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Catalysis with homogeneous membranes loaded with nanoscale metallic clusters and their preparation

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Abstract

Catalytically powerful, non-porous membranes were manufactured from two highly gas permeable poly(amide imides) consisting of structures with moieties of 3,3′-dimethylnaphthidine and hexafluoroisopropylidene (6F) or hexafluoroisopropylidene-2,2-bis(phthalic acid anhydride) (6FDA) and 6F. The catalysts are pure precious metals or precious metal alloys dispersed on a nanoscale uniformly throughout the membrane. The membranes are characterized by electron microscopy, gas permeability, hydrogen uptake and, as a model reaction, the decomposition of nitrous oxide by hydrogen to nitrogen and water catalyzed by Pd/Ag. The permeance to hydrogen and nitrous oxide is round $2 \cdot 10^{-6}$ cm^3 (STP)/cm$^2 \cdot$ s $\cdot$ cmHg for membranes of 40–50 μm in thickness.

1. Introduction

Development of catalytic membranes and processes, known since about two decades, is still a challenge. Catalytic membranes may consist of porous or nonporous membranes based on inorganic materials or organic polymers. The catalytic separation layer of non-porous membranes in most cases is composed of palladium or palladium alloy foils. Reduction in thickness by film deposition on porous supports increases the hydrogen permeability and reduces the costs for the precious metals.

Reviews [1,2] covering the main results on catalytic membrane research summarize the state of the art. We present in this contribution a method to generate nanoscale precious metal clusters uniformly distributed inside of non-porous polymer membranes, their characterization and a test of their performance using a model reaction.

2. Experimental

2.1. Polymers

Recently developed poly(amide imides) (PAI) with very high gas permeability and high selectivity were used. Their synthesis and properties are reported elsewhere [3]. The structures are given in Fig. 1.

2.2. Membrane formation

Uniform non-porous films of 40–50 μm thickness were prepared from ~ 10% tetrahydrofurane (THF) solution. Residual solvent was exchanged by immersing overnight in methanol. The membranes were dried to constant weight in a vacuum

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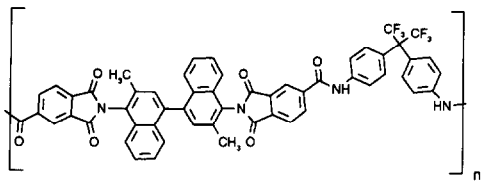

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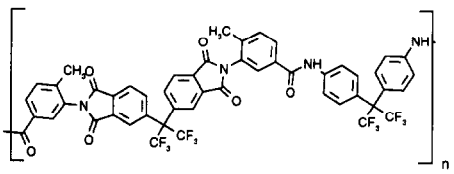

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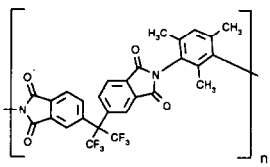

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Fig. 1. Structures of the polymers used.

oven at 110°C at below 1 mbar. TGA measurements to control the quality exhibited no residual solvent or water. The first step to catalytic membranes is the preparation of salt-filled membranes. These were prepared from ~10% N-methyl-2-pyrrolidone (NMP) solution of the polymer and admixing of the required amount of palladium acetate and/or silver acetate (all from MERCK). This solution was cast on a glass plate and heated at 80°C in a dust free atmosphere overnight. The peeled off, salt filled membrane containing 5–10% residual solvent (checked by TGA) was immersed for 15 min in a freshly prepared solution of $NaBH_4$/MeOH. The brown color of the membrane immediately turned to black (Pd and Pd/Ag) or silvery–blackish (Ag). In no case bleeding-out of the precious metal was observed. During this step a shrinking of the membrane by 5–10% in diameter was observed. This is probably due to washing out of the residual solvent (see above) and reduced volume of the metallic particles compared to the salt, e.g. Pd to PdAc. Washing with methanol and drying in vacuum (110°C; overnight below 1 mbar) results in solvent and pore free membranes of 40–50 μm thickness containing nanoscale metal clusters. The clusters are distributed uniformly throughout the membrane. Metal contents from 0 to 30 wt.-% are possible without effect on the mechanical properties. Membranes with 15 wt.-% metal clusters are no longer soluble in THF or NMP.

2.3. Permeability measurement and detection of the model reaction by mass spectroscopy

Permselectivities were measured at 30°C as reported previously [3]. The $NaBH_4$/MeOH treatment of films of the pure polymer did not change the polymer structure as indicated by IR spectra of thin films.

Feed gas for the model reaction was compounded from steel cylinders by flow-meters connected to a gas mixing device (MKS Baratron μbar™). Membrane area was 13.2 cm^2 (Millipore cell); feed gas stream was 100 ml/min; feed and retentate composition were nearly identical indicating a low stage cut. Feed, retentate and permeate were supplied sequentially to the gas inlet of the mass spectrometer (Faraday-type, Alcatel) and recorded to stable results (feed, retentate 3–5 min; permeate 5–10 min).

3. Results and discussion

3.1. Polymer selection

Polymers with high gas permeability are favored for the use as non-porous catalytic membranes. A pre-selection from reviews [4,5] pointed out poly(imides) (PI) to have the best properties. Attempts to prepare usable films with metallic clusters from the PI 3 (structure see Fig. 1) failed because at the reduction step ($NaBH_4$/MeOH) the film curled and crumpled resulting in visible holes by inspection. The recently developed PAI (1, 2; Fig. 1) have favorable gas permselective properties and overcome these difficulties. Catalytic membranes prepared according to the experimental section have superior mechanical properties and are stable to sol-

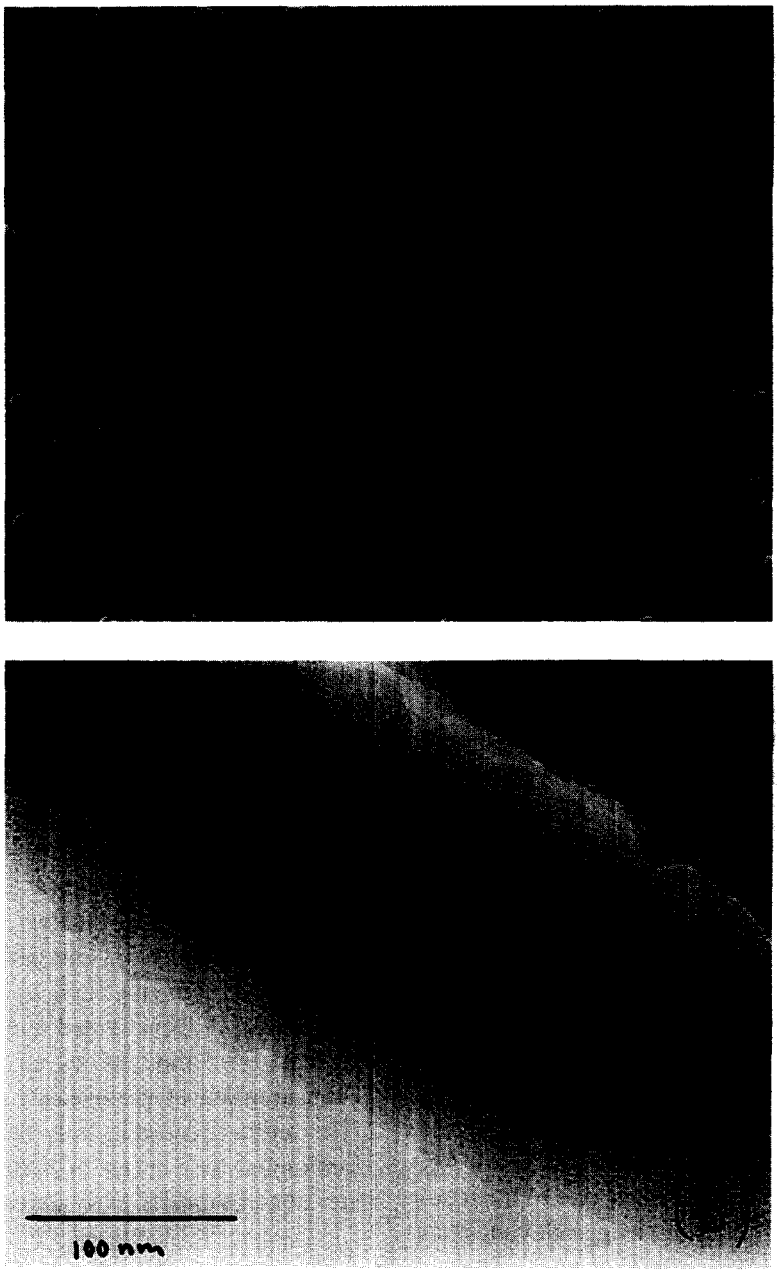


Fig. 2. SEM (a) and TEM (b) micrographs of nanoscale precious metal clusters containing membrane from polymer 1 with 15% Pd/Ag (77/23). SEM: fractured plane, sputtered by Cr. TEM: thin film section, unstained.

vents, even to THF and NMP, the solvents they were prepared from. Shrinking of the membrane by 5–10% in diameter during the reduction step did not result in crumbling; the membranes are flat, pore-free and uniform in thickness.

3.2. Characterization of catalytic membranes

Characterization by electron microscopy and density measurement

Transmission and scanning electron micros-

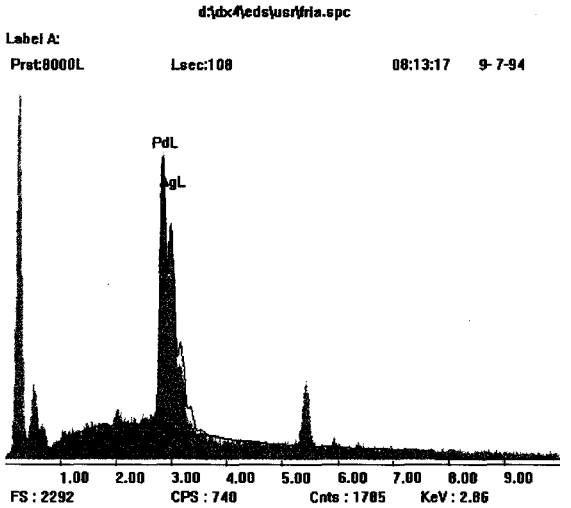


Fig. 3. EDAX analysis of fractured plane of membrane from polymer 1 (sputtered by Cr).

copy (TEM and SEM) were used to characterize the membrane microstructure. SEM micrographs at high magnification show the nodular structure of the catalytic membrane (see Fig. 2); differences between metal free and loaded membranes are not discernible (not shown). Energy dispersive analysis of X-rays (EDAX), however, clearly detects the metals. In Fig. 3 the EDAX analysis is shown for a membrane from polymer 1 with 15 wt.-% Pd/Ag (77/23 w/w) bimetallic clusters. The detected ratio (Pd/Ag = 76.7/23.3) is in good agreement with the calculated one from the membrane composition. EDAX analysis resulting from membranes with compositions of Pd/Ru/Co (89/10/1) and, moreover, Pd/Ag (10/90) deviates markedly from the calculated one (by EDAX: Pd/Ru/Co: 82/18/0.5; Pd/Ag; Pd/Ag: 41/59). This is probably due to the inaccuracy of the method without using relevant standards.

Thin film sections of unstained TEM micrographs, however, clearly indicate the presence of heavy atom clusters in cross-sections of the 40–50 μm membrane. Clusters in diameters of about 2 nm are distributed uniformly throughout the membrane (see Fig. 2b). The boundary layer of the clusters cannot be seen very clearly; this may result from the limited resolution of the electron microscope or may be caused by not well defined boundary layers of the clusters.

On a macroscopic level membrane properties such as density should change by incorporation of metallic particles. The density of the membranes was measured using a method reported previously [3]. The membrane density increases with increasing portion of noble metal. Pd/Ag alloy membranes show lower density than those with the same content of only Pd, due to the lower density of Ag over Pd (see Table 1).

Characterization by gas permselectivity

Inorganic fillers used with polymers, normally, are not permeable to gases and therefore act as diffusion barrier [6,7]. Sorption effects are negligible when using nonporous fillers with diameters on a μm level. The sorption behavior is expected to change by using nanoscale clusters of precious metals. Calculating the surface of palladium clusters, assuming spheres, results in surfaces of 0.025 m^2/g (diameter: 20 μm) and 250 m^2/g (diameter: 2 nm). As detected by electron microscopy, the cluster diameter is about 2 nm. Pd clusters with such high surfaces should behave differently to gases like CO_2, H_2, He and O_2. CO_2 and He may be non-interacting; H_2 should dissolve markedly in the clusters, and O_2 may oxidize the surface. Time-lag and permeability measurements were performed and are reported in Table 2 and Table 3. Deactivated membranes (subjected at least for 3 days to dry air) were used for the measurement of permselectivity and diffusivity. The redox-process is fully reversible, even after prolonged time in air or hydrogen. For CO_2 the permeability, diffusivity and solubility decreases

Table 1
Density of various membranes

Polymer	Density/g/cm^3
Polymer 1	
pure	1.307
15% Pd	1.546
20% Pd	1.586
15% Pd/Ag (77/23)	1.519
Polymer 2	
pure	1.399
15% Pd/Ag (77/23)	1.605

Table 2
Diffusivity, solubility and permeability of pure and noble metal cluster containing membranes from polymer 1 and 2

Polymer	D_{CO_2}[a]	S_{CO_2}[b]	P_{CO_2}[c]	D_{H_2}[a]	S_{H_2}[b]	P_{H_2}[c]	P^c_{He}
Polymer 1							
pure	2.8	0.39	109	>100	<0.01	98	86
with 15% Pd	1.0	0.31	31	0.57	0.95	54	87
dto. after 1 h evacuation	–	–	–	2.78	0.24	67	–
dto. after 1 h O_2 treatment	–	–	–	0.49	1.1	54	–
dto. after 2 h O_2 treatment	–	–	–	0.38	1.1	41	65
with 20% Pd	1.8	0.31	55	0.55	0.87	48	87
dto. after 1 h O_2 treatment	–	–	–	0.51	1.0	53	–
15% Pd/Ag (77/23) 47 μm	1.6	0.34	55	2.3	0.39	89	82
15% Pd/Ag (77/23) 50 μm	1.8	0.32	57	2.3	0.40	93	74
15% Ag	0.71	0.27	19	>100	<0.005	49	46
Polymer 2							
pure	2.1	0.35	73	>100	<0.009	86	114
15% Pd/Ag (77/23)	–	–	–	1.2	0.38	46	70

[a] Diffusivity (D) in 10^{-3} cm^2/s. [b] Solubility (S) in cm^3 (STP)/cm^3·cmHg. [c] Permeability (P) in barrer.

in the presence of clusters, due to hindrance by the clusters. Permeability of He decreases similarly; diffusivity could not be measured precisely in spite of the short time-lag of below ca. 1 s.

In contrast to this, the diffusivity of hydrogen (D_{H_2}) decreases by 2 to 3 orders of magnitude accompanied by an increase in solubility by two orders (see Table 2). Membranes with Pd/Ag are less effective in H_2 sorption than those with pure Pd; membranes with Ag only showed a decrease in permeability and no measurable change in diffusivity. Reexamining of the diffusivity after 1 h of evacuation results in an increase of diffusivity (0.57 to 2.8 e^{-8}·cm^2/s) and a decrease in solubility for H_2. After treatment with O_2 for about 15 min and evacuating for 1 h, data similar to the initial values of H_2 diffusivity and solubility were found (see Table 2).

Table 3 reports the O_2 diffusivity data (D_{O_2}) of membranes from polymer 1. In general, D_{O_2} decreases compared to unfilled membranes (from 8.4 to about 3 e^{-8}·cm^2/s). Measuring D_{O_2} after exposure to H_2 and evacuation for 1 h, two steps in D_{O_2} can be identified from the time-lag curve, indicating an interaction with the metallic clusters. This is presumably due to the reaction of O_2 with residual H_2 followed by a surface oxidation of Pd clusters [8–10]. Sweeping with oxygen may be

Table 3
O_2 diffusivity of polymer 1 filled with various nanoscale noble metal clusters tested after H_2 exposure and 1 h vacuum

Membrane	D_{O2} (e^{-8} cm^2/s)	Remarks
Pure	8.4	1 step only
15% Pd	2.0	1. step
	0.19	2. step
	2.6	test, after O_2; 1 h vac.; 1 step only
	3.7	test, after O_2; 1 h vac.; 1 step only
20% Pd	2.5	1. step
	0.40	2. step
15% Pd/Ag 47 μm	2.4	1. step
	0.85	2. step
	3.1	test, after O_2; 1 h vac.; 1 step only
15% Pd/Ag 50 μm	2.89	1. step
	1.09	2. step
15% Ag	1.1	1 step only

Table 4
Permeance and diffusivity of catalytic membranes with 15% Pd/Ag (77/23) from polymer 1 and 2

Polymer	Permeance[a]					Diffusivity[b]	
	H_2	N_2O	He	Ar	CH_4	H_2	N_2O
1	1.9	2.3	1.7	–	–	2.3	2.5
2	1.2	1.1	1.8	0.048	0.022	1.2	1.2

[a] Unit: 10^{-6} cm^3 (STP)/cm^2·s·cmHg. [b] Unit: 10^{-8} cm^2/s.

Table 5
Ideal separation factors of membranes from pure polymers and with 15% Pd/Ag (77/23)

Polymer	$p(H_2/He)$	$p(H_2/Ar)$	$p(H_2/CH_4)$	$p(N_2O/He)$	$p(N_2O/Ar)$	$p(N_2O/CH_4)$
1	1.1	–	–	1.4	–	–
Pure 1	1.1	–	33	–	–	–
2	0.66	24	52	0.61	23	48
Pure 2	0.75	–	56	–	–	–

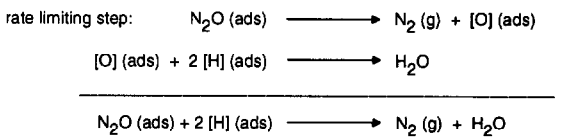
used to reactivate the catalyst [10]. Only membranes with Pd or Pd/Ag clusters show this behavior; for membranes with Ag clusters, even after H_2 exposure and evacuation, only 1 step in time-lag for D_{O_2} was detected. At the experimental conditions (1 bar feed gas pressure, 30°C), Ag clusters do not sorb H_2, therefore no residual H_2 can react with O_2.

Characterization by model reaction

Hydrogenation of nitrous oxide was selected as a model reaction. Activity to various noble metals, measured electrochemically by electroreduction of N_2O to N_2 using a gas electrode [11], indicating Pd to be most effective. Only Pd/Pt (1/1) alloys are more powerful.

Table 6
Ratios (v/v) of feed gas mixtures used in the model reaction using membranes from polymer 1 and 2, with 15% Pd/Ag (77/23) clusters

Run	Diluting gas	N_2O	H_2	Diluting gas	N_2O/H_2	X/Diluting gas
Polymer 1						
1	He	16.7	33.3	50	1/2	1/1
2	He	25	25	50	1/1	1/1
3	He	35	–	35	1/–	1/1
4	He	35	–	–	1/–	1/–
5	He	–	–	200	–/–	–/1
6	He	35	–	75	1/–	~1/2
7	He	25	25	50	1/1	1/1
Polymer 2						
8	He	25	25	50	1/1	1/1
9	He	16.7	33.3	50	1/2	1/1
10	He	8.3	41.7	50	1/5	1/1
11	Ar	8.3	41.7	50	1/5	1/1
12	Ar	–	41.7	50	–/1	~1/1
13	Ar	–	–	65	–/–	–/1
14	Ar	35	–	65	1/–	~1/2
15	CH_4	25	25	50	1/1	1/1
16	CH_4	8.3	41.7	50	1/5	1/1



Scheme 1.

Scheme 1 summarizes the reaction. According to the literature [12,13] the rate limiting step is the decomposition of sorbed nitrous oxide at the surface of Pd. Therefore highest available surface area of metal clusters is favorable for efficiency of the process.

For testing of the model reaction, membranes from polymer 1 and 2 with 15% Pd/Ag (77/23) were used. They differ in permeance for the tested gases except for He, and they differ by a factor of two in diffusivity for H_2 and N_2O (see Table 4).

The composition of the feed gas mixtures varied in N_2O/H_2 from 1/5 to 1/1 (v/v); diluting gases were He, Ar or CH_4. The diluting gas in the feed rarefies the reactants; selectivity of the diluting gas to the reactants ranges from about 1 to 50 (see Table 5). In Table 6 the applied feed gas mixtures are summarized. With H_2 of at least molar ratio to N_2O in the feed gas, no N_2O was detected in the permeate (Table 6 and Table 7; runs 1, 2, 7–11, 15, 16; m/e: 44, 30 (N_2O) at background level). When turning off the H_2 (runs 3, 4, 6, 14) N_2O was identified in the permeate (within the response time of the MS detector). By switching on H_2 again (runs 7, 15), the signal for N_2O decreased rapidly to the background level of the MS detector. Runs 5, 13 were used to sweep the membrane with He (run 5), Ar (run 13) or H_2/Ar (run 12), respectively.

Additionally, the reaction products H_2O (m/e: 18) and N_2 (m/e: 28) were identified in the permeate. Their amounts in the permeate are propor-

Table 7
Selected results of MS analysis of feed and permeate

Run	Gas comp. ($N_2O/H_2/He$)	N_2O^a (m/e: 44/4)	H_2^a (m/e: 2/4)	H_2O^a (m/e: 18/4)	N_2^a (m/e: 28/4)
Polymer 1					
1 Feed	16.7/33.3/50	0.84	3.49	0.10	0.15
1 Perm		0.00	1.66	0.88	1.02
2 Feed	25/25/50	1.54	3.87	0.16	0.26
2 Perm		0.01	0.18	1.16	2.00
6 Feed	35/–/75	0.76	0.00	0.01	0.14
6 Perm		0.75	0.00	0.21	0.16
7 Feed	25/25/50	1.54	3.87	0.16	0.26
7 Perm		0.00	0.61	1.07	1.58
Polymer 2					
8 Feed	25/25/50	1.54	3.87	0.16	0.26
8 Perm		0.01	0.72	0.78	0.77
9 Feed	16.7/33.3/50	0.84	3.49	0.10	0.15
9 Perm		0.00	2.04	0.53	0.00
10 Feed	8.3/41.7/50	0.42	4.24	0.06	0.08
10 Perm		0.00	3.43	0.28	0.00

[a] Peak intensity relative to He.

tional to the ratios of N_2O in the feed gas (see Table 6 and Table 7; runs 1, 2, 7–10). The data are not corrected for partial overlap of the peaks, e.g. N_2O and N_2.

4. Conclusion

A new and efficient method to manufacture catalytically powerful membranes was developed. The membranes consist of poly(amide imides) with nanoscale noble metal clusters distributed uniformly throughout the membrane. Any metallic clusters or metal alloy (bimetallic clusters) can be generated. The method is limited only by the solubility of the metal salts in high boiling solvents like NMP and the accessibility to fast reduction by, e.g. active hydrogen. The membranes obtained are not soluble anymore in organic solvents and can be used in catalytic reactions, for example the catalytical nitrous oxide reduction in gas streams.

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