

Catalytic Hydrogenation and Gas Permeation Properties of Metal-Containing Poly(phenylene oxide) and Polysulfone

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SYNOPSIS

Metal-containing polymers, PPO-DPP-Pd, PPO-CPA-Pd, PSF-DPP-Pd, PSF-CPA-Pd (DPP = diphenylphosphinyl, CPA = *o*-carboxy phenyl amino), PPO-M (M = Pd, Cu, Co, Ni), and PSF-Pd, were prepared by incorporating metal chloride with either modified or unmodified poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and polysulfone (PSF). The Pd-containing polymers exhibit catalytic activity in the hydrogenation of cyclopentadiene under mild conditions (40°C, 0.1 MPa) both in alcohol solution and in the gas phase. The selectivity in the hydrogenation of diene to monoene in the gas phase can be controlled by adjusting the hydrogen partial pressure. The metal-containing polymers, PPO-M and PSF-Pd, can be cast easily into the membranes. The H₂/N₂ permselectivity for PPO-M is higher than that for unmodified PPO, whereas the permeability of H₂ changes slightly. The H₂ permeability and H₂/N₂ permselectivity for the PPO-Pd membrane are up to 67.5 barrers and 135, respectively. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Metal-containing polymeric materials have been studied extensively because of their potential applications as versatile materials.¹⁻⁶ Much effort has been expended in studying these materials as catalysts, which are presumed to combine the virtues of both homogeneous and heterogeneous catalysts in various chemical reactions such as hydrogenation, carbonylation, oxidation, and polymerization.⁷⁻¹⁰ It has been indicated that in these materials metal complexes or metal ions, surrounded by giant polymer chains, show interesting physical properties and chemical reactivities that are different from those of the corresponding ordinary metal complexes or metal ions. On the other hand, many studies have also reported that the doping or coordination of metal ions or complexes, which may selectively and reversibly coordinate gases, into polymers is one approach to improve the permeability and permselectivity of the polymeric membranes.¹¹⁻²³

However, up to now, there has been no report dealing with metal-containing polymeric materials

to be used in both catalytic reactions and gas separation. Recently, we prepared several metal-containing polymeric materials by incorporating transition metal chlorides into modified or unmodified poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and polysulfone (PSF). The catalytic activities in the hydrogenation of cyclopentadiene and isoprene as well as the H₂ and N₂ permeabilities of these polymeric materials have been investigated.

EXPERIMENTAL

Preparation of Materials

Preparation of PPO-DPP-Pd and PSF-DPP-Pd

The brominated PPO substituted with bromine at aromatic carbon (PPO, Shanghai Institute of Synthetic Resin, $M_w = 14,000$), which was prepared according to Ref. 24, was treated with LiPPh₂ (Ref. 25) under nitrogen atmosphere and stirred for 2 h at room temperature. The phosphinated PPO was precipitated in ethanol and dried in vacuum (PPO-DPP, P content 0.2 wt %). It was then stirred in the refluxing ethanol-benzene (3 : 1) solution of PdCl₂ for 5 h. After filtration, washing, and drying in vacuum, the Pd-containing PPO (PPO-DPP-Pd,

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Pd content 0.51 and 1.90 wt %, respectively) was obtained. The Pd-containing PSF (PSF, Dalian Plastic Factory, $M_w = 3900$), PSF-DPP-Pd (Pd content 0.4 wt %), was prepared in the same way as mentioned above.

Preparation of PPO-CPA-Pd and PSF-CPA-Pd

The brominated PPO substituted with bromine at the benzylic carbon, which was prepared according to the literature,²⁶ was stirred in the refluxing ethanol solution of anthranilic acid for 10 h. The product was washed with ethanol and dried in vacuum and the N-containing PPO (PPO-CPA, N content 2 wt %) was obtained. This PPO-CPA was then refluxed in the ethanol solution of PdCl₂ for 3 h. The resulting product was washed with ethanol and dried in vacuum and the Pd-containing PPO (PPO-CPA-Pd, Pd content 0.6 wt %) was obtained. The Pd-containing PSF (PSF-CPA-Pd, Pd content 0.4 wt %) was prepared by the reaction of chloromethylated PSF (Cl content 4.5 wt %, prepared according to Ref. 27) with anthranilic acid in methanol, and the product was then treated with PdCl₂ in ethanol in the same way as mentioned above.

Preparation of PPO-M (M = Pd, Co, Cu, and Ni) and PSF-Pd

A mixture of MCl₂, PPO, and ethanol was stirred for 10 h at refluxing temperature. After filtration, the product was washed with ethanol several times until the filtrate became colorless, then dried in vacuum, and PPO-M was obtained. The PSF-Pd was prepared from the incorporation of PSF with PdCl₂ in ethanol-benzene (3 : 1) in the same way.

Hydrogenation

Hydrogenation of Cyclopentadiene in Solution

The hydrogenation was carried out in a 50 mL three-necked, jacketed bottle closed with a self-sealing silicon rubber cap, connected to the vacuum, hydrogen lines, and constant pressure gas buret. The temperature of the circulating water passing through the jacket was maintained by a thermostat. After the catalyst was added and the atmosphere was replaced with hydrogen, ethanol was injected and stirred for 20 min. Then, cyclopentadiene was added and hydrogen uptakes were followed by a constant-pressure gas buret. The products were analyzed by gas chromatography.

Hydrogenation of Olefins in the Gas Phase

The hydrogenation was carried out in a reactor connected to a circulating pump, mercury manometer, and constant pressure gas buret. The total volume of the reaction system was 400 mL and the circulation speed was 120 mL/min. After the catalyst (50 mg) was placed in the reactor, the atmosphere of the reaction system was removed by evacuation. Then, cyclopentadiene (or isoprene), H₂, and N₂ were added, respectively, according to the required partial pressures of the feed, which were measured by the mercury manometer. By starting the gas circulation and connecting the reaction system with the constant-pressure gas buret, the hydrogen uptakes were followed by the gas buret and the products were analyzed by gas chromatography at different time intervals.

Preparation of Membranes

A chloroform solution of the metal-containing polymer (in 12 wt %) was cast on a glass plate. After the evaporation of solvent at room temperature for 24 h, a colored membrane was obtained. The permeation measurements of the membrane were taken with a stainless-steel cell modeled after that reported in the literature.²⁸ The cast membranes were cut to appropriate size and placed in the cell and tested for small leaks. Permeation rates were measured several times for each membrane and repeated at least twice for another membrane from the same casting solution.

RESULTS AND DISCUSSION

Catalytic Hydrogenation Properties of Pd-containing PPO and PSF

The catalytic activities and selectivities of PPO-DPP-Pd, PPO-CPA-Pd, PSF-DPP-Pd, PSF-CPA-Pd, PPO-Pd, and PSF-Pd in the hydrogenation of cyclopentadiene in ethanol under mild conditions (40°C, 0.1 MPa) were investigated and the results are shown in Table I. These Pd-containing polymers, except PSF-Pd, are effective catalysts for the selective hydrogenation of cyclopentadiene. The activities of the Pd-containing PSF polymers are higher than those of the Pd-containing PPO polymers, but the latter display better selectivity for cyclopentene than do the former. It is also noteworthy that the activity of PPO-Pd is lower than that of PPO-DPP-Pd and that PSF-Pd is inactive for this

Table I Hydrogenation of Cyclopentadiene Catalyzed by Pd-containing PPO and PSF in Ethanol

| Pd-containing Polymer | Pd (μmol) | Initial Activity (mol H ₂ /mol Pd min) | Selectivity ^a (%) |
|-----------------------|------------------------|---|------------------------------|
| PPO-DPP-Pd | 2.5 | 10.4 | 97 |
| PPO-CPA-Pd | 2.8 | 1.0 | 87 |
| PPO-Pd | 8.9 | 2.7 | 98 |
| PSF-DPP-Pd | 1.9 | 26.4 | 88 |
| PSF-CPA-Pd | 1.9 | 5.5 | 77 |
| PSF-Pd | 7.8 | 0.0 | — |

^a Selectivity for cyclopentene (cyclopentene/cyclopentene + cyclopentane) when the moles of H₂ uptake equal the moles of cyclopentadiene added. Reaction conditions: catalyst 50 mg; cyclopentadiene 1 mL. Solvent: absolute ethanol 10 mL, 40°C, 1.0×10^5 Pa.

reaction. These results indicate that the polymer matrix and the functional groups in the polymer matrix strongly affect the activity and selectivity of the Pd-containing polymers in the hydrogenation of cyclopentadiene.

The catalytic behaviors of PPO-DPP-Pd and PPO-Pd in the hydrogenation of cyclopentadiene and isoprene in the gas phase at 40°C under different hydrogen partial pressures were also investigated. The results are given in Tables II and III. It is shown that the activities of catalysts are increased with increase of hydrogen partial pressure, but the selectivities for diene hydrogenated to monoene are decreased. This may be related to the fact that with the increase of hydrogen partial pressure the hydrogenation rate of monoene formed from diene is increased, indicating that the monoene has been hydrogenated before it dissociates from the Pd active species. These data also indicate that the selectivity for the formation of monoene can be controlled by adjusting the hydrogen partial pressure of the reaction system.

The data shown in Tables I and II also reveal that the activity and selectivity of the catalysts in the hydrogenation of cyclopentadiene are lower in the gas phase than those in the ethanol solution. One reason for the higher hydrogenation rate in solution is that the concentration of cyclopentadiene in solution (1.22 mmol/mL) is much higher than that in the gas phase (5.0×10^{-3} mmol/mL). The other reason is that, unlike the reaction in solution, the polymeric matrix is not swollen in the gas-phase reaction. Therefore, only those Pd species that locate on the surface of the polymer can act as a catalyst. It is generally accepted that the selectivity of diene hydrogenated to monoene depends on the efficiency of diene inhibiting the further hydrogenation of monoene because diene is more strongly coordinated on palladium species than is the corresponding monoene. The higher selectivity of the formation of cyclopentene in solution may be due to the fact that very low solubility of hydrogen in ethanol (3.1×10^{-3} mmol/mL) leads to a low hydrogen concentration around the Pd active species. In this case,

Table II Hydrogenation of Cyclopentadiene Catalyzed by PPO-DPP-Pd and PPO-Pd in the Gas Phase

| Pd-containing Polymer | Hydrogen Partial Pressure (Pa) | Initial Activity (mol H ₂ /mol Pd min) | Selectivity ^a (%) |
|-----------------------|--------------------------------|---|------------------------------|
| PPO-DPP-Pd | 8.7×10^4 | 4.30 | 90.0 |
| | 3.9×10^4 | 1.30 | 92.0 |
| | 1.6×10^4 | 0.60 | 95.0 |
| PPO-Pd | 7.9×10^4 | 0.84 | 90.4 |
| | 3.9×10^4 | 0.28 | 93.2 |
| | 1.6×10^4 | 0.15 | 96.4 |

^a Selectivity for cyclopentene when the conversion of cyclopentadiene is 50%. Reaction conditions: catalyst 50 mg (Pd content, 1.90 wt %); partial pressure of cyclopentadiene 1.3×10^4 Pa, 40°C. The remaining gas is nitrogen, which makes a total pressure of 1.0×10^5 Pa.

Table III Hydrogenation of Isoprene Catalyzed by PPO–DPP–Pd and PPO–Pd in the Gas Phase

| Pd-containing Polymer | Hydrogen Partial Pressure (Pa) | Initial Activity (mol H ₂ /mol Pd min) | Selectivity ^a (%) |
|-----------------------|--------------------------------|---|------------------------------|
| PPO–DPP–Pd | 7.9 × 10 ⁴ | 7.90 | 91.5 |
| | 3.9 × 10 ⁴ | 3.10 | 94.0 |
| | 1.6 × 10 ⁴ | 1.30 | 97.2 |
| PPO–Pd | 7.9 × 10 ⁴ | 0.35 | 90.6 |
| | 3.9 × 10 ⁴ | 0.21 | 93.3 |
| | 1.6 × 10 ⁴ | 0.10 | 94.8 |

^a Selectivity for monoene when the conversion of isoprene is 30%. Reaction conditions are the same as those in Table II.

cyclopentadiene (the concentration of which is much higher than that of hydrogen [244 : 1]) can be coordinated easily and inhibit efficiently the further hydrogenation of cyclopentene, whereas in the gas-phase reaction, the concentration ratios of diene to hydrogen (1 : 6, 1 : 3, and 1 : 1.2) are low, so the inhibition effect of cyclopentadiene is no longer as strong.

Permeation Studies with Metal-containing PPO and PSF

The metal-containing PPO and PSF materials were used to cast membranes. Unfortunately, PPO–CPA–Pd and PSF–CPA–Pd cannot be cast into membranes and the membranes made of PPO–DPP–Pd and PSF–DPP–Pd are fragile. However, PPO–M (M = Co, Cu, Ni, or Pd) and PSF–Pd can be cast easily into membranes. The permeability of H₂ and N₂ in unmodified PPO and PSF and the metal-modified membranes are presented in Table IV. It is noticed

that the incorporation of metal chlorides such as PdCl₂, CuCl₂, CoCl₂, and NiCl₂ into PPO membranes results in a decrease in the permeability of N₂ and an increase in the H₂/N₂ permselectivity. The decrease of permeability of N₂ can be understood as a result of the loss in free volume available for solution of gas in the membrane by the incorporation of metals with the polymer. This effect is less pronounced in the case of a small molecule, such as hydrogen, than it is in nitrogen. The permeability of H₂ in PPO–Pd and PPO–Ni membranes is higher than that in the unmodified PPO membrane. Since hydrogen can be easily coordinated with Pd and Ni species, the higher permeability in PPO–Pd or PPO–Ni membranes can be explained by the modified dual-mode transport theory as that described by Nishide et al.¹²: the Henry's law sorption of H₂ to the polymer domain and an additional Langmuir sorption to the polymer–Pd (or Ni) species. The hydrogen transport is expected to be accelerated by this additional Langmuir mode in addition to the

Table IV Permeability and Permselectivity of Metal-containing PPO and PSF

| Metal-containing Polymer | Metal Content (wt %) | Permeability (P) ^a | | Selectivity (α _{H₂/N₂)} |
|--------------------------|----------------------|-------------------------------|----------------|--|
| | | H ₂ | N ₂ | |
| PPO | 0.00 | 60.6 | 6.00 | 10 |
| PPO–Co | 0.31 | 32.3 | 0.60 | 54 |
| PPO–Ni | 0.47 | 100.0 | 3.70 | 27 |
| PPO–Cu | 0.66 | 47.0 | 1.90 | 25 |
| PPO–Pd | 0.38 | 80.8 | 2.60 | 31 |
| PPO–Pd | 0.58 | 49.4 | 1.00 | 49 |
| PPO–Pd | 1.90 | 67.5 | 0.50 | 135 |
| PSF | 0.00 | 5.0 | 0.15 | 33 |
| PSF–Pd | 1.65 | 3.0 | 0.10 | 30 |

^a Unit of P, barrer (10⁻¹⁰ cm³ [STP] cm/cm² S cmHg); driving pressure 1 MPa, room temperature.

Henry mode. On the other hand, the PSF-Pd membrane exhibits no advantage over pure PSF membrane with respect to H_2 permeability and H_2/N_2 permselectivity, just as the incorporation of $RuCl_3$ into cellulose acetate membrane has no effect on the H_2/CO permselectivity reported by Feldman et al.¹⁶ These results reveal that the effect of incorporating metal compounds into polymeric membranes on the permeability and permselectivity of gases is influenced both by the properties of metal compounds and the polymer matrix.

The data shown in Table IV illustrate that the H_2/N_2 permselectivity of the PPO-Pd membrane is increased with increase of the Pd content, while the permeability of H_2 is changed only slightly. Similar phenomenon has been also reported by Tsuchida et al. on the transport of oxygen in the membranes of the polymer-coordinated cobalt Schiff base.¹³ When the Pd content is 1.9 wt %, the H_2/N_2 permselectivity of the PPO-Pd membrane is up to 135. It is much higher than that of the unmodified PPO membrane.

CONCLUSIONS

The incorporation of metal chlorides such as $CuCl_2$, $CoCl_2$, $NiCl_2$, and $PdCl_2$ into PPO membranes can enhance the H_2/N_2 permselectivity. The Pd-containing PPO exhibits both catalytic hydrogenation activity and good H_2-N_2 separation property. The H_2/N_2 permselectivity for PPO-Pd is much higher than that for unmodified PPO, while the H_2 permeability is changed slightly. The selectivity of PPO-Pd in the catalytic hydrogenation of diene to monoene in the gas phase can be controlled by adjusting the hydrogen partial pressure. It is also shown that PPO-CPA-Pd and PSF-CPA-Pd cannot be cast into membranes and the membranes made of PPO-DPP-Pd and PSF-DPP-Pd are fragile, but they are very active catalysts in the hydrogenation of cyclopentadiene.

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