

Catalytic Behaviors and Gas Permeation Properties of Palladium-Containing Phenolphthalein Poly(ether sulfone)

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SYNOPSIS

Palladium supported on a high-temperature-withstanding polymer, phenolphthalein poly(ether sulfone) (PES-C), exhibits very high catalytic activity both in the carbonylation of allyl bromide and in the hydrogenation of 1-octene at 40°C and atmospheric pressure. The initial activities are up to 345 mol CO/mol Pd min and 493 mol H₂/mol Pd min, respectively. The polymer-supported palladium catalysts prepared by refluxing the mixture of PdCl₂ and PES-C immersed in benzene/ethanol ($\frac{1}{3}$, v/v) prior to the preparation of the catalyst show higher catalytic activity than those obtained by refluxing the mixture of PdCl₂ and PES-C in benzene/ethanol. The Pd-containing PES-C membranes made from the polymer-supported palladium catalysts are endowed with a very specific permeability of H₂ and the corresponding Pd-containing membrane catalysts can also exhibit considerable catalytic activity for the hydrogenation of 1-octene. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Metal-containing polymeric materials can be prepared by chemically bonding a transition-metal compound to a polymer or by blending a transition-metal complex and a polymer.^{1,2} These materials have been extensively studied as catalysts which lie in between those generally classified as "heterogeneous" and those classified as "homogeneous."³⁻⁵ Generally speaking, can polymers be used as the suitable supports of transition-metal compounds only after they are modified by introduction of ligating atoms in their polymer chains.⁶⁻⁹ It has been indicated that in these metal-containing 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. Recently, studies on the permeation

or separation by means of metal-containing polymeric materials have shown 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.¹⁰⁻¹⁴ Especially, explorations on catalytic polymeric membrane reactors involving permeation of gases have begun to attract more and more attention.^{2,15,16} However, up to now, there have been only a few reports to study both the catalytic behaviors and gas permeation of metal-containing polymeric materials.^{9,16} There is no question that it is challenging work to investigate the metal-containing polymeric materials endowed with catalytic and separative properties.

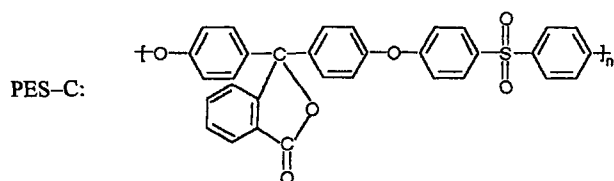
As one part of our research on catalytic polymeric membrane reactors, we have been searching for the polymeric materials which can be easily cast into membranes and used as the support of transition-metal catalysts.^{9,16,17} PES-C itself is a membrane-forming polymeric material and there are lactonate groups with a fair coordination ability in its polymer chains. In addition, PES-C is endowed with a high-temperature-withstanding property that is very im-

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portant for a polymeric material to be used to build a catalytic polymeric membrane reactor. It seems that PES-C is a potential material for a catalytic polymeric membrane reactor. In this article, the properties for PES-C to be used as the support of polymer-supported palladium catalysts and the gas permeation and catalytic properties of the Pd-containing PES-C membranes were investigated. Some interesting results were obtained.

EXPERIMENTAL

PES-C ($\eta = 0.68$) was purchased from Changchun Institute of Applied Chemistry, Chinese Academy of Sciences.¹⁸ The polymer was dried at 120°C for 4 h prior to use. Other reagents were used as supplied.



Preparation of the Polymer-supported Palladium Catalysts

Method a: To the mixed solvent of benzene/absolute ethanol ($\frac{1}{3}$, v/v), PES-C and PdCl₂ were added and then the mixture was refluxed for 4 h with vigorous stirring. After allowing it to cool, the mixture was filtered. The solid was washed with benzene and absolute ethanol successively and then extracted with absolute ethanol for 2 h by using a Soxhlet extractor. After the solvent was evaporated at room temperature, the solid was dried at 110°C. Thus, the polymer-supported palladium catalyst was obtained. **Method b:** To a mixture of benzene/absolute ethanol ($\frac{1}{3}$, v/v) and PES-C immersed in this solvent for 20 h at room temperature, PdCl₂ was added. The mixture was refluxed for 4 h and the solid was treated in the same way as mentioned in Method a.

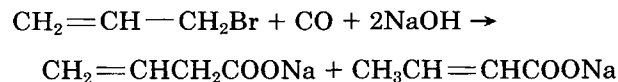
Preparation of Palladium-containing Membranes

The transparent membrane of pure PES-C was prepared by dissolving it in CHCl₃. The solution was filtered and degassed under reduced pressure and then the thick solution of the polymer (PES-C concentration ca. 12 wt %) was cast on a glass plate with a scalpel at 25°C. After slow evaporation of the solvent in air, the glass plate was immersed in water

and the membrane was taken from the glass plate. Water on the membrane was removed by filter paper and the membrane was then dried under an IR lamp. Its thickness was 29 μm . The Pd-containing PES-C membranes were similarly made by dissolving the polymer-supported palladium catalysts in chloroform (PES-C concentration ca. 12 wt %). Their thickness was in the range of 15–25 μm . The permeation measurements of the membrane were taken with a stainless-steel cell modeled after that reported in the literature.¹⁹ 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. The membrane catalysts were obtained by cutting the Pd-containing membranes into chips.

Carbonylation of Allyl Bromide

The carbonylation was carried out in a 60 mL three-necked, jacketed bottle closed with a self-sealing silicon rubber cap and connected to the vacuum, carbon monoxide lines, and a constant pressure CO gas buret. After the catalyst and NaOH were added and the atmosphere was replaced with CO, the solvent was added. The mixture was stirred at the reaction temperature for 30 min; then, allyl bromide was added through the silicon rubber cap via a syringe. After the reaction was complete or stopped and the reaction mixture cooled to room temperature, the aqueous phase was acidified with excess hydrochloric acid and then used for the analysis of butenoic acids by HPLC (Shimadzu LC-5A, 4.6 mm i.d. \times 25 cm Zorbax ODS column, ion pair mobile phase containing H₃PO₄/KH₂PO₄: [v/v] MeOH : H₂O = 50 : 50) and analysis of allyl alcohol by GC (2 m DEGS column). The organic layer was used to determine the unreacted substrate by GC. The carbonylation was conducted according to the following equation:



Hydrogenation of 1-Octene

The reactor was the same as that for the carbonylation of allyl bromide. After the atmosphere of the reactor containing the catalyst was replaced by hydrogen, the reactor was connected to a constant

Table I Preparation of the Polymer-supported Palladium Catalysts

Catalyst	Method of Preparation	Pd Content (Wt %)	Corresponding Membrane Catalysts
P-1 ^a	<i>a</i>	0.20	M-1
P-2 ^a	<i>b</i>	0.28	M-2
P-3 ^a	<i>a</i>	0.04	M-3
P-4 ^a	<i>b</i>	0.05	M-4
Pd-PPO ^b	<i>a</i>	0.50	—
Pd-PSF ^c	<i>a</i>	0.50	—

^a The polymeric support is PES-C.

^b PPO = poly(2,6-dimethyl-1,4-phenylene oxide).

^c PSF = polysulfone.

pressure H₂ buret and then the solvent was added. After the mixture was stirred at the reaction temperature for 30 min, 1-octene was added. The reaction was monitored by H₂ uptake. The liquid samples were analyzed by GC.

RESULTS AND DISCUSSION

The data in Table I indicates that under the same conditions the polymeric support (PES-C) immersed in benzene/ethanol prior to the preparation of the catalyst could support more palladium species than could the polymer which was not immersed before use. The reason may be that the sufficient swelling of the polymer prior to the preparation of the catalyst exposes more ligating groups originally embedded in the body of the polymer and then leads to a more effective interaction between the ligating atoms in the polymer chains and the palladium species, which results in an increase of the content of the supported palladium.

Polymers can be used as the supports of transition-metal complex catalysts. The polymer-supported transition-metal catalysts usually exhibit poor catalytic activity and stability (sometimes no activity) when the polymeric supports contain only ligating atoms with a weak coordination ability in their polymer chains. Only after being modified by introduction of ligating groups containing phosphorus, sulfur, nitrogen, or oxygen atoms can these functionalized polymers be used as the suitable supports. It can be seen from Tables II and III that the polymer-supported palladium catalysts (Pd-PPO or Pd-PSF) prepared by refluxing the mixture of PdCl₂ and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) or polysulfone (PSF) in benzene/ethanol showed nearly no catalytic activity for the carbonylation of allyl bromide and hydrogenation of 1-octene at 40°C and atmospheric pressure. Due to the very weak coordination ability of the oxygen atoms of the ether bonds and sulfur atoms of the sulfone groups in the polymer chains of PPO and PSF to transition-metal atoms, the palladium species in Pd-PPO and Pd-

Table II Carbonylation of Allyl Bromide Catalyzed by the Polymer-supported Palladium Catalysts

Catalyst	Initial Activity (mol CO/mol Pd min)	Conversion ^a (%)	Isomer Ratio ^b ($\beta, \gamma/\alpha, \beta$)	Yield of Butenoic Acids (%)
P-1	66	87 (330)	1.9	79.3
P-2	68	97 (330)	3.8	93.2
P-3	345	84 (480)	4.3	78.3
P-3 ^c	334	92 (480)	6.7	88.0
P-4	219	80 (480)	4.0	75.7
Pd-PPO	Nil	— (300)	—	—
Pd-PSF	Nil	— (300)	—	—

^a The values in parentheses are the time for a given conversion of allyl bromide (in min).

^b $\beta, \gamma/\alpha, \beta$ is the mole ratio of β, γ -butenoic acid to α, β -butenoic acid.

^c Twenty milligrams of SnCl₂·2H₂O was added. Reaction conditions: 0.1 MPa, 40°C; catalyst, 40 mg; NaOH, 25 mmol; solvent, benzene (10 mL) + water (10 mL); allyl bromide, 1 mL.

Table III Hydrogenation of 1-Octene Catalyzed by the Polymer-supported Palladium Catalysts and Membrane Catalysts

Catalyst	Initial Activity (mol H ₂ /mol Pd min)	Conversion (%)	Selectivity (%)	
			<i>n</i> -Octane	2-Octene + 3-Octene
P-1	95	92 (240)	67.8	32.2
P-2	179	97 (240)	91.0	9.0
P-3	493	84 (300)	73.1	26.9
P-4	389	92 (300)	89.4	10.6
M-1	17	51 (240)	48.1	51.9
M-2	18	62 (240)	47.9	52.1
M-3	83	49 (300)	45.0	55.0
M-4	81	66 (300)	44.0	56.0
Pd-PPO	Nil	— (300)	—	—
Pd-PSF	Nil	— (300)	—	—

Reaction conditions: 0.1 MPa, 40°C; catalyst, 40 mg; absolute ethanol, 10 mL; 1-octene, 1 mL.

PSF catalysts were easily dissociated and eluted in the course of the reaction, these types of catalyst showed only very poor catalytic activity and were easily deactivated. It is known that PPO and PSF can be used as the suitable supports of transition-metal catalysts after active ligating atoms (or groups) were introduced into their polymer chains^{9,17} and so can polystyrenes.^{6,7} It can be expected that PES-C may be a suitable support to prepare a polymer-supported transition-metal catalyst according to its structural features.

Carbonylation of Allyl Bromide Catalyzed by the Polymer-supported Palladium Catalysts

The carbonylation of allyl bromide catalyzed by transition-metal compounds offers a synthetic method of β,γ -unsaturated butenoic acid, but this method usually needs relatively high CO pressure, and the selectivity for the desired product was moderate.²⁰ In view of the application, the use of polymer-supported palladium catalysts is an approach to improve the catalytic properties of the corresponding homogeneous catalysts.

It can be seen from Table II that in the cases using the catalysts containing relatively high Pd contents (0.20–0.28 wt %), the P-2 catalyst prepared by Method *b* exhibited higher catalytic activity and selectivity for β,γ -butenoic acid than did its corresponding analog (P-1) prepared by Method *a*, but in the cases using the catalysts with very low Pd contents (0.04–0.05 wt %), the catalysts prepared by different methods showed comparable catalyst efficiency in spite of different initial activities. These

results can be understood as follows: (a) In the case of using a catalyst containing a relatively high content of palladium, more palladium species can be available on the surfaces of the catalyst in the course of the reaction; and (b) on the surfaces of the catalysts with very low Pd contents, the content of the available palladium species may be comparable because more palladium species were embedded in the body of the polymeric support immersed prior to the preparation of the catalyst. An increase of the available palladium species may result in an increase in the catalytic activity. The additive SnCl₂ · 2H₂O can improve the catalytic activity of the polymer-supported catalyst for the carbonylation. As compared with the reported homogeneous catalysts^{21,22} and other polymer-supported transition-metal catalyst systems,²³ these polymer-supported palladium catalysts with low Pd contents showed much higher catalytic activity and efficiency.

Hydrogenation of 1-Octene

Hydrogenation of 1-Octene Catalyzed by the Polymer-supported Palladium Catalysts

1-Octene can be easily isomerized to the internal octenes, which, in turn, inhibit the hydrogenation of the substrate (Fig. 1). The preparation of the catalysts showed obvious influences on the catalytic activity of these catalysts (Table III). The catalysts prepared by Method *b* exhibited much higher catalytic activity than did those prepared by Method *a*, although the initial activity of catalyst P-3 was higher than that of catalyst P-4. The effect of sol-

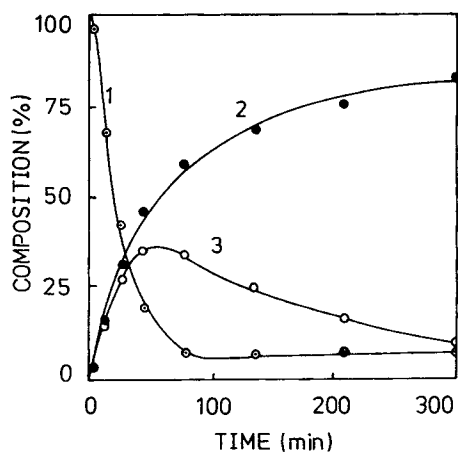


Figure 1 Hydrogenation of 1-octene catalyzed by catalyst P-4: (1) 1-octene; (2) *n*-octane; (3) 2-octene + 3-octene. The reaction conditions are shown in Table III.

vents on the hydrogenation is very obvious. For example, catalyst P-2 exhibited only poor catalytic activity for the hydrogenation of 1-octene in benzene/ethanol (Fig. 2). The excessive swelling of PES-C in benzene/ethanol easily led to a gathering of the Pd-PES-C catalyst which may, in turn, result in an assembly of the catalytically active palladium species and then a deactivation of the catalyst. Decreasing the content of benzene in the mixed solvent can reduce the excessive swelling of the polymer-supported palladium catalyst and then improve the catalytic activity for the hydrogenation and lessen the isomerization of the substrate. To some extent, the optimum catalytic activity of the polymer-supported palladium catalyst (Fig. 2) is attributed to the fairly favorable swelling of the polymeric support in ethanol, which is also in accordance with the reported results.²⁴

Hydrogenation of 1-Octene Catalyzed by the Pd-containing Membrane Catalysts

As compared with their corresponding polymer-supported palladium catalysts, the Pd-containing membrane catalysts showed much lower catalytic activity for the hydrogenation of 1-octene (Table III and Fig. 3). Using the membrane catalysts, 1-octene was easily isomerized to the internal octenes. The kinetic curve of hydrogenation indicates that the membrane catalyst is endowed with good stability, which may be attributed to a more even distribution of palladium species on the surfaces and more effective coordination of the palladium species to the ligating atoms in the polymer chains than to

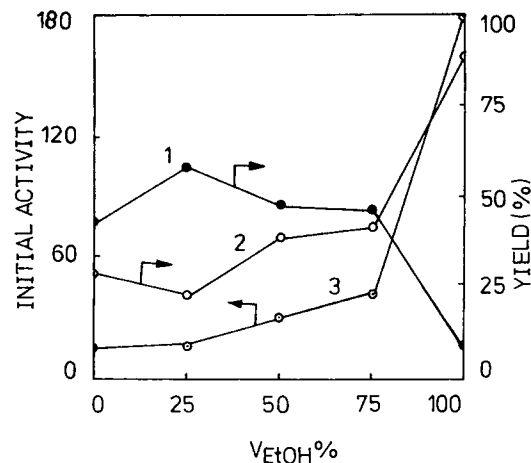


Figure 2 Effect of solvents on the hydrogenation of 1-octene catalyzed by catalyst P-2: (1) 2-octene + 3-octene; (2) *n*-octane; (3) initial activity. Reaction time is 240 min; other reaction conditions are the same as those shown in Table III.

those of the polymer-supported catalyst. For the polymer-supported catalysts, we confirmed by the TEM technique that the palladium species were distributed mainly on the surfaces of the polymeric support,¹⁷ but for the homogeneous membrane catalysts, the palladium species were evenly distributed on the surfaces and in the body of the polymeric support. In addition, the available surface area of the membrane catalyst is much smaller than that of the polymer-supported catalyst. These differences led to such a result that the catalytically active palladium species in the course of the reaction are more

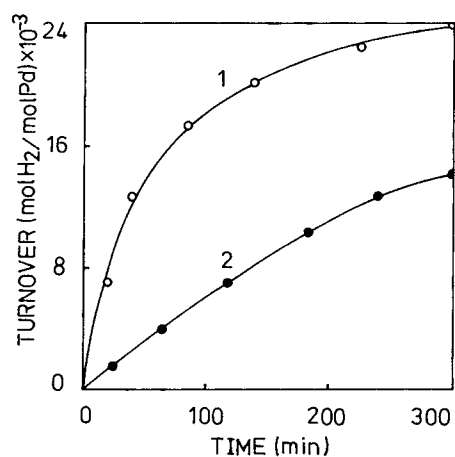


Figure 3 Hydrogenation of 1-octene catalyzed by the polymer-supported catalyst and its corresponding membrane catalyst: (1) polymer-supported catalyst P-4; (2) membrane catalyst M-4.

readily available from the polymer-supported catalyst than from the membrane catalyst. Therefore, the membrane catalyst usually gave a lower catalytic activity than did the polymer-supported catalyst.

Gas Permeation Properties of Pd-containing PES-C Membranes

The Pd-containing PES-C can be easily cast into membranes. It is noticed from Figure 4 that the incorporation of palladium species into PES-C membranes improved the permeability of H₂ in these Pd-containing PES-C membranes, among which the membrane with 0.05 wt % of palladium gave the largest permeability of H₂. The permeabilities of H₂ in Pd-PES-C membranes are much higher than those in the pure PES-C membrane. Since hydrogen can be easily coordinated with palladium species, the higher permeability in Pd-PES-C membranes can be explained by the modified dual-mode transport theory as that described by Nishide et al.²⁵: the Henry's law sorption of H₂ to the polymer domain and an additional Langmuir sorption to the Pd-polymer species. The hydrogen transport is expected to be accelerated by this additional Langmuir mode in addition to the Henry mode. Under the same conditions, nitrogen and dioxygen cannot permeate these membranes, which can be understood as a result of the loss in free volume available for sorption of gas in the membrane by the incorporation of palladium with the polymer. This effect is less pronounced in the case of a small molecule, such as hydrogen, than it is in the cases of nitrogen and dioxygen. These results reveal that the effect of incorporating a metal compound into polymeric membranes on the permeability of gases is influenced by the properties of the metal compound and the polymer matrix. It may be related to the contents and states of the palladium species that the Pd-PES-C membrane containing 0.05 wt % of palladium could give the largest permeability of H₂ and other Pd-PES-C membranes showed comparable permeabilities of H₂.

CONCLUSIONS

PES-C can be used as a suitable support for the polymer-supported palladium catalysts. The swelling effect of the polymeric support both in the preparation of the catalyst and in the course of reaction can show great influence on the catalytic activity and selectivity of the polymer-supported palladium

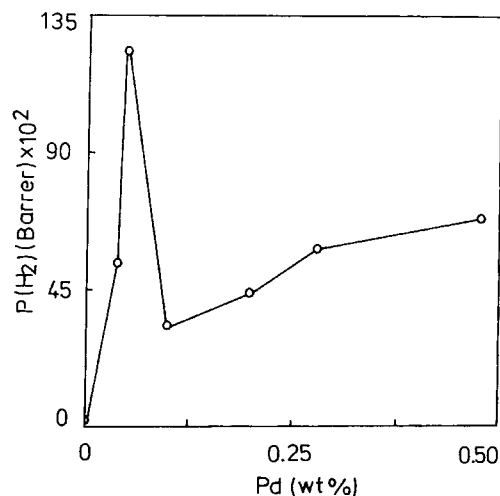


Figure 4 Plot of the Permeability of H₂ of the Pd-containing PES-C membranes vs. Pd contents. Determination conditions: 1.0 MPa, 15°C; membrane area, 13.2 cm². 1 Barrer = 1 × 10⁻¹⁰ cm³ [STP] cm/cm² cm Hg s.

catalysts. The Pd-containing polymeric material Pd-PES-C with 0.05 wt % of palladium exhibits the largest catalytic activity for the carbonylation of allyl bromide and hydrogenation of 1-octene and the largest permeability of H₂. As far as the catalytic activity and the permeability of gases are concerned, Pd-PES-C with 0.05 wt % of palladium may be a promising material to build a catalytic polymeric reactor for the gas-phase hydrogenation and dehydrogenation at relatively high temperatures.

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