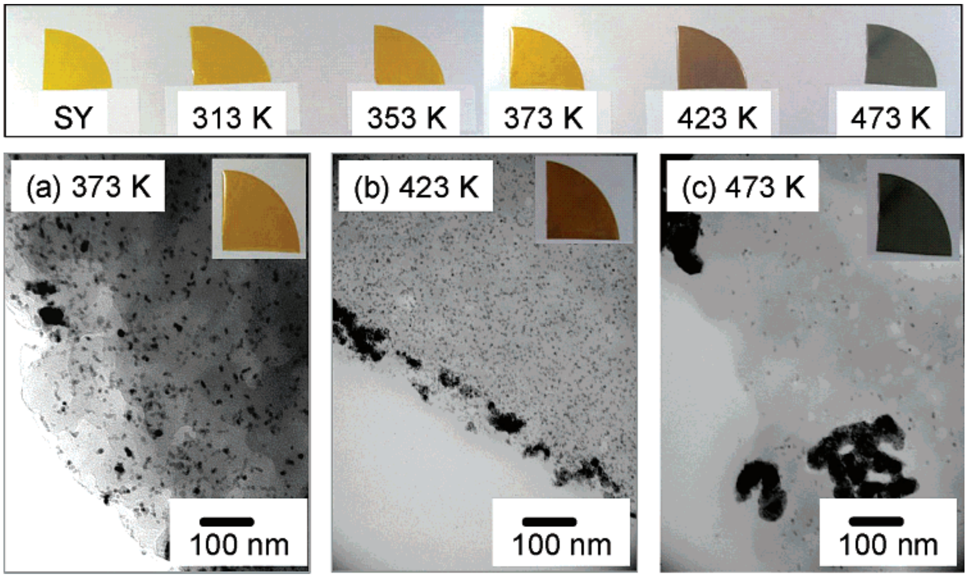

Figure 6. TEM Photographs of Pd-doped SY films prepared at (a) 373 K, (b) 423 K, and (c) 473 K The impregnating pressure and time were 19.6 MPa and 9 h, respectively.

(Figure 6b). Aggregated Pd particles were also observed on the surface. At the higher temperature, 473 K, large surface Pd particles were observed frequently, and the density of fine particles inside the film decreased (Figure 6c).

These differences of particle dispersion may be related to the diffusion of acetylacetonate complex into the polyimide network. As described, in the Experimental Section, we had confirmed that neither SY nor KP films showed significant swelling and melting phenomena in $scCO_2$ under our experimental conditions. However, the microscopic thermal relaxation either with or without $scCO_2$ swelling effect needs to consider. Surface precipitation at 473 K for both samples seems to be a consequence of thermal decomposition of the impregnating chelates. As described in the section on solubility measurements, decomposition of the chelates was observed at 473 K. If decomposition occurs, both solubility in $scCO_2$ and diffusion in the polyimide film will be drastically decreased and the decomposed chelates will precipitate on the surface of the film. The decomposition temperature under atmospheric pressure was, however, at least 523 K for both Pt(II)$(acac)_2$ and Pd(II)$(acac)_2$, as shown by the DSC analyses. Studies on the thermal decomposition of both chelates in $scCO_2$ are required for further clarification.

The reason Pd particles were highly dispersed could be related to the melting behavior of Pt(II)$(acac)_2$ and to chemical interactions with the carboxyl structures of polyimide. Pt(II)$(acac)_2$ has a clear melting point at 523K, whereas Pd(II)$(acac)_2$ showed an undivided melting and decomposing point in the thermal analysis in air. Therefore, aggregation of Pt(II)$(acac)_2$ during thermal treatment would be more prevalent than in Pd(II)$(acac)_2$. The possible interaction between Pd(II)$(acac)_2$ polymers was already mentioned in the study of Pd/block copolymer composite derived from Pd(II)$(acac)_2$.[16] Interaction between the carbonate in polyimide and Pd(II)$(acac)_2$ could conceivably diminish the growth and aggregation of the Pd particles.

Effect of the Type of Film. Figure 7 shows TEM photographs of Pt- and Pd-doped KP and SY films generated under the same impregnation conditions. Smaller Pt and Pd particle sizes and more homogeneous dispersion were observed in SY film than in KP film for both samples. The best Pt dispersion in polyimide was observed in an SY film impregnated at 523 K, where the average Pt particle size ($n = 46$) was 12 nm.

The difference between the KP and SY films is probably caused by the arrangement of the polymer network. The SY film was fabricated by casting the precursor solutions, whereas conventional KP film is made via a drawing process. The KP film therefore has a tighter and more inflexible polyimide network structure, hence inhibiting the diffusion of both acetylacetonate and $scCO_2$. Physical structures rather than chemical structural differences in polymers need to be carefully considered prior to $scCO_2$ impregnation.

CMS Membrane and Gas Permeability. Pt- and Pd-doped CMS membranes were successfully prepared by carbonization of acetylacetonate-impregnated SY and KP films. Figure 8 shows TEM images of Pd-doped CMS membrane prepared by calcination of Pd-doped SY film at 1273 K. Pd(II)$(acac)_2$ was impregnated into the SY precursor at 473 K, 19.6 MPa for 9 h. The Pd particles were dispersed all over the membrane as in SY film. Due to shrinkage during calcinations, the particle density in the membrane was higher than that in SY films. Large surface-aggregated particles were rare in the CMS. The majority of Pd particles were under 5 nm in diameter. These sizes were similar to that in the SY films. The structure of the carbon matrix was almost the same as the CMS without Pd doping.[1]

An example of gas permeability measurements on Pd-doped CMS is shown in Table 1. The permeabilities of both nitrogen and hydrogen were decreased on Pd-doped CMS samples, but blocking of nitrogen is more effective than hydrogen. As a result, its hydrogen selectivity was

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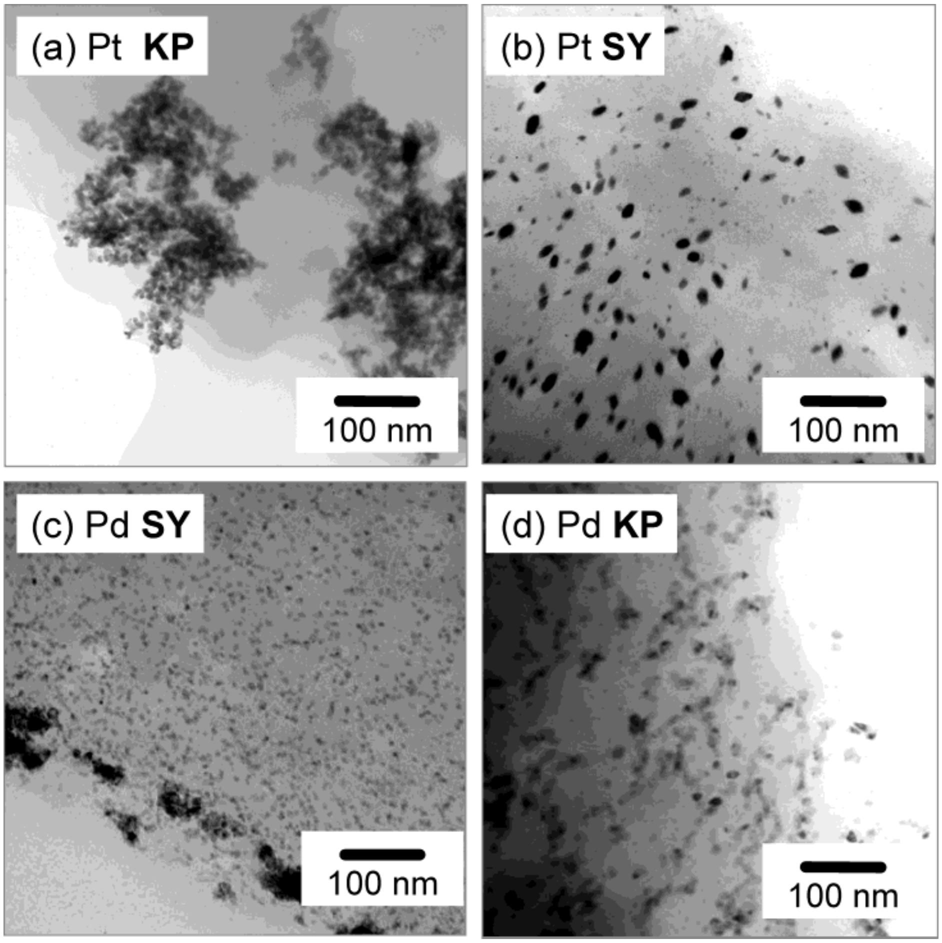

Figure 7. TEM photographs of (a) Pt-doped SY, (b) Pt-doped KP, (c) Pd-doped SY, and (d) Pd-doped KP film prepared at 423 K, 19.6 MPa for 9 h.

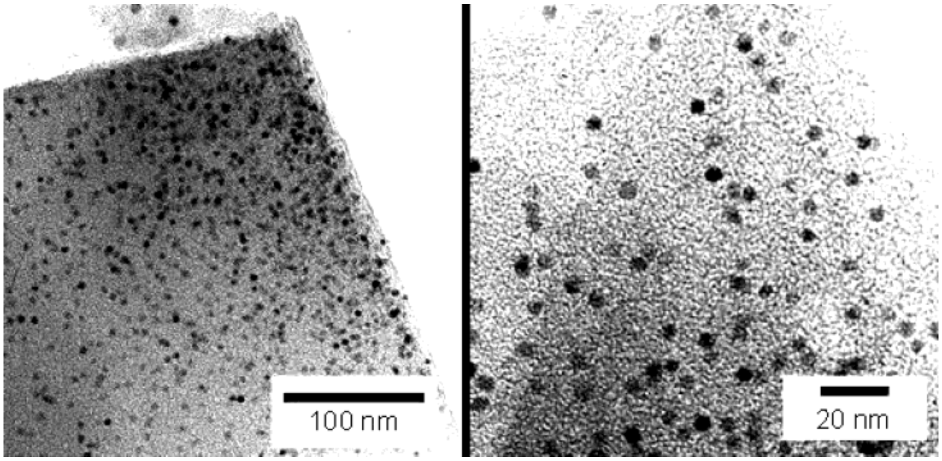

Figure 8. TEM photographs of Pd-doped CMS membrane prepared by carbonation of Pd-doped SY film (Pd(II)(acac)$_2$ was impregnated at 473 K, 19.6 MPa for 9 h) at 1273 K.

Table 1. Gas Permeability of Pd-Doped CMS Membrane Determined by the Time-Lag Method

	P_{H_2} (Barrer)	P_{N_2} (Barrer)	α[a]
CMS	49.4	0.15	330
Pd-CMS	34.4	0.0061	5640

[a] $a = P_{H_2}/P_{N_2}$.

17 times higher than that of CMS membrane. The Pd particles would act as a mass transport inhibiter of nitrogen.

Conclusions

Pt- and Pd-nanoparticle-doped polyimide films as precursors of CMS were successfully prepared by supercritical impregnation. Pt(II)(acac)$_2$ and Pd(II)(acac)$_2$ are confirmed to be useful in the preparation. We conclude that the decisive parameter for scCO$_2$ impregnation is relaxation of the polymer network. In the case that thermal relaxation of the polymer is effective, the thermally stable metal compounds, even though their solubility is low, were useful. We anticipate that many useful combinations of polymers and metal chelates, not only those useful for carbon membranes, could be generated by our method.

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