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Chemical Engineering Journal 85 (2002) 303–311

Chemical Engineering Journal
www.elsevier.com/locate/cej

Catalytic membrane reactor to simultaneously concentrate and react organics

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Received 30 January 2001; accepted 6 April 2001

Abstract

Catalytically active membranes containing palladium nanoclusters of 3–5 nm were prepared from poly(ether-*b*-amide) (PEBA) and the catalyst precursor palladium diacetate in a solution-casting-reduction procedure. These membranes were used to simultaneously concentrate and react organics by catalytic pervaporation. The model reaction considered is the hydrogenation of 4-chlorophenol in aqueous solution using dissolved hydrogen as reducing agent. The reaction produced phenol and, in smaller yields, cyclohexanone and cyclohexanol were detected in the permeate but also in the feed solution. Conversion of 4-chlorophenol is up to 80% after 20 h of operation. However, a considerable amount of 4-chlorophenol passed the membrane unreacted. Pervaporative enrichment of the organics was by a factor of 100. The effectivity of the process was influenced by the palladium cluster size, feed temperature and permeate pressure. A significant conversion is realized only when employing the catalytic membrane in the pervaporation mode. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: 4-Chlorophenol; Catalytic pervaporation; Polymer membrane reactor

1. Introduction

Coupling of a semi-permeable membrane to a chemical reactor represents a new reactor configuration theoretically having several advantages. In its simplest design a membrane process is coupled directly to a state of the art reactor to accomplish the separation of the effluent and optionally feeding back the retentate to the reactor. In a more sophisticated type of reactor the membrane itself is catalytically active. Some major tasks are identified to favor the membrane reactor concept over common reactors: ability to shift the overall conversion above thermodynamic equilibrium by selective product removal, distributed addition of reactants (dosing) alongside the reactor to improve selectivity, and control of reactant contact to amend safety, selectivity and conversion [1,2]. All the various combinations in membrane reactor design have their merits and needs to be adjusted to improve a specific reaction. Most discussed reactions today are in the high-temperature range from 300 to 1000 °C [2]. However, besides applications in the field of biosynthesis, also low-temperature processes for, e.g. production of fine chemicals may profit from the membrane reactor concept. At low temperature (room temperature (RT) up to about 150 °C) also polymer membranes can be considered as integral component of the membrane reactor and could have some advantages over the more expensive inorganic membranes made from ceramic or metals [3–5]. On principle, polymer membranes may be either porous or dense (homogeneous). Porous polymer membranes can be used as catalytic filters [6,7], whereas dense polymer membranes, in use to separate gases, vapors or liquids from mixtures by a sorption–diffusion mechanism, can be made catalytically active and then be used to separate and react in one step. By pervaporation liquid mixtures, including azeotropes, are separated effectively. High separation factors up to >1000 have been observed. The elastomer poly(ether-*b*-amide) (PEBA) is known as a polymer that effectively concentrates slightly polar chemicals such as phenols, higher alcohols and the like from water [8,9]. We have prepared PEBA membranes with various concentrations of different catalytically active metal nanoclusters and utilized these membranes to simultaneously react and separate 4-chlorophenol as a model compound from diluted aqueous solutions. Halogenated phenols are very persistent to biodegradation, however, are widely used in agriculture or for wood protection. Catalytic hydrodechlorination may be used to decrease the toxicity of these compounds. Fig. 1 summarizes the hydrogenation reactions of 4-chlorophenol. It has some advantages as a model compound for catalytic pervaporation:

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PII: S1385-8947(01)00159-0

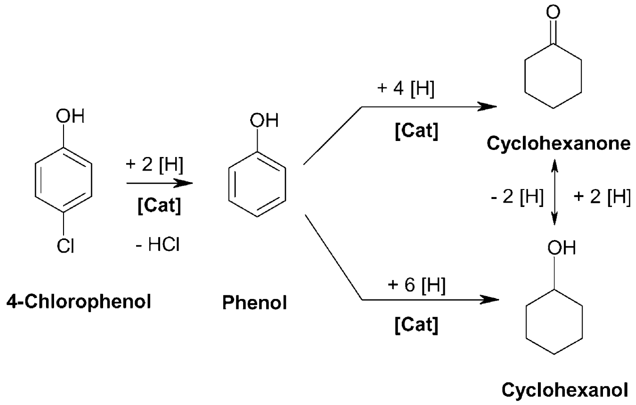

Fig. 1. Hydrogenation reactions of 4-chlorophenol.

1. Literature data of pervaporation of phenols are available; high enrichment factors are reported.
2. It is a fast, consecutive reaction were the reaction products have lower boiling points and, therefore, are more easily removed by pervaporation; product distribution may be changed by this combined separation/reaction compared to a batch reactor with normal, supported catalyst.
3. The influence of the side product hydrochloric acid as a catalyst poison on the catalyst's stability can be monitored because the membrane process is a continuous process.

Various experimental conditions such as hydrogen pressure, temperature, noble metal loading, membrane thickness were applied to understand the process parameters of reactive pervaporation.

2. Experimental

2.1. Materials

N,*N*-dimethylacetamide (DMAc), *n*-butanol (BuOH) and 4-chlorophenol were purchased from Merck and were used without further purification. Palladium diacetate ($PdAc_2$, Chempur) and sodium borohydride (Aldrich) were kept under dry conditions and used as received. The PEBA (PEBAX® grade 4033, Atochem) granulate was washed with isopropanol/water (1:3) and dried at 80 °C for 2 days. The woven fabrics made from poly(ethylene-tetrafluoroethylene) copolymer (Scrynel COP 70, Sefar Inc.) and polyester (Estal 58, Schweizer Seidengaze Fabrik) were used as received.

2.1.1. Preparation of Pd–PEBA membranes

PEBA was dissolved in DMAc at 110 °C (6 wt.% solution) and kept at 100 °C for 30 min. $PdAc_2$ was dissolved in DMAc (8–10 wt.% solution) at RT a few minutes before use. The dark-red solution was added dropwise under vigorous stirring to the hot PEBA solution to avoid precipitation of the polymer at temperatures below 80 °C. A few minutes after completion, the hot, dark-red solution was poured immediately on a glass plate thermostated at 40 °C. In order to reinforce the membranes the glass plate was covered by a woven fabric (Scrynel or Estal) before casting the polymer solution. The solvent was allowed to evaporate slowly overnight, the remaining dark-red, translucent membrane was removed from the glass plate and dried in the oven at 50–60 °C for 1 day.

The reduction of the homogeneously distributed $PdAc_2$ was carried out either chemically or by heat treatment.

1. Chemical reduction was done by sodium borohydride solution (1 wt.% in H_2O/methanol (1:1)). The color of the membrane turned to black within a few seconds and small gas bubbles escaped. After 15 min, the black and non-transparent membrane was rinsed several times with water and dried at 50–60 °C for 1 day.
2. Reduction was also performed at 120 °C in a vacuum oven to exclude oxygen and to remove the emitted acetic acid. The oven was evacuated to <1 mbar. After 20 h at 120 °C the red membrane had turned to black. The heat treatment did not affect the membrane polymer properties.

The resulting membranes were tested for leaks by measuring the water flux density in pervaporation. The cluster size of palladium was estimated by XRD (Siemens D5000 diffractometer using Cu radiation and a graphite secondary monochromator [10]). SEM was performed on a Jeol 6400 F scanning electron microscope with Everhart–Thornley detector, the samples were prepared by microtome cutting at -200 °C.

2.1.2. Reduction of 4-chlorophenol under pervaporative conditions at 1 bar hydrogen pressure

The pervaporation apparatus used is depicted in Fig. 2a. For gas inlet a glass frit (porosity 1) was introduced to the feed vessel. A volume of 2000 ml aqueous solution of 4-chlorophenol were kept at 30 °C and saturated with hydrogen gas by bubbling through the frit for at least 30 min. The membrane area of the test cell was 100 cm^2, it is flowed radially from the aisle to the center (circulation speed 1.5 l/min) to avoid concentration polarization. The permeate side of the membrane was evacuated to <0.1 mbar to generate a high driving force for the membrane permeation. The membrane was allowed to reach equilibrium for 30 min, already under vacuum, and then the permeate was collected for 2–3 h in a trap by cooling with liquid nitrogen. Flux densities were estimated by weight in terms of g/m^2h. Concentrations of feed, retentate and permeate were analyzed for 4-chlorophenol, phenol, cyclohexanone and cyclohexanol by gas chromatography (Hewlett–Packard, 30 m Supelcowax capillary column, film thickness 1 μm) and pH was measured by pH strips (Acilit 0-6, Merck). The phase-separated permeates were diluted before analysis with a small amount of ethanol to obtain a homogeneous solution. Enrichment

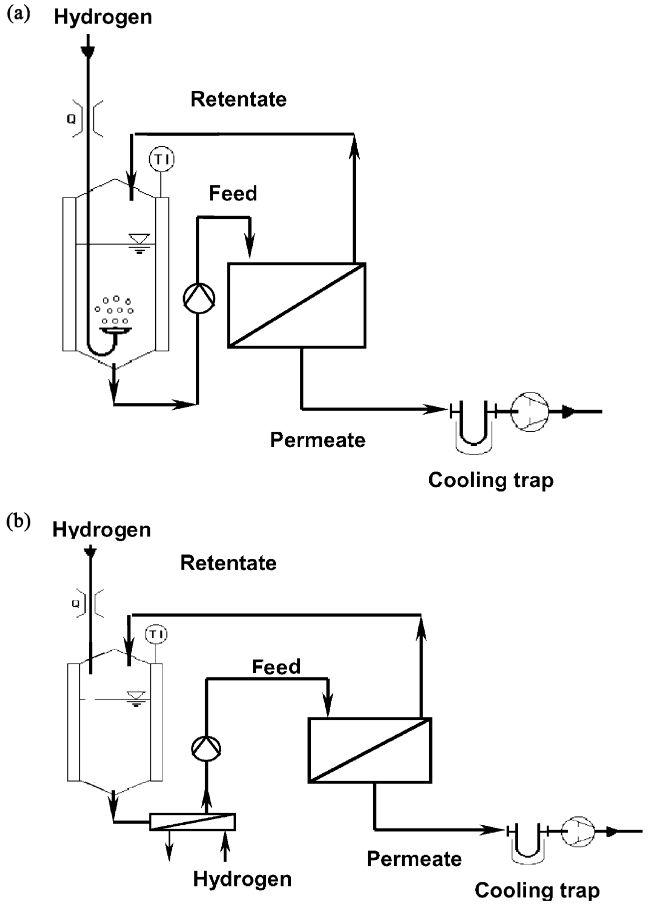

Fig. 2. (a) Pervaporation apparatus with gas inlet through the frit; (b) pervaporation apparatus with hollow fiber gas inlet.

factor is calculated by $\beta =$ concentration (organic in permeate)/concentration (organic in feed).

2.1.3. Reduction of 4-chlorophenol under pervaporative conditions at 5 bar hydrogen pressure

The high-pressure suited pervaporation apparatus consists of stainless steel with a total vessel volume of 2200 ml (Fig. 2b). The vessel and the membrane test cell were kept at 30 °C by immersion into a water bath. Hydrogen gas was applied by circulating the aqueous solution through a hollow fiber module (membrane area 200 cm^2, polysulfone support coated with silicone rubber, manufactured at GKSS) on the inner side of the fibers. The outer side was set under 5 bar hydrogen pressure. Additionally, the feed vessel itself was held under 5 bar hydrogen pressure. First the hydrogen was allowed to reach saturation in the solution. The content of dissolved hydrogen in the solution was measured by a H_2-sensor placed in a by-pass (electrochemical H_2-sensor equipped with a Saran membrane, Model 3600 analyzer, Orbisphere Laboratories, Switzerland). The catalytic PEBA membrane (100 cm^2) used was reinforced by a woven fabric. During pervaporation measurements the permeate side of the membrane was evacuated to <0.1 mbar. The experiments were conducted identically to those at 1 bar pressure.

2.1.4. Reduction of 4-chlorophenol or phenol by the catalytic membrane without pervaporation

A volume of 2000 ml of aqueous solutions of 4-chlorophenol or phenol were thermostated at 30 °C and circulated through the membrane test cell (100 cm^2) as described above. The membrane was allowed to become saturated with 4-chlorophenol or phenol for 2 days (uptake of phenolic compounds about 5% of the membrane's weight). Hydrogen supply was from the opposite ("permeate") side of the membrane. By means of two valves, an excess pressure of 0.4 bar H_2 was applied to the membrane. The hydrogen gas stream along the membrane was 100 ml/min. Feed samples were taken every 3 h, tested on acidity and analyzed by gas chromatography. Identical experiments were conducted at an excess pressure of 1 bar hydrogen using reinforced membranes.

2.2. Results

2.2.1. Preparation of Pd–PEBA membranes

PEBA are available commercially with a wide variety of properties. Depending on the block length and the type of polyether segment, block copolymers with different polarity and, therefore, differing pervaporation properties [8,9] were identified previously. Aromatic compounds, in particular phenol, showed excellent selectivities and good fluxes in pervaporation by PEBA membranes. Due to the outstanding film forming properties of PEBA and its solubility, homogeneous membranes can be formed by membrane casting. To activate the membranes with a heterogeneous catalyst, a previously applied, simple method [10,11] was used. A metal precursor ($PdAc_2$) was co-dissolved with the polymer and immediately cast on a heated glass plate. After evaporation, a translucent, flexible and tough membrane was obtained. No crystallization of $PdAc_2$ up to about 13 wt.% was observed. A fast reduction step by sodium borohydride in water/methanol solution or a heat treatment at 120 °C formed nano-sized palladium clusters homogeneously distributed throughout the membrane.

Two solvents were used for membrane casting: BuOH and DMAc. Alcohols and to lesser extent also DMAc are able to reduce Pd-salts [12] at elevated temperatures in solution. Preparing the membranes from BuOH solution yielded dark brown membranes prior to final reduction, although the $PdAc_2$ solution was admixed shortly before membrane casting. The color indicated some decomposition of the precursor during the preparation step. Following the same procedure, from DMAc solutions dark-red colored membranes were obtained. After reduction, the color of the membranes changed identically to black. Upon examination of the cluster size, however, cluster sizes of 2–4 nm were detected for the DMAc based membranes and larger clusters of 5–7 nm for those from BuOH (see Table 1).

Reinforcement was shown previously to improve the membrane stability [13]. A polyester fabric of high chemical stability was used preferentially to reinforce membranes

Table 1
Properties of Pd–PEBA membranes[a]

Membrane number	Palladium content (wt.%)	Membrane thickness (μm)	Solvent	Pd cluster size by XRD[b] (nm)	Reinforcement	Water flux density at 30 °C (g/m^{2}h)
1	5.7	55–60	DMAc	2.94 ($\pm$0.85)	None	45
2	13	53	BuOH	5.0 ($\pm$0.9)	None	50
3	12.2	70–80	DMAc	2.37 ($\pm$0.72)	None	28
4	8.85	135	BuOH	5.40 ($\pm$1.2)	Estal (PES)	30
5[c]	12.2	50	DMAc	2.98 ($\pm$0.8)	None	
5			DMAc	2.66 ($\pm$0.96)	None	
6[c]	12.6	55–70	DMAc		None	
7	9.24	260–280	DMAc		Scrynel (ETFE)	
8	12.1	260–280	DMAc		Scrynel (ETFE)	
9	12.1	260–280	DMAc	4.40 ($\pm$1.1)	Scrynel (ETFE)	30
10	12.8	250–270	DMAc		Scrynel (ETFE)	30

[a] Reduction of the palladium diacetate by sodium borohydride unless noticed otherwise.

[b] Method see [10].

[c] Reduction by temperature (120 °C/12 h).

cast from BuOH. By changing to the solvent DMAc, however, no uniform membranes were formed and both layers could be separated easily. The adhesion of PEBA cast from DMAc solutions was improved by use of ETFE fabric. The palladium content of the membranes ranged from 6 to 13 wt.% (Table 1).

Fig. 3a depicts the SEM picture of a homogeneous PEBA membrane of 50 μm thickness in cross section. The distribution of the palladium clusters was measured along the straight white line by the intensity of back scattered electrons [14]. The scattering line below reveals that a uniform distribution of the palladium clusters was obtained over the membrane.

Fig. 3b shows a reinforced PEBA membrane in cross-section. The polymer forms a thick homogeneous layer of about 60 μm on top of the fabric (ETFE). Although not compatible with the fabric, PEBA encloses the fabric completely by a thin polymer layer. This configuration guarantees the stability of the membrane even under high swelling conditions [13]. The reinforcement did not alter the distribution of the palladium clusters in the PEBA polymer as is shown in the profile line. The fabric takes up no palladium, it shows no swelling in DMAc.

2.2.2. Reductive pervaporation of 4-chlorophenol and phenol with hydrogen supply from aqueous solution

2.2.2.1. Pervaporation—short introduction. Pervaporation denotes a membrane process for the separation of liquid mixtures. The liquid feed phase is divided by the membrane from the vaporous permeate, which is maintained by evacuation, generating a concentration gradient as the driving force. Pervaporation selectivity is governed not primarily by differences in vapor pressure, but by differences in transport rate through the membrane as a result of differences in solubility and diffusivity of the components to be separated in the membrane polymer. Practical applications, thus, include the separation and, at the same time, enrichment of minority components from diluted solutions: hydrophilic pervaporation (dehydration of organic solvents) and organophilic pervaporation (removal or recovery of volatile organic compounds).

The process is characterized by the enrichment factor of the preferentially permeating species in the permeate and the permeation rate (flux density). Total flux density includes the partial flux densities of all the permeating compounds. Process parameters to be regarded are: Temperature, permeate pressure, membrane thickness and feed concentration.

2.2.2.2. Pervaporation—process parameters. Temperature affects solubility and diffusivity of the permeants and their interaction with the polymer. In consequence, the flux density increases with temperature. Unfortunately, the increase of diffusivity is higher for smaller molecules, in this case water, and lead to a slight decrease of the enrichment factor at higher temperatures. In the temperature range of 30–60 °C the total flux increased from 30 to 160 g/m^{2}h, while the enrichment factor for 4-chlorophenol decreased from 100 to 80 (membrane number 2, 0.45 wt.% 4-chlorophenol, permeate pressure $<$ 1 mbar) [15].

The permeate pressure is crucial in pervaporation of high boiling compounds like phenols to establish a concentration gradient at the feed side of the membrane. Especially, when pervaporating low concentrations of these compounds, a permeate pressure below 1 mbar is essential to obtain a maximum organic flux [8]. The influence on the major component water, having a rather high vapor pressure, is negligible. For example, the partial flux of phenol (membrane number 1, feed concentration 0.1 wt.%, 30 °C) was 4.25 g/m^{2}h at $<$0.1 mbar, but only 1.5 g/m^{2}h at 5 mbar. In contrast, the flux of water was measured to 45 g/m^{2}h at $<$0.1 mbar and 43 g/m^{2}h at 5 mbar. Resulting enrichment factors are 86 ($<$0.1 mbar) or 34 (5 mbar). Experiments on pervaporative reduction were performed at permeate pressures $<$0.1 mbar.

The influence of membrane thickness on the performance of catalytically active PEBA membranes is shown in Fig. 4

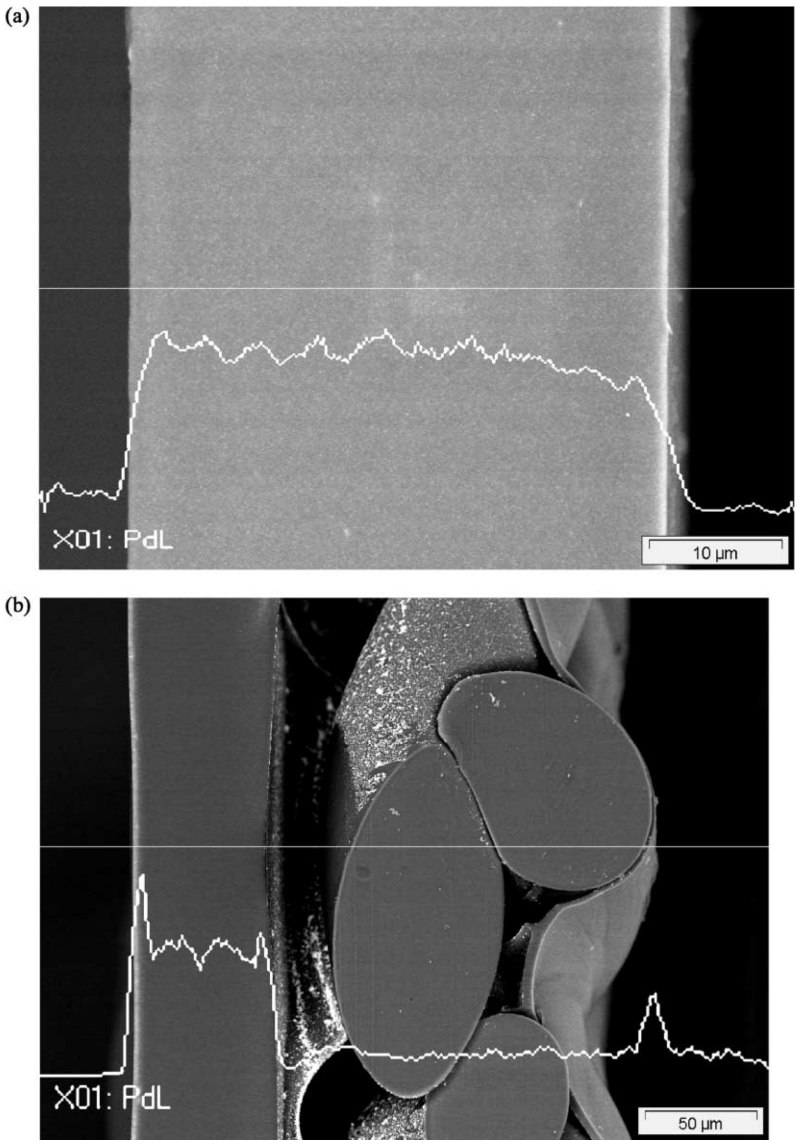

Fig. 3. (a) Homogeneous Pd–PEBA membrane number 5 (magnification: 2000); (b) Pd–PEBA membrane number 7, reinforced with Scrynel fabric (magnification: 350).

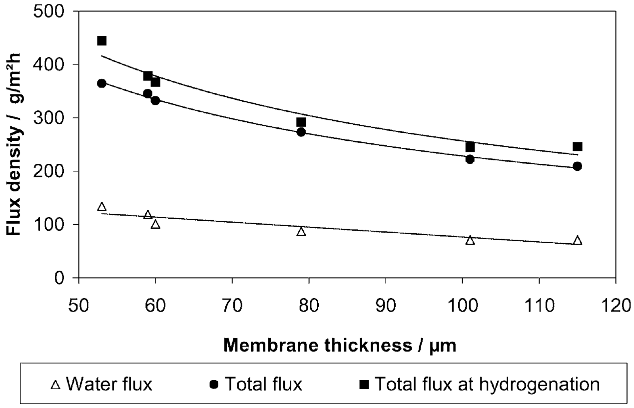

Fig. 4. Influence of membrane thickness on pervaporation flux densities under different conditions. Chlorophenol (0.4 wt.%) in feed, 57 °C, 1 bar H_2.

(feed concentration 0.4 wt.% 4-chlorophenol, 57 °C) [15]. The water flux decreased linearly, while the total flux density showed an exponential decrease as membrane thickness increased. The mechanical stability of PEBA membranes in the swollen state depends on the membrane thickness. Thinner membranes are more sensitive to fail at higher phenol concentration. Addition of hydrogen to the solution (1 bar H_2 by frit) increased the flux of chlorophenol further. This flux increase may be due to a coupled transport of H_2 and chlorophenol. Membranes used in the pervaporative reduction have thicknesses of 50–70 μm.

The partial flux density of 4-chlorophenol is directly proportional to its concentration in the feed up to 1–2 wt.%. At higher concentrations of 4-chlorophenol the membrane swells extremely, since the PEBA polymer is soluble in the pure chlorophenol. The chlorophenol from solution

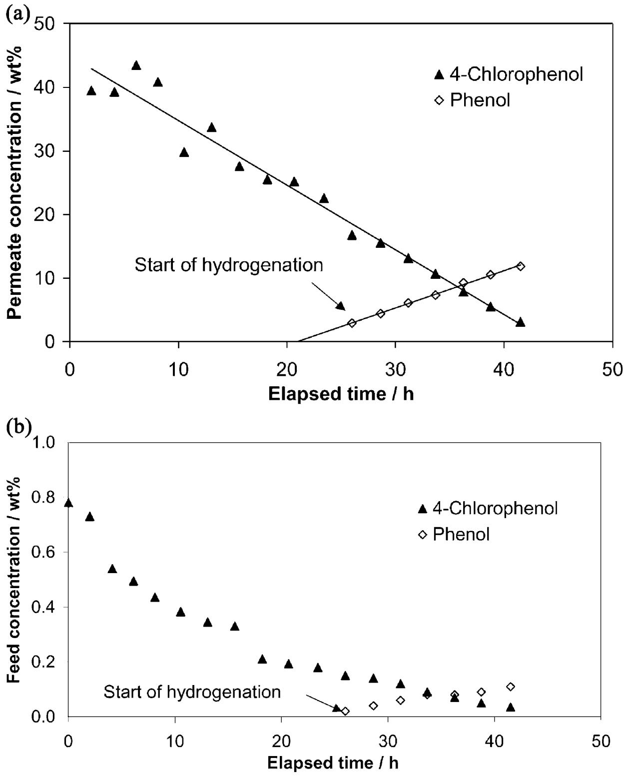

Fig. 5. (a) Permeate concentration of 4-chlorophenol phenol without/with reduction, respectively by H_2 at 1 bar. Membrane number 3, 30 °C, starting feed concentration 0.78 wt.% chlorophenol; (b) feed concentration during pervaporation of 4-chlorophenol without/with reduction by H_2 at 1 bar. Membrane number 3, 30 °C.

dissolves in the membrane preferentially over water, enrichment factors of 100 and more were obtained [8].

2.2.2.3. Reduction of 4-chlorophenol under pervaporative conditions at 1 bar hydrogen pressure. Fig. 5a depicts the permeate concentrations obtained within a series of 16 experiments during 40 h of pervaporation, starting at a concentration of 0.78 wt.% 4-chlorophenol in feed (membrane number 3, 30 °C). Permeate concentrations were measured to about 40 wt.% and higher for the first experiments in row, the enrichment factor increased from 50 to 100 and above. During the operation time chlorophenol was removed from the feed solution by pervaporation. With decreasing feed concentration also the permeate concentration declines, although the enrichment factor increases simultaneously. After 25 h of pervaporation hydrogen was bubbled to the solution by a frit and reduction starts immediately without induction period. The concentration of dissolved hydrogen was measured to 1.5 mg/l at 30 °C. The reaction product phenol subsequently appeared in the following permeates. Nevertheless, a considerable amount of the chlorophenol permeated the membrane without reaction. Details are given in Table 2.

The permeate concentration of the product phenol increased with time due to the increase of phenol concentration in the feed. Comparison of the total masses of phenol in permeate and feed showed that phenol was accumulated predominantly in the feed solution (relation 0.5:1). A driving force exists to both sides of the membrane: The concentration of the product phenol in the feed is zero at the beginning and is kept at zero by a vacuum at the permeate side. Consequently, the measured phenol flux of each experiment is a combination of the phenol produced in the membrane and the enrichment of the phenol, diffused from the membrane to the feed solution.

In Fig. 5b, it is depicted that the concentration change in the feed during pervaporation of 4-chlorophenol without and after about 25 h with reduction by H_2. To about 16 h of running normal pervaporation conditions the 4-chlorophenol concentration decreased exponentially and changed into linear decrease after about 18 h. Starting the reduction of chlorophenol by bubbling hydrogen into the feed after 25 h did not change the linear decrease of chlorophenol concentration. The product phenol, diffusing to the feed solution after reaction inside the Pd-activated PEBA membrane,

Table 2
Reductive pervaporation of 4-chlorophenol[a]

Time (h)	$Conc_{Feed}$ Cl-phenol (wt.%)	Flux H_2O (g/m^2h)	Flux Cl-phenol (g/m^2h)	Flux phenol (g/m^2h)	Flux cyclohexanone (g/m^2h)	Flux total (g/m^2h)	Enrichment Cl-phenol	Enrichment phenol	Enrichment cyclohexanone
0	0.180								
3	0.165	28.6	6.0	1.05	<0.01	35.7	100	200	–
5.5	0.145	28.9	5.6	1.60	<0.01	36.1	110	150	–
8	0.130	28.2	4.6	2.14	<0.01	34.9	100	120	–
10.5	0.100	27.9	3.6	2.50	0.01	34.0	110	100	–
13	0.080	27.3	2.6	3.06	0.01	32.0	100	120	–
15.5	0.060	27.5	1.8	3.46	0.01	32.8	90	120	–
18	0.035	28.1	1.0	3.92	0.05	33.1	90	110	–
21	0.019	28.6	0.2	3.84	0.14	32.8	40	100	370
25	0.008	29.2	0.2	3.95	0.22	33.6	70	100	480
28	0.003	28.7	0.1	3.33	0.20	32.3	70	90	270
31	0.001	29.1	<0.1	2.86	0.22	32.4	60	90	160

[a] H_2 pressure 1 bar (frit), 30 °C, membrane number 3.

Table 3
Reductive pervaporation of 4-chlorophenol[a]

H_2 pressure (bar)	Conc$_{feed}$ Cl-phenol (wt.%)	Conc$_{feed}$ phenol (wt.%)	Conc$_{permeate}$ Cl-phenol (wt.%)	Conc$_{permeate}$ phenol (wt.%)	Cyclohexanone (wt.%)	Cyclohexanol (wt.%)	Flux density (g/m^{2}h)
1	0.10	0.08	10.7	7.3	0.015	N.D.	34.0
5	0.15	0.07	10.2	6.8	0.022	0.097	34.7
1	0.08	0.08	7.9	9.3	0.023	N.D.	32.9
5	0.08	0.09	4.2	7.2	0.987	0.104	30.3

[a] Comparison of experiments at two different hydrogen pressures, 30 °C, membrane number 3 at 1 bar (frit), membrane number 9 at 5 bar (hollow fiber).

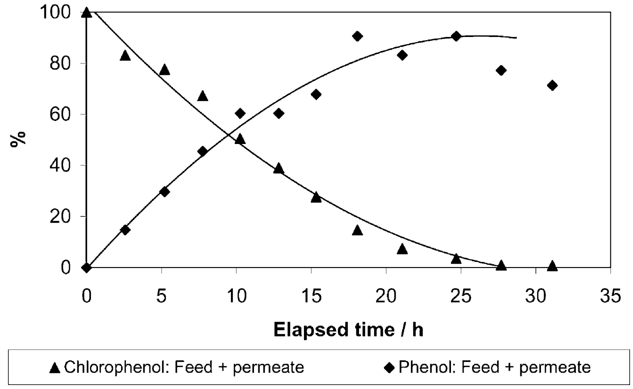

Fig. 6. Conversion during the pervaporative reduction of 4-chlorophenol by H_2 at 1 bar. Membrane number 3, 30 °C; starting feed concentration 0.18 wt.% chlorophenol.

increased in the feed by time. This increase followed most likely in logarithmic order. Because in the permeate are found also small amounts of the phenol reduction products cyclohexanone and cyclohexanol (see Table 3) we conclude that as well as phenol also its products diffuse to the feed. However, they could not be measured precisely because of the high dilution in the feed.

Fig. 6 describes the conversion of 4-chlorophenol to the major product phenol during 30 h of catalytic pervaporation. The decrease of chlorophenol over reaction time includes the non-reduced chlorophenol from the permeate. The conversion to phenol was necessarily incomplete, since the chlorophenol permeating without reaction was irreversibly removed from the feed.

Due to the by-product hydrochloric acid the pH value of the feed solution decreased from 5 to 2. The permeates were only slightly acidic, indicating that hydrochloric acid was only in very minor parts permeating through the membrane. Independent pervaporation experiments of diluted HCl using pure PEBA membranes indicated no permeation of HCl.

The increase of acidity in the feed during up to 40 h of pervaporation did not affect the catalyst's activity as it is reported for batch experiments using conventional supported Pd or Ru catalyst [16,17]. Catalytic pervaporation, thus, does not require pH control to prevent poisoning of the catalyst by HCl.

The reduction of an aqueous solution of phenol showed low conversion to cyclohexanone (less than 30% after 30 h of operation). Palladium metal catalyst is not especially suited for the hydrogenation of the aromatic ring [18]. Nevertheless, the phenol flux density and enrichment was in accordance with the results obtained by a homogeneous PEBA membrane without palladium: 14 g/m^{2}h and $\beta = 100$ at 30 °C at a phenol feed concentration of 0.3 wt.%.

2.2.2.4. Reduction of 4-chlorophenol under pervaporative conditions at 5 bar hydrogen pressure. To improve the hydrogen supply to the solution, a hollow fiber module was installed, allowing the direct transport of hydrogen gas into the water without bubbles up to 5 bar (Fig. 2b). The measured hydrogen concentration in the feed solution was 8–10 mg/l (compared to 1.5 mg/l at normal pressure). In Table 4, a typical series of experiments is presented. The yield of phenol was at the same level as the experiments at 1 bar with the frit, indicating that the yield of phenol was estimated by the amount of catalyst and not of the hydrogen. But the clearly higher conversion to cyclohexanone and cyclohexanol showed that the amount of hydrogen available improved the subsequent reaction of phenol to cyclohexanone and cyclohexanol (Table 3).

2.2.3. Reduction of 4-chlorophenol or phenol by the catalytic membrane and hydrogen supply through the membrane (without pervaporation)

To clarify the influence of pervaporation on the reduction of chlorophenol, experiments without pervaporation were conducted with the same catalytically active PEBA membranes. The apparatus was slightly changed by using a modified test cell. The permeate side was fitted with an inlay identical to the one on the feed side, allowing gas in and out by applying 0.5–1 bar hydrogen pressure as H_2 source. The hydrogen purge was very slow to avoid stripping of organic compounds on the "permeate" side. The 4-chlorophenol solution was circulated on the membrane's feed side. By diffusion through the membrane, the palladium clusters were loaded by hydrogen, the chlorophenol was absorbed by the PEBA membrane and the reaction took place inside the membrane. The produced phenol diffused back into the feed solution. The by-product hydrochloric acid also accumulated

Table 4
Reductive pervaporation of 4-chlorophenol[a]

Time (h)	Conc$_{Feed}$ Cl-phenol (wt.%)	Flux H_2O (g/m^{2}h)	Flux Cl-phenol (g/m^{2}h)	Flux phenol (g/m^{2}h)	Flux cyclohexanone (g/m^{2}h)	Flux total (g/m^{2}h)	Enrichment Cl-phenol	Enrichment phenol	Enrichment cyclohexanone
0	0.34								
3	0.31	28.9	8.2	1.9	0.23	39.2	70	150	430
6	0.25	28.5	9.8	2.5	0.34	41.1	90	120	230
9	0.17	31.6	5.2	2.2	0.24	39.2	60	90	120
12	0.13	28.8	3.5	2.4	0.32	35.0	70	90	140
16	0.09	28.3	4.3	2.9	0.30	35.8	110	100	110
19	0.07	26.8	1.3	2.2	0.30	30.6	50	80	100
23	0.05	29.2	2.0	3.2	0.28	34.7	110	90	60
26	0.04	28.4	1.1	2.8	0.27	32.6	90	90	60

[a] H_2 pressure 5 bar (hollow fiber), 30 °C, membrane number 9.

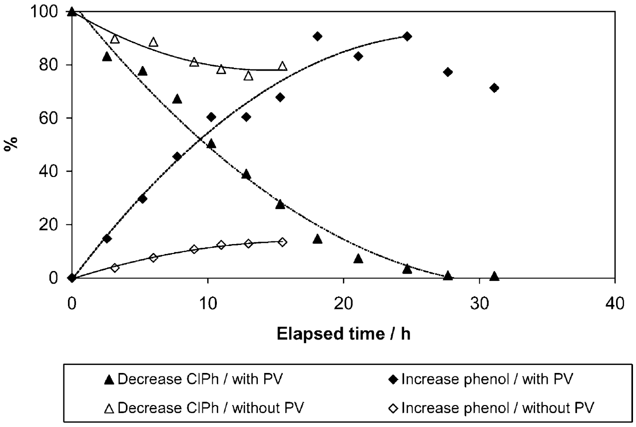

Fig. 7. Conversion of 4-chlorophenol with (filled symbols) and without (open symbols) pervaporation. PV: membrane number 3, 1 bar H_2 by frit into feed; and without PV: membrane number 5 (0.5 bar) and membrane number 8 (1 bar H_2 directly to membrane backside).

within the feed solution, causing a decrease of pH from 5 to 2.5. Fig. 7 compares the conversion of 4-chlorophenol with and without pervaporation. In combination with pervaporation the amount of phenol generated by the reduction was much higher. After 10 h of operation without pervaporation, about 10% of the stoichiometrically possible amount of phenol was generated, compared to 50% of phenol by pervaporative reduction. The mobility of the chlorophenol in the membrane is higher, when driven by the concentration gradient to the permeate and also, the probability of passing by a catalyst cluster increases.

If the palladium catalyst would be affected by the hydrochloric acid, experiments using phenol should enable a direct comparison of hydrogenation with or without pervaporation.

The entire result of this reduction was comparable to the chlorophenol reduction, although on a lower level of conversion (Fig. 8). The rather steep decrease of phenol concentration with pervaporation is due not only to the reaction to cyclohexanone but also to the permeation of non-reacted phenol. Nevertheless, the amount of cyclohexanone produced was more than doubled by pervaporation. The conclusive distinction, however, was in the concentration of the produced cyclohexanone. Coupled to pervaporation, the major amount of the cyclohexanone was found in the permeate, hardly detectable in the feed solution (<20 ppm). The concentration of cyclohexanone in the permeate was stable at 0.7–0.8 wt.% during the operation time, while the concentration of phenol in the permeate decreased proportionally to the feed concentration. Without pervaporation and with hydrogen supply through the membrane the produced cyclohexanone was dissolved in 2000 ml of feed solution, resulting in the very low concentration of about 50 ppm.

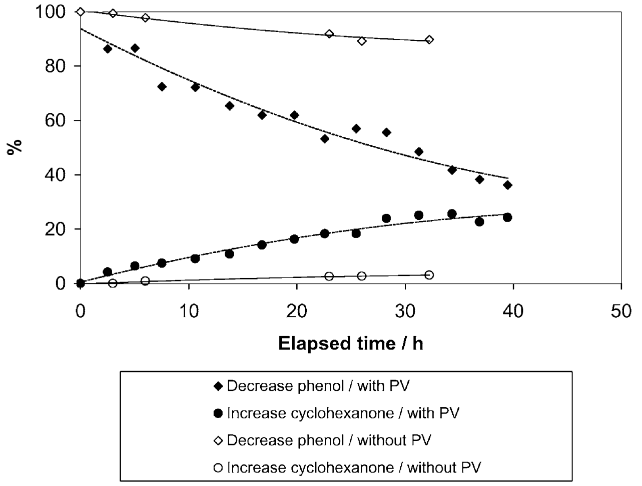

Fig. 8. Conversion of phenol with (filled symbols) and without (open symbols) pervaporation. PV: membrane number 3, 1 bar H_2 by frit into feed; and without PV: membrane numbers 5 and 7, 0.5 bar H_2 directly to membrane backside.

3. Conclusions

Enrichment and reaction of organic compounds in one step by pervaporation was demonstrated. As a test compound, the feasibility of the reduction of 4-chlorophenol by dissolved hydrogen in aqueous solution at 30–50 °C was demonstrated. The palladium nanoclusters incorporated in the PEBA membrane allow easy start of the reaction. Although the acidity in the feed solution decreased to pH 2 after 10 h of operation, no poisoning of the catalyst by the by-product hydrochloric acid was detected. The polymer itself is impermeable to HCl as tested by independent experiment.

The cluster size of the palladium in the membrane is crucial for catalytic performance: Small clusters of about 3 nm allow a conversion of chlorophenol of up to 80% after 20 h of operation, while larger clusters of about 5 nm show hardly any conversion. The cluster size depends on the preparation conditions of the membranes: membranes made from DMAc contain clusters of about 3 nm. BuOH is a reducing agent for $PdAc_2$ at elevated temperatures, the membranes prepared from BuOH solution contain Pd clusters of 5–7 nm.

The amount of hydrogen dissolved in the feed solution hardly influences the total phenol production because the diffusion of hydrogen in PEBA polymer is slow. Increasing hydrogen pressure, however, clearly enhances the yield of the subsequent hydrogenation products, cyclohexanone and cyclohexanol.

A palladium content of the membranes up to 12% by weight was possible, but amounts to only 1% by volume. In contrast to hydrogen, chlorophenol has no special affinity towards palladium. As a consequence, a notable amount of the chlorophenol passes the membrane without meeting reaction sites. To improve the degree of conversion we suggest to increase the volume concentration of the catalyst by using a support, to enhance the chance of the reactants meeting the reactive sites of the catalyst.

The reaction product was not permeating exclusively to the permeate. A considerable amount diffused back from the membrane to the feed solution and was subsequently transferred to the permeate by normal pervaporation.

Pervaporative reduction of phenol to cyclohexanone with Pd–PEBA membranes showed conversion of less than 30% after 30 h of operation, although Pd is not described in literature as a catalyst for phenol reduction at the applied temperature.

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