

Selective Hydrogenation Reactions with a Microporous Membrane Catalyst, Prepared by Sol–Gel Dip Coating

C. Lange, S. Storck, B. Tesche, and W. F. Maier¹

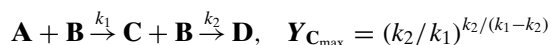
Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim a.d. Ruhr, Germany

Received September 9, 1997; revised November 24, 1997; accepted December 5, 1997

Catalytically active microporous thin film membranes were prepared by dip coating of an asymmetric ceramic support membrane in a Na₂PtCl₆ containing sol based on Ti(OiPr)₄. After drying and calcination, the membrane (thickness of the top layer, 0.2–0.4 μm) shows separation properties typical for microporous membranes with low defect concentration (nanofiltration). After activation with hydrogen at 250°C the membranes exhibit a hydrogenation activity significantly higher than those of comparable batch catalysts. At conditions of reaction control and limitation of hydrogen availability, 2-hexyne is semihydrogenated with such a membrane with 100% selectivity to *cis*-2-hexene. 1,3-Hexadiene is semihydrogenated selectively to 1-hexene. The unusual selectivity observed is attributed to the prevention of back-mixing through the use of the membrane contactor. © 1998 Academic Press

INTRODUCTION

Secondary reactions represent a common problem in the production of bulk and fine chemicals involving reactions such as oxidation, hydrogenation, alkylation, and halogenation.



Often **C** as the desired product is rapidly converted upon formation to undesired products **D** (chemical waste). The well-known kinetic consequences of such *successive* reactions (1) require often low conversion, short residence time and reaction control (no transport limitation) to achieve acceptable selectivities for **C**. These requirements usually impose undesirable conditions on the chemical production, responsible for inefficient use of energy, high process costs, and chemical waste. The selectivity and yield are strongly dependent on the ratio of k_1/k_2 . The $Y_{\mathbf{C}_{\max}}$, the maximum yield of **C**, approaches rapidly zero, if k_2 is larger than k_1 and for $k_2 = k_1$ the maximum yield is just 37% (holds for plug flow and batch reactor, for a CSTR another expression is valid leading to even lower yields). The major problem

here is the back-mixing of products with reagents by the stirring and the turbulence of batch-type reactor systems.

Natural catalysts like enzymes overcome this problem in a more elegant way by preventing the product from secondary reactions through chemical recognition and reaction selectivity. Only the starting material has sufficient access to the active center through structural recognition of the enzyme pocket or the cell limits accessibility of reactants through their membranes.

Heterogeneous catalysts are not yet capable of molecular recognition and therefore other approaches have to be examined to improve the technical control over successive reactions. Such a new approach is the use of catalytically active membranes, where through permselective addition of reagent or removal of product, conversion and selectivity of desired reactions can be controlled (2). Besides nonporous metal membranes for permselective hydrogen transport (3), porous inorganic membranes are increasingly being used in catalytic membrane reactors (4). The potential of membrane reactors has been nicely demonstrated in the liquid phase hydrogenation of nitrobenzene, where the hydrogen limitation of the conventional reaction conditions were overcome by the use of a membrane catalyst (5).

In organic membranes, permselectivities are achieved by the different solubility of the components in the organic matrix (6). Inorganic membranes, which are much more rigid, exhibit radically different separation behavior. Figure 1 sketches the principal dependence of molecular separation in inorganic porous membranes from the mean pore diameter (λ)/(d_{pore}). In pores larger than the mean free pathway there is no separation. In pores smaller than the mean free path (<1 μm) molecular diffusion is governed by impulse exchange, which means small molecules have higher speed and achievable separation is limited to the square root of the ratio of molecular weights (Knudsen diffusion).

When pore diameters approach molecular dimensions (<1–2 nm) separation can be affected by surface diffusion, pore condensation, or even molecular sieving. Among the special diffusion phenomena found in this range of pore dimensions is the single-file diffusion (7), which describes

¹ To whom correspondence should be addressed.

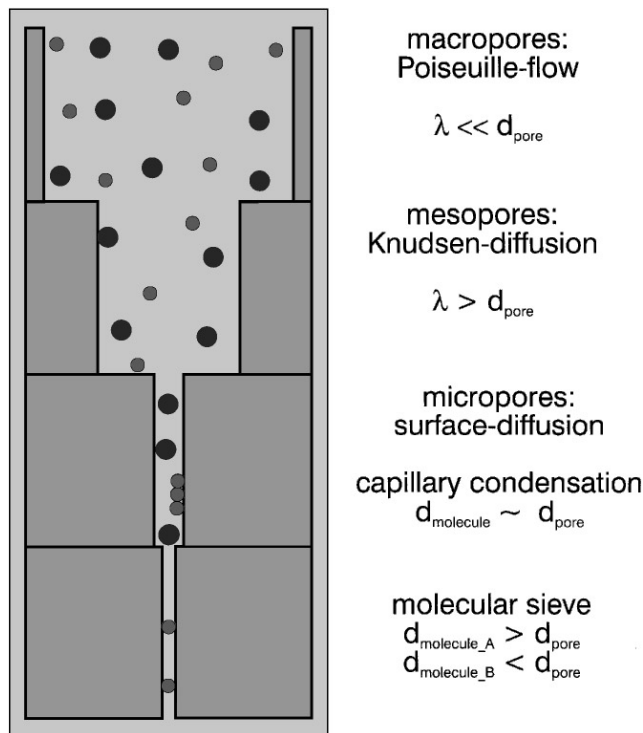


FIG. 1. Effect of pore diameter in inorganic membranes on flow behavior.

the diffusion of molecules too large to pass each other in a restrictive pore environment. Such a molecular queuing may provide a new scenario for avoiding secondary reactions. Figure 2 illustrates the principle. We assume the reaction of **A** + **B** (**A** could be a diene or a hydrocarbon and **B** may be hydrogen or oxygen) to give **C** (a monoene or a ketone), which is of comparable or higher reactivity than **A**. Secondary reactions can be avoided, when **C**, once formed, has no further contact with **B**. This can be realized in a single-file diffusion regime, where **B**, once consumed, cannot be replaced due to the one-dimensional movement

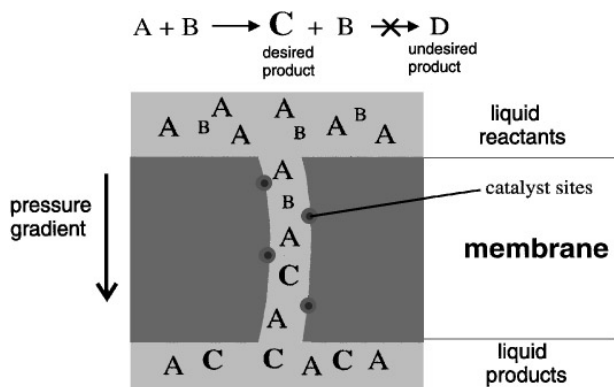


FIG. 2. Model of the prevention of secondary reactions by single-file diffusion in microporous membranes.

through the membrane brought about by a pressure gradient across the membrane. In Fig. 2 this is illustrated by the mixture of molecules entering the pores. **A** and **B** are consumed at the next catalytic site, and the product **C** is forced to leave the membrane.

For such a scenario to function, a thin membrane and a narrow pore size distribution is required with a pore diameter small enough to prevent molecular passing. Such a requirement is more readily fulfilled if reagents **A** and **B** are of similar molecular size, but in the proposed reactions of small molecules like hydrogen or oxygen with much larger organic molecules, molecular passing may not be avoidable and the single-file regime should be regarded as an idealized case. Direct evidence for the described scenario has been reported recently in an excellent study on the permeation characteristics of a zeolite membrane, where strongly hindered permeation of hydrogen by the presence of butane in the pores was documented (8). Also, if the membrane is thin enough, access of the smaller molecules to the active site may still be restricted sufficiently by the hindered diffusion, pressure, solubility and reactant concentration. The required narrow microporosity is only available with zeolites or sol-gel materials (9). The preparation of defect-free membranes from zeolites is very difficult (10) because of the particulate nature and the problem of closing intercrystalline voids. The method of choice for membrane preparation is therefore the sol-gel process.

In 1993 we successfully prepared titania-, zirconia-, and silica-based microporous membranes by the sol-gel process, which showed molecular sieving properties (11). At the same time, sol-gel silica-based membranes of similar quality were reported by other groups (12). The size exclusion properties of such membranes in catalytic reactions have been utilized in the poison resistant hydrogenation of alkenes with microporous Pt-containing titania membranes (13). It was shown that catalyst poisons, such as octahydroacridine, which effectively block hydrogenation reactions under batch conditions, have no effect on the rate of hydrogenation in a membrane reactor, where due to pore size the active sites can only be accessed by hydrogen. Another important, often ignored, property of heterogeneous catalysts as well as of membranes is their surface polarity, which strongly affects the mass transport properties and thus catalytic performance and permeation. Surface polarity of the sol-gel materials can be controlled by copolycondensation of Me-Si(OR)_3 with Si(OR)_4 , essentially replacing polar surface hydroxyl groups by nonhydrolyzable methyl groups. The effectiveness of this technique was demonstrated recently by the selective oxidation of alkenes on $\text{AMM-Ti}_x\text{-Si}$ -based catalysts, where the hydrophilic materials deactivate rapidly and can only utilize organic hydroperoxides, while the hydrophobic materials show no deactivation and even allow the use of hydrogen

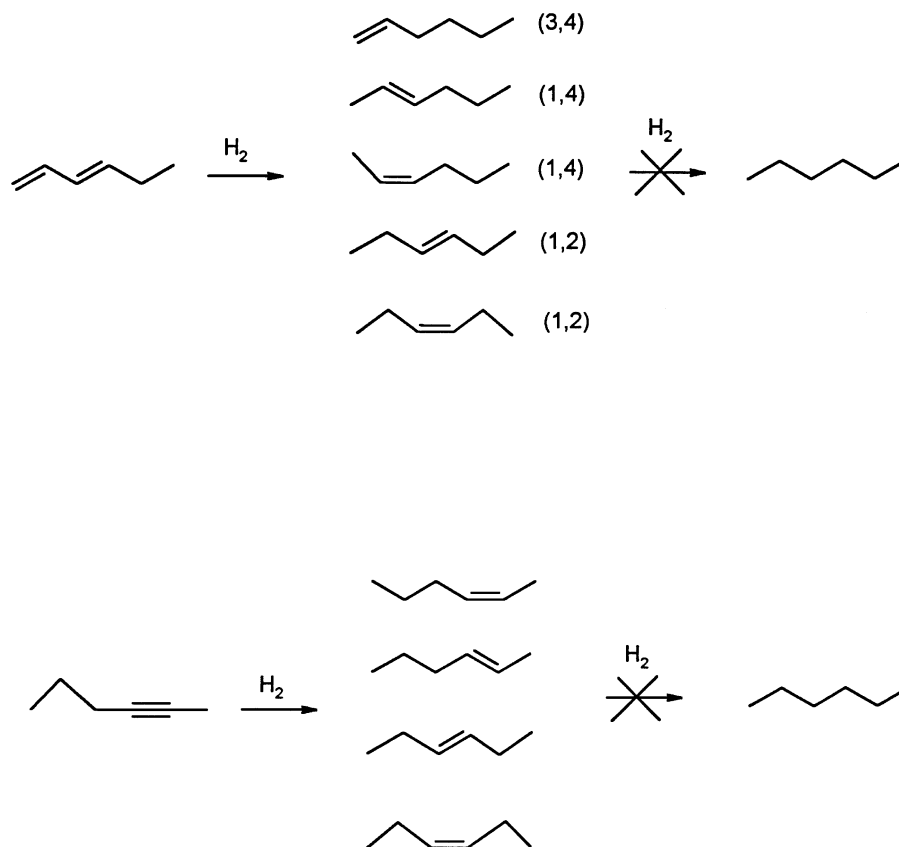
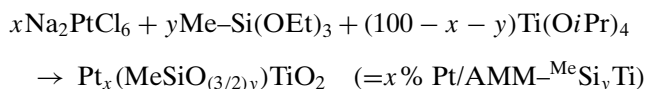


FIG. 3. Selected model reactions to study the suppression of secondary reactions.

peroxide in water as oxidation reagent (14). No effects of surface polarity on catalytic activity or selectivity have been identified so far. As long as the hydrophobic groups are not part of the active center, such effects are also not to be expected. For membrane applications preliminary studies have shown that hydrophobic membranes are much easier to handle and show less deactivation, higher permeation, and a more reproducible catalytic behavior than the hydrophilic materials. It was therefore decided to use exclusively hydrophobic membranes in this study. The preparation of the catalyst membrane material in the sol-gel reaction is summarized in the following equation:



In this manuscript we provide the first evidence for the successful application of catalytic membrane reactors to prevent secondary reactions. In order to study our above hypothesis on the control of secondary reactions, a suitable reaction had to be chosen and a defect-free catalytically active microporous membrane with a monomodal pore size distribution and pore diameters comparable to the size of organic molecules had to be prepared. Of critical impor-

tance is the absence of larger pores, since transmembrane flux increases rapidly with pore size. As a model reaction, a successive reaction with comparable rate constants seemed a good choice. Such reactions are selective hydrogenation reactions of alkynes or dienes.

Selective hydrogenations of alkynes are well-studied reactions (15). Pd is the most selective catalyst for this reaction, and highly *cis*-selective semihydrogenation is commonly achieved by the addition of poisons, which reduce the hydrogenation rate of the *cis*-olefin (k_2) more than that of the alkyne (k_1) (16). The selectivity shows a surface structure sensitivity, most selective are the low index surfaces of Pd (17). Despite high selectivities reported for Pd-catalyzed hydrogenation of alkynes, an intrinsic parallel reaction to the direct total hydrogenation can for mechanistic reasons not be avoided (18). Pt is a poor catalyst for these reactions, it shows no *cis*-hydrogenation selectivity and k_2 is often larger or identical with k_1 . Therefore we have chosen the hydrogenation of 2-hexyne as a model reaction on a Pt-containing membrane catalyst in the absence of modifier or poison (see Fig. 3).

Selective hydrogenation of dienes is another important challenge in heterogeneous catalysis. Especially conjugated dienes are difficult to semihydrogenate, since the product is usually a mixture resulting from 1,2-, 3,4-, and, 1,4-hydrogen

addition as well as overhydrogenation. In batch reactions, 1,3-butadiene is unselectively hydrogenated with *n*-butane formation as the major product on Pt catalysts (19), while on Pd selective formation of butenes by 1,2- and 1,4-hydrogen addition was observed (20). Most likely due to the shorter residence time in the gas phase flow hydrogenation of 1,3-pentadiene with Pt selective formation of monoenes with a 16:52:32 ratio of 1,2-, 3,4-, and 1,4-addition respectively has been reported (21). For the sake of simplicity of product analysis, we have chosen 1,3-hexadiene hydrogenation on Pt-containing catalysts as the second model reaction (see Fig. 3).

EXPERIMENTAL SECTION

Preparation of the Pt-Containing Titania Sol

All liquids used for sol preparations were filtered through an Anopore filter with pore size $0.02\ \mu\text{m}$ directly before use for the removal of dust, germs, and other small particles. A solution of 9.5 mL (32 mmol) of titanium(IV) isopropylate and 2.5 mL (12.5 mmol) of methyltriethoxysilane, dissolved in 40 mL of dried ethanol, was stirred for 30 min followed by dropwise addition of 0.1 mL of 8 N HCl. After 2 min, 0.1 mL of hydrochloric acid was added; then after 5 min 0.3 mL of hydrochloric acid was added; 0.3 mL of hydrochloric acid was then added after each of two 10 min intervals. After 60 min, 0.105 g of $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, dissolved in 10 mL of ethanol, was added. A clear yellowish solution was obtained. This solution was stirred at room temperature for

24 h. Without stirring the sol was kept loosely covered for another day. The sol was then used for dip coating.

Preparation of the Pt-Containing Titania Reference Catalyst

After dip coating the sol-gel solution was dried in a hood for 10 days. After the gel was hard and brittle, it was heated in air to 65°C at a heating rate of $0.1^\circ\text{C}/\text{min}$, kept at this temperature for 100 min, and then heated at the same heating rate to the final calcination temperature of 250°C . This temperature was kept for 5 h. The cooling rate to room temperature was smaller than $5^\circ\text{C}/\text{min}$. The calcined gel was milled for 10 min in a ball mill to a fine powder (particle size 1–10 μm).

Sorption Studies

Ar adsorption isotherms in liquid Ar were obtained with an Omnisorb 360. Figure 4 shows the isotherm obtained from catalyst powder **I**, and the insert in Fig. 4 shows the pore size distribution calculated from the isotherm by the method of Horvath and Kawazoe. All materials prepared displayed such type I isotherms typical for microporous materials with narrow pore size distribution. The isotherm confirms the complete absence of larger pores in the powdered materials.

Membrane Preparation

Membranes **I–III** were fabricated by dip coating a disc of a commercial ceramic alumina membrane, $\varnothing = 47\ \text{mm}$,

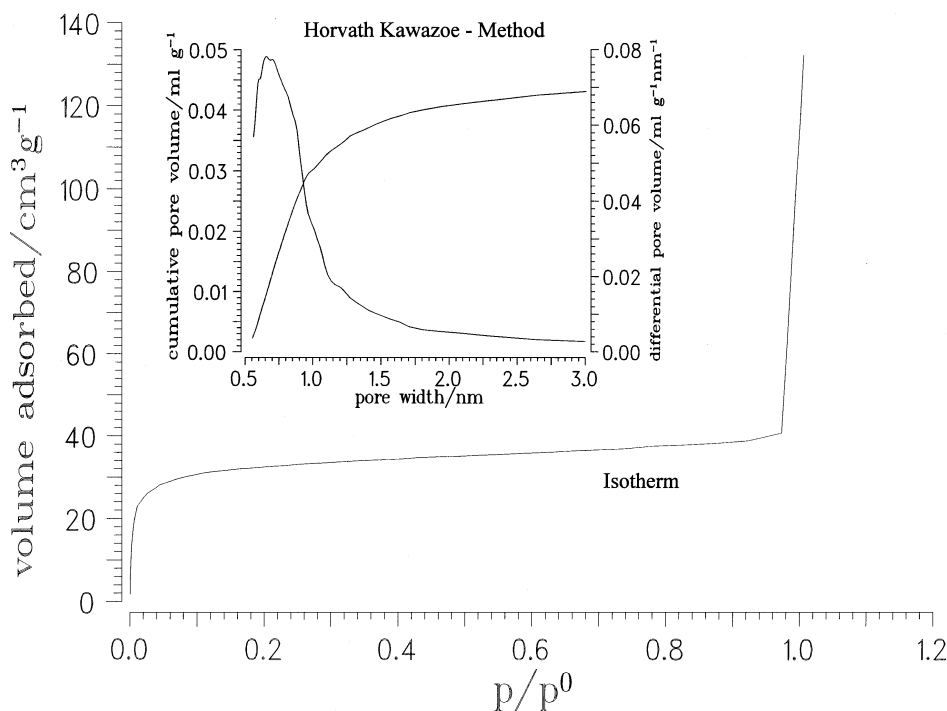


FIG. 4. Ar-adsorption isotherm and pore size distribution of catalyst **I**, representative of all catalysts of this study.

thickness 1 mm, nominal pore diameter of the last layer, 5 nm (Hermsdorfer Institut für Technische Keramik). The preparation procedures of all three membranes were identical. The alumina disc was first cleaned by boiling in a 3 : 2 : 1 mixture of acetone : pentane : isopropyl alcohol followed by an ultrasonic treatment in an acetone bath for 1 h. The ceramic support was then calcined in an oven at 450°C for 8 h. For dip coating the beaker containing the titania sol was placed into a large glass container, which was covered with a glass plate designed with a hole. The ceramic disc was attached to a string passing through a small hole in the glass plate cover of the glass container and connected to a motor. Before dip coating, the atmosphere in the container was saturated by injecting ethanol onto the glass bottom. Saturation is achieved when condensation takes place on the walls. The membrane was then immersed in the sol and pulled vertically continuously and free of vibrations at a constant speed of 3 mm/min out of the sol. When the membrane had been completely removed from the solution, the motor was stopped and the still hanging membrane was allowed to dry slowly under such mild conditions for 1 week in the glass cylinder. During that time the atmosphere of the container was allowed to slowly exchange with the laboratory atmosphere. Thereafter the membrane was dried in an oven at normal pressure in air. The membrane was heated from room temperature to 65°C at a heating rate of 0.1°C/min, kept at this temperature for 100 min, and then heated to the final calcination temperature of 250°C at the same heating rate. This temperature was kept constant for 5 h. The cooling rate to room temperature was smaller than 5°C/min. After this procedure the membrane was ready for use. Before and after dip coating, the dry weights of the membranes were determined and the mass difference (between 2 and 7 mg) was used as the catalyst mass in the calculation of kinetic data.

Membrane **IV** was prepared by following the procedure described by Leenaars and Burggraaf (22) in the last dip coating step. This dip coating was done in a clean room of class 1000.

Based on the mass of the membrane films and the Pt concentration of the sol the following amounts of Pt have been estimated for membranes **I–IV**, respectively: 5.8×10^{-8} , 2.3×10^{-7} , 3.3×10^{-7} , 5.6×10^{-8} mol Pt (used for TOF calculations).

Electron Microscopy

For high-resolution transmission electron microscopy (HRTEM) a Hitachi HF-2000 instrument (acceleration voltage 200 keV) was used. Energy dispersive X-ray analysis (EDX) was performed using a Noran EDX system with a liquid nitrogen cooled Si(Li) detector. For sample preparation the catalyst powders were ground, suspended in methanol, and deposited on Holey carbon grids (Cu, 400 mesh, 3 mm diameter).

Scanning electron microscopy was obtained on a ISI 60 at varying acceleration voltages. Energy dispersive X-ray analysis (EDX) was carried out with a KeveX system cooled with a liquid nitrogen Si(Li) detector. The ISI microscope is equipped with an external data treatment system (PRODAS). During the investigation, different sample preparations were studied and high- and low-vacuum conditions in the specimen chamber were applied. For the low-vacuum studies, the microscope was equipped with a second low-pressure pump system. This extra equipment allows the detection of backscattered electrons (Robinson detector) at increased pressure in the specimen chamber. The chamber pressure was adjusted with purified laboratory air. For preparation the membranes were embedded in a SPURR medium followed by grinding and a three-stage polishing procedure. To obtain sufficient resolution and for sufficient signals in the EDX analysis, the specimen had to be coated by means of a special electron impact evaporator with gold or carbon. The thickness of the carbon films varied between 3 and 10 nm, whereas the gold films were kept in the range of 10 nm. After embedding, these specimen were cut and the membrane cross-section was examined. Elemental distributions were examined by standard line scan analysis with EDX.

Membrane Reactor

The experiments were carried out in a special disc membrane reactor shown in Fig. 5. The reactor is similar to the one described earlier (23). The membrane catalyst is situated on a perforated supporting metal plate (thickness 1 mm, $\varnothing = 47$ mm, hole diameters = 1 mm) with the membrane layer facing the retentate (on top). The plate is necessary to avoid cracking of the ceramic membrane at higher pressure gradients across the membrane. Carbon gaskets are situated above the membrane and below the supporting plate to seal the retentate chamber. The membrane is fixed by a steel cylinder. Gas entries are located on top of the retentate and permeate chamber. The gas flow is controlled by a mass flow detector. The liquid phase is placed above the membrane and is stirred by a magnetically coupled mechanical stirrer. The reactor can be heated up to 300°C and pressurized up to 10 bar.

Before membranes are used in catalytic experiments, their separation quality had to be tested. The separation of alkylated benzenes (24) was used as control measurement. The membrane was heated in the reactor at 250°C under argon with a pressure gradient of 0.3 bar across the membrane for 4 h. It was then cooled to 100°C and 10 mL of a solution of equal parts by weight of benzene, toluene, propylbenzene, butylbenzene, heptylbenzene, decylbenzene, and dodecylbenzene, which were added in the retentate chamber and stirred. The composition of the permeate was analyzed by gas chromatography. Membranes of good quality separate these alkylbenzenes by their molecular weight as

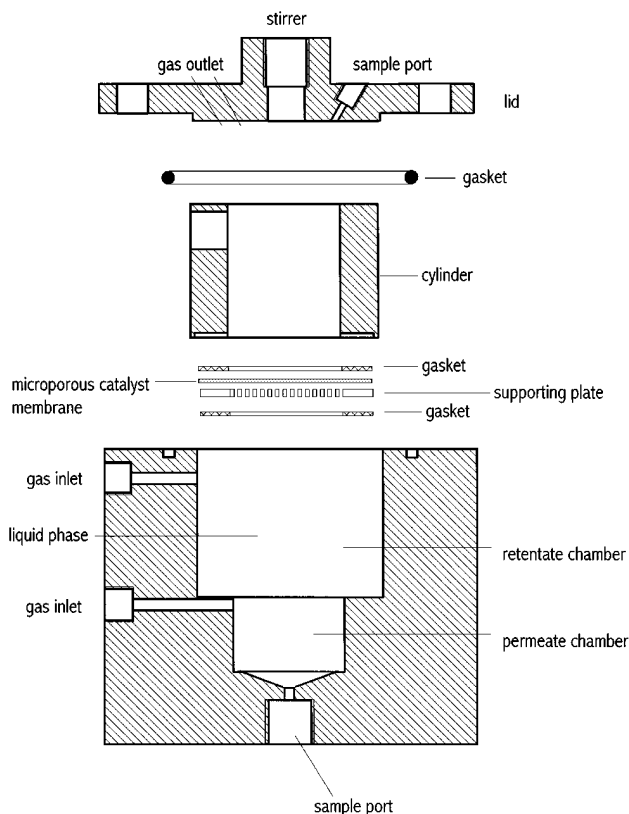


FIG. 5. Cross-section of the membrane reactor.

described (10). Another, simpler test for membrane quality is the single gas permeation of Ar and H₂, which should result in a separation factor slightly better than the Knudsen factor. In the experiments described below only membranes that fulfill these criteria were used.

Hydrogenation Experiments in the Membrane Reactor

In the membrane reactor an excess hydrogen pressure of 0.3 bar was applied to the lower surface of the ceramic membrane, so that a flow rate of 10–15 mL/min was observed at the gas outlet on top of the reactor. The reactor was heated to 250°C, and the membrane was activated at that temperature for 12 h and then cooled to the starting temperature (60–120°C). Hydrogen flow was then stopped, and the reactor was flushed with pure Ar (0.3 bar excess pressure) for 5–10 min through the membrane from below. (1.78×10^{-4})–(4.45×10^{-3}) mol of 2-hexyne (or 1.75×10^{-3} mol of 1,3-hexadiene) in 5 mL of decane or heptane was added to the reaction chamber on the upper surface of the membrane and stirred (stirring speed 300 min^{-1}) while the Ar flow from below was stopped. An Ar/H₂ mixture (7.5% H₂) was now introduced from the top of the reactor with a specific pressure (variation of excess pressure in various experiments, 0.05–1.5 bar). The lower surface of the membrane (permeate chamber) was kept open to ambient pres-

sure. The influence of the temperature (60–120°C) and of the concentration of substrate ((0.36×10^{-4}) –(0.89×10^{-3}) mol/mL) on the hexene yield was tested. The permeate was collected by opening the permeate chamber and condensing the permeate in a small sample glass cooled by dry ice. The permeate mixture was analyzed by gas chromatography (all 30 min).

Control Experiments in a Batch Reactor

100 mg of catalyst powder (1.1 wt% Pt/AMM–^{Me}Si₃₀Ti, particle size <10 μm) was used in a batch reactor to hydrogenate 4.45×10^{-3} mol of 2-hexyne (or 1,3-hexadiene) in 50 mL of decane. The mixture was stirred vigorously ($n = 2000 \text{ min}^{-1}$) in a hydrogen atmosphere at normal pressure at a temperature of 60 and 90°C. The reaction was monitored by gas chromatography.

Results and Discussion

In previous studies Pt/TiO₂, prepared by a single-step sol-gel procedure, has been shown to provide a highly active hydrogenation catalyst of stable Pt dispersion. Membranes prepared by dip coating from such a sol have shown new poison resistance in hydrogenation reactions due to size exclusion of the bulky poison from the active sites in the membrane pores (13). The membranes here were prepared by dip coating of a porous support asymmetric alumina membrane, composed of three layers. The bulk support is a ceramic membrane formed from α-alumina particles, which is covered by an intermediate layer of α-alumina particles with 60 nm pores. The top layer of the support (thickness 3 μm) consists of γ-alumina with a narrow pore size distribution and pore diameters of about 5 nm. On top of this layer a thin layer (0.3–0.5 μm) of Pt-containing TiO₂ was added by the dip coating procedure described above. Micrographs of the top of membrane cross-sections, obtained by scanning electron microscopy (SEM) are displayed in Fig. 6. Figure 6a, displaying a membrane from preliminary studies, shows that the TiO₂ layer penetrates the underlying alumina layer. This membrane was prepared with a sol of very low viscosity. Apparently substantial amounts of the sol particles are smaller than 5 nm. Figure 6b shows membrane I prepared with a more viscous sol (sol formation time 48 h). Here the three layers of the support membrane can nicely be recognized. The coarse support structure on the left is followed by the particulate intermediate layer. The γ-alumina on the right appears as a continuous material. On top of this layer, the microporous TiO₂ film was deposited. Figure 6c shows a cross-section of the top layer. Due to poor contrast, the microporous film cannot be clearly recognized. Only EDX line scans across the structure (Fig. 6d) show the exclusive presence of Ti on the outer surface of the material (see 3rd line scan), while the bulk of the membrane top layer consists of alumina (lowest line scan). The Pt-containing TiO₂ membrane layer on the top is therefore

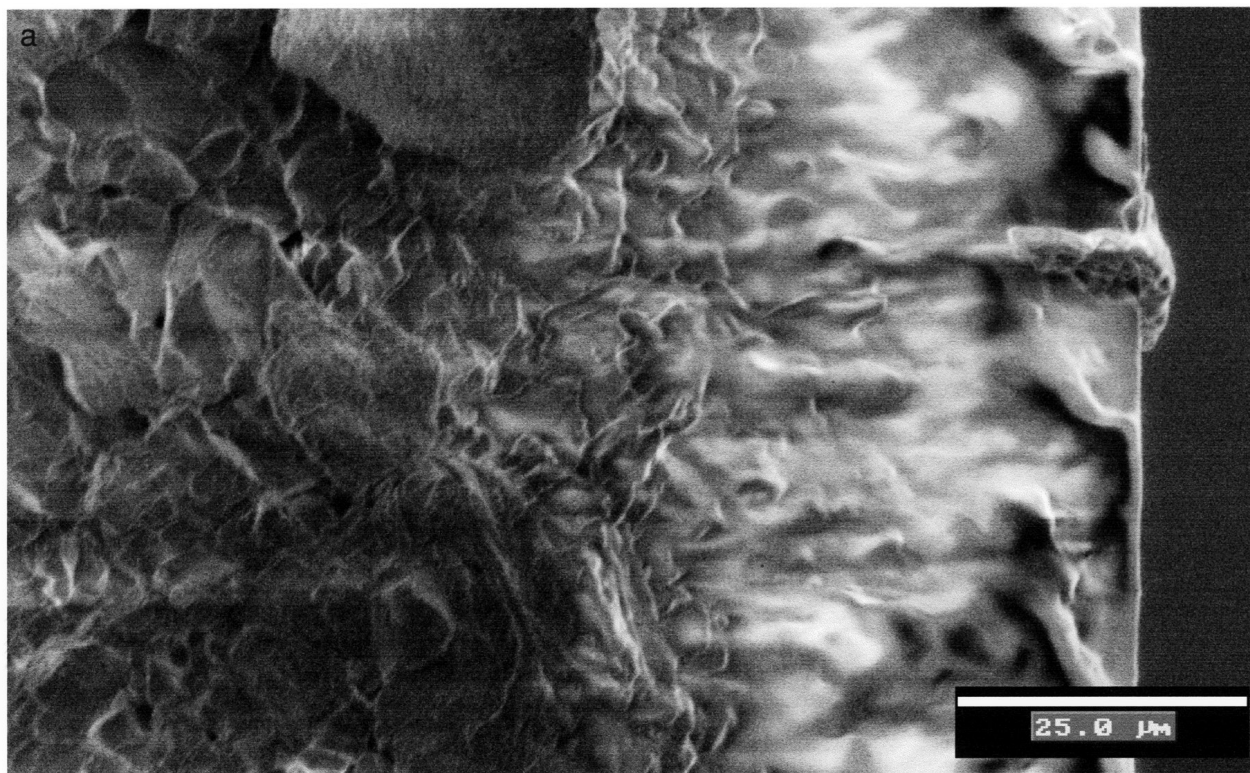


FIG. 6. SEM micrographs of catalyst membrane cross-sections. (a) Sol-gel-penetrated membrane. s.8 (b) Nonpenetrated membrane **I**. s.9 (c, d) Nonpenetrated membrane **I** with EDX line scans documenting the separation of the titania top layer from the alumina support layer (Cl = chlorine, BG = background, Ti = titanium, Al = aluminum). The crack is an artefact of the specimen preparation. The white line identifies the line scan position with the elemental distributions given below.

clearly visible, while its low Pt-content was not registered. The crack is an artefact of specimen preparation. This membrane has been used for the selective hydrogenation experiments.

During the dip coating procedure only a small portion of the sol is consumed and the remaining material was used to prepare powdered reference catalysts to be used as materials for the hydrogenation reactions in the batch reactor. The powders obtained after drying and calcination of the gel were characterized by high-resolution transmission electron microscopy (TEM) and adsorption isotherms. TEM studies have been obtained from fresh and used catalysts and membranes. Representative micrographs are presented in Fig. 7. Figure 7a shows a high-resolution micrograph of the used powdered catalyst **I**. The material shows amorphous TiO_2 ; however, very few small regions of microcrystalline TiO_2 were detectable. Pt is present only as large crystallites (dark spots). No Pt is detectable by EDX in other amorphous regions. Figure 7b shows particles removed from membrane **I** prepared from the same sol as powdered catalysts **I**. The bulk structure is also amorphous, the Pt is present as discrete crystallites, although smaller than in the powder. There is no evidence for a homoge-

neous distribution of Pt in high dispersion throughout the membrane.

Due to the small quantity of only a few mg per membrane film, no adsorption isotherms could be measured. Membrane quality has been evaluated by the drop of permeation relative to the support membrane. Membranes of lower quality, identified by higher permeation, most likely contain a larger number of broader pores resulting from defects or a broader size distribution. Such membranes do not show the selectivity of the high-quality membranes reported below. It is therefore assumed that the pore size distribution of the selective membranes must be as good or better as that of the associated catalyst powders shown in Fig. 4.

Selective Hydrogenation in the Membrane Reactor

Of special importance for the total permeation is the molecular size of the solvent. Table 1 shows the decrease in permeation (liquid volumes) with increasing solvent size and the decreasing temperature, documenting the expected strong dependence of permeation on the solvent size as a result of small pore diameters. The conversions given for the membrane reactor are based on permeated molecules

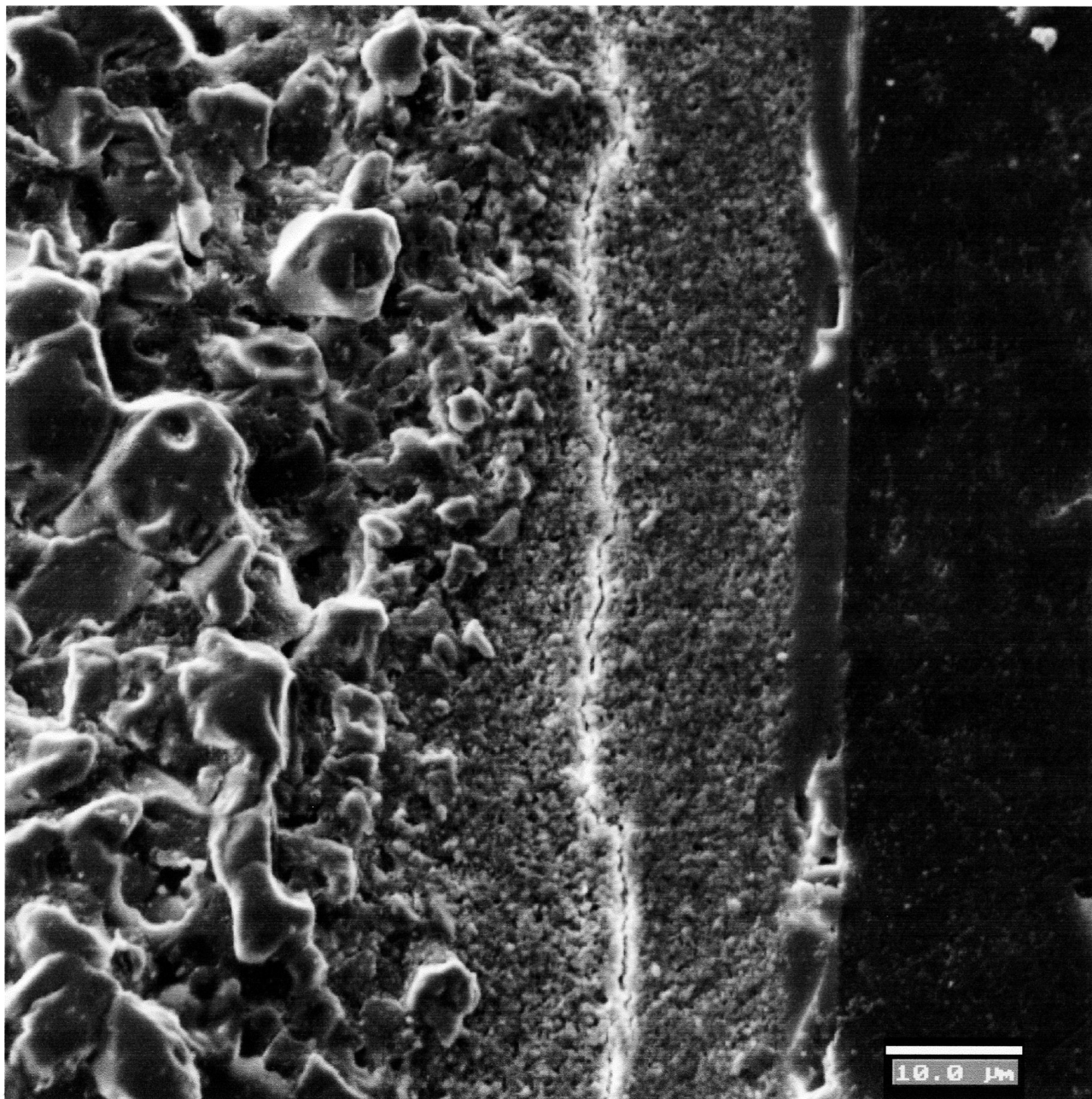


FIG. 6—Continued

only; these conversions are rather stable over the time of the experiment. Since the integral conversion of the batch reactor cannot be compared to the differential conversions obtained with the membrane reactor and since the differential conversions of the membrane reactor are dependent on permeation and thus different residence times, the turnover frequency (TOF) was calculated as a comparable measure of catalyst activity. The TOF was calculated from the measured conversion divided by the reaction time and amount of Pt in the catalyst (mol/mol h).

Table 2 shows the results of 2-hexyne hydrogenations obtained in decane as solvent on several catalyst membranes (I–III) prepared by the same procedure. All three membranes show identical selectivities and comparable activities at identical reaction conditions. Entry 1 (membrane I) shows the exclusive formation of *cis*-2-hexene (an *S* of 99% means other products are barely detectable by FID–GC at lowest attenuation) indicating a highly *cis*-selective semihydrogenation by the membrane catalyst at 60°C. Increase in the gas pressure should increase the hydrogen

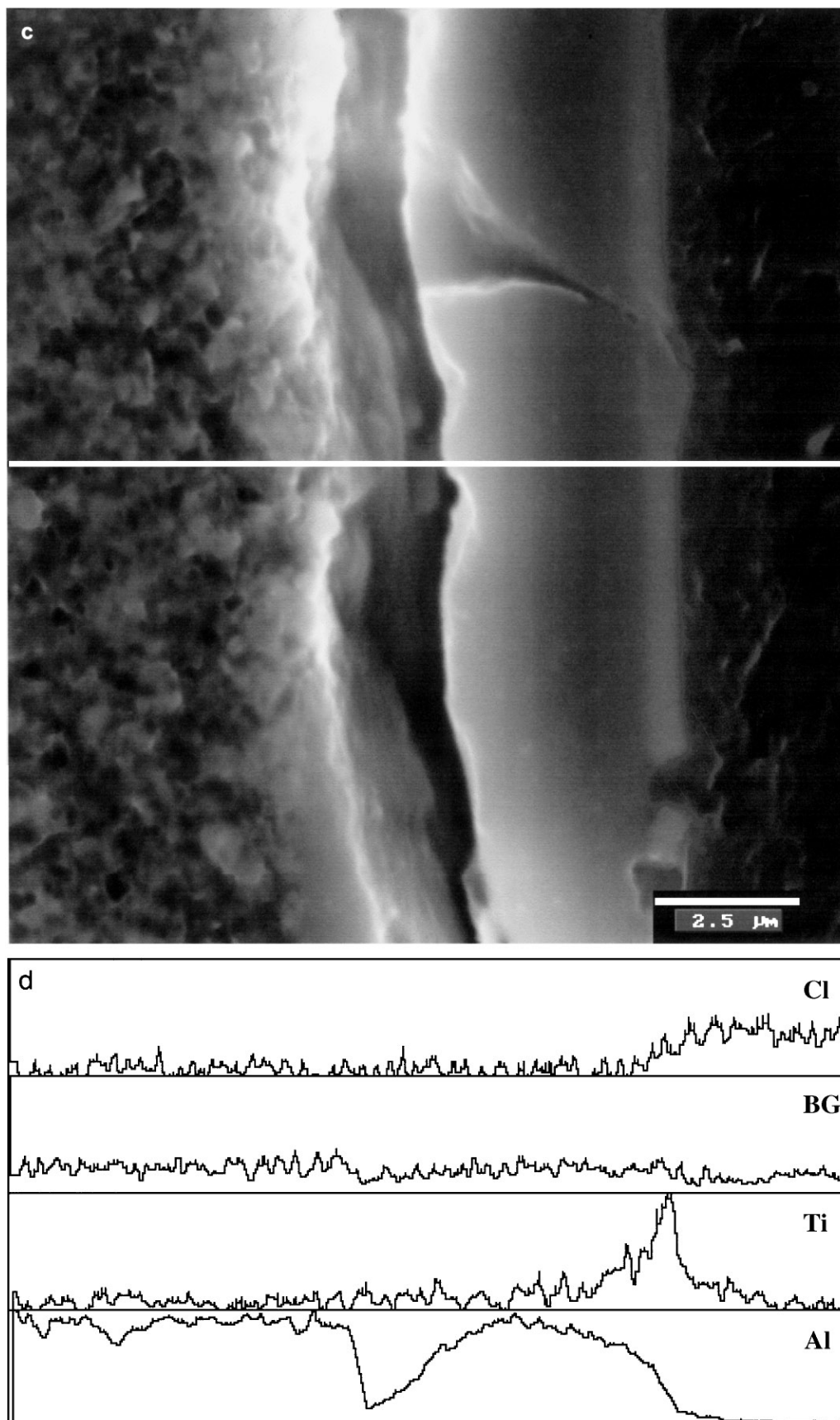


FIG. 6—Continued

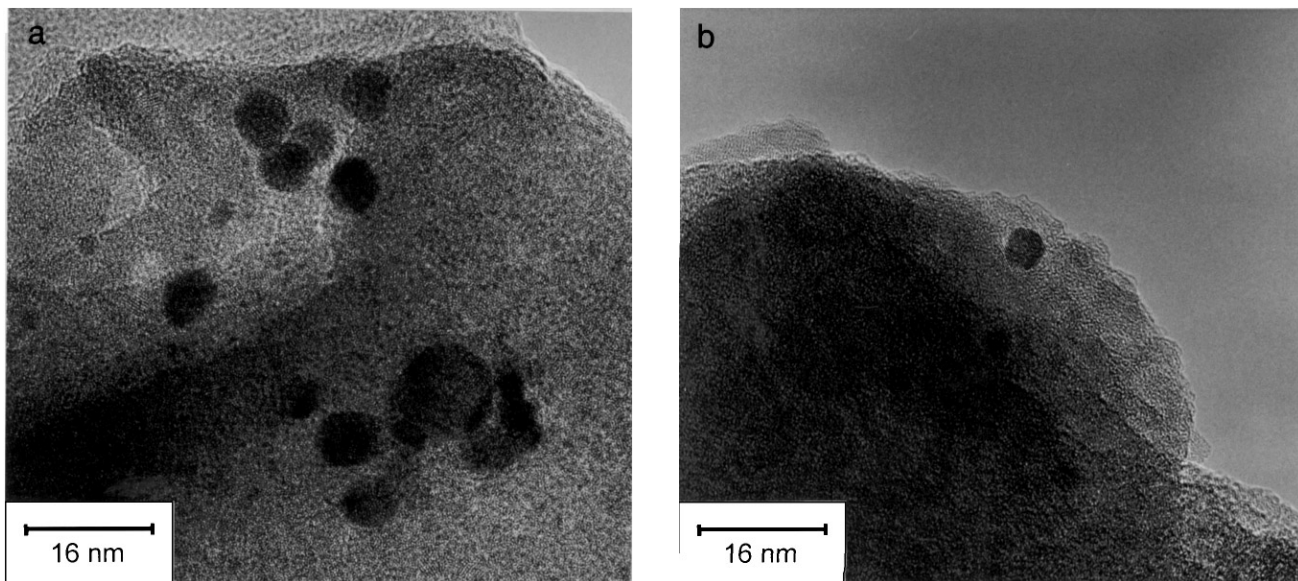


FIG. 7. TEM micrographs of powdered (a) and membrane (b) catalyst I.

concentration in the liquid and the pores and thus result in overhydrogenation. This was observed as expected, a pressure increase from 0.05 to 0.3 bar resulted with the formation of *n*-hexane in a decrease in hydrogenation selectivity to 91%. With a further increase to 0.6 bar (entry 3) the selectivity dropped to 84% with only a small increase in total conversion. Apparently, the steady state hydrogen concentration in the pores is with the higher pressures already high enough to promote overhydrogenation.

In entry 4 the 2-hexyne concentration was increased and the temperature was raised to 90°C. The result was an increase in the TOF and the permeation rate, while hydrogenation selectivity remained at 100%. Switching from dilute hydrogen to pure hydrogen (entry 5) with membrane II and a high concentration of 2-hexyne, the TOF was low and the selectivity was high. Doubling the hydrogen pressure to 0.1 bar and reducing the 2-hexyne concentration finally resulted in the expected formation of *n*-hexane ($S = 84\%$).

At identical reaction conditions, but without excess pressure (continuous flow of hydrogen), 100% selectivity was obtained at a comparable TOF of 3. Increasing the temperature to 120°C and the 2-hexyne concentration by a factor of 4 results in a high conversion of 32% at a high permeation corresponding to a TOF of over 31 (entry 8). With membrane III (entries 9 and 10) the increase in temperature from 90 to 120°C reproduced the increase in conversion and permeation, but now *n*-hexane was formed as a side product and the selectivity dropped to about 90%.

When the reaction was carried out in pentane as a solvent, permeation increased and good conversions were obtained at a much lower temperature. However, we could not locate conditions with high semihydrogenation selectivity. At all conditions applied, *n*-hexane formation was detectable. We assume that the smaller sized pentane allowed a more effective hydrogen diffusion and therefore overhydrogenation could not be avoided. Therefore, the slightly larger *n*-heptane was used as solvent and some of the data obtained are compiled in Table 3. The largest difference is the increase in permeation by a factor 3 relative to *n*-decane, while the TOF remained comparable. Doubling of the 2-hexyne concentration (entries 1 and 2) resulted in a decrease of the conversion indicating reaction limitation of the effective rate at 99% selectivity (assuming constant H_2 concentration). With temperature increase (entry 3) to 120°C high selectivity remained, permeation and conversion increased, resulting in a 10-fold increase in the TOF. Membrane II at the same temperature, but using the 10-fold concentration of 2-hexyne, showed the same selectivity but a much lower TOF. Doubling the pressure to 0.1 bar with membrane I at 90°C caused an increase in the TOF (entry 5). With further increase of the pressure to

TABLE 1

Permeation Rate [$mL h^{-1} cm^{-2} bar^{-1}$] of Selected Solvents (as Liquids) with Membrane Catalyst I

$T [^{\circ}C]$	Decane	Octane	Heptane	Isooctane	Pentane
30	n.p.	n.p.	n.p.	n.p. ^a	0.1
40	n.p.	n.p.	n.p.	n.p.	0.12
50	n.p.	n.p.	0.03	n.p.	0.2
60	0.01	0.04	0.05	n.p.	—
70	0.02	0.0, 04	0.06	n.p.	—
90	0.05	0.08	0.08	0.04	—
120	0.1	0.13	0.14	0.06	—

^a n.p., no permeate after 1 h.

TABLE 2
Hydrogenation of 2-Hexyne in Decane with Membrane Catalysts

Entry no.	Excess pressure [bar] or flow ^a	Membrane	Concentration [mol/L]	Temp. [°C]	Conv. [%]	Selectivity to <i>cis</i> -2-hexene [%]	TOF [h ⁻¹]	Permeation ^b [mL/h]
1	0.05 Ar/H ₂	I	0.036	60	10	99	19	0.1
2	0.3	I	0.036	60	11	91	19	0.1
3	0.6	I	0.036	60	15	84	28	0.1
4	0.05 Ar/H ₂	I	0.09	90	7	99	32	0.15
5	0.05 H ₂	II	0.9	90	0.4	99	5	0.15
6	0.1 bar H ₂	II	0.18	90	1.8	84	4	0.15
7	10 mL/min H ₂	II	0.18	90	1.4	99	3	0.15
8	10 mL/min H ₂	II	0.045	120	32	99	32	0.25
9	10 mL/min H ₂	III	0.09	90	18	99	10	0.1
10	10 mL/min H ₂	III	0.09	120	26	91	10	0.15

^a At ambient pressure.

^b Liquid volume.

0.3 bar conversion and TOF still increased (entry 6), but at 0.6 bar (entry 7) the conversion and TOF increase finally were accompanied by the undesired hexane formation. In the absence of pressure with pure hydrogen a high conversion at 99% selectivity was obtained (entry 8).

With membrane **III** the temperature increase from 90 to 120°C resulted in an increase of conversion like with membrane **I**, but now the selectivity dropped to 93% (*n*-hexane formation).

By quantitative gas analysis, no hydrogen could be detected in these experiments on the permeate side of the membrane, confirming that hydrogen is completely consumed in the pores of the membrane. This also means that the total conversion must result from the H₂ concentration in the pores. It was of interest to know, whether this pore concentration is identical to the solubility of H₂ in the solution. From the literature (25) the H₂ solubility in decane at 25°C is 3.3×10^{-3} mol/L and we have measured a solubility of

1.6×10^{-3} mol/L at 90°C in decane in the absence and presence of 2-hexyne. It was found that in all experiments about 1.5 to 2 times more H₂ has been consumed in the pores than could be present due to its solubility. This indicates that the hydrogen concentration in the pores is higher than in the solution (permselectivity) or that some additional hydrogen can still be delivered through the filled pores. Overall, there is excellent agreement between the solubility of the hydrogen in the reaction solution and the conversion obtained.

The data obtained from heptane as solvent confirm the trends observed with decane. *cis*-Selective semihydrogenation is obtained with Pt in a microporous membrane. With an increase in pressure overhydrogenation is observed readily, while an increase in 2-hexyne concentration has little effect on the selectivity. Increase in temperature results in a higher permeation rate and an increase in conversion. In some cases this overall increase of the TOF was

TABLE 3
Hydrogenation of 2-Hexyne with Membrane Catalysts in heptane

Entry no.	Excess pressure [bar]	Membrane	Conc. [mol/L]	Temp. [°C]	Conv. [%]	S ^a [%]	TOF [h ⁻¹]	Permeate ^b [mL/h]
1	0.05 Ar/H ₂	I	0.045	60	4.3	99	10.1	0.3
2	0.05 Ar/H ₂	I	0.09	60	1.9	99	8.9	0.3
3	0.05 Ar/H ₂	I	0.09	120	6.7	99	83.9	0.8
4	0.05 Ar/H ₂	II	0.9	120	0.4	99	2.1	0.6
5	0.1 Ar/H ₂	I	0.09	90	1.7	99	26.6	0.5
6	0.3 Ar/H ₂	I	0.09	90	3.3	99	25.8	0.5
7	0.6 Ar/H ₂	I	0.09	90	8.2	71	64.2	0.5
8	10 mL/min H ₂	I	0.09	90	4.4	99	41.3	0.6
9	0.05 H ₂	III	0.18	90	3.5	99	27.6	0.4
10	0.05 H ₂	III	0.18	120	8.6	93	27.8	0.6

^a S = selectivity to *cis*-2-hexene.

^b Liquid volume.

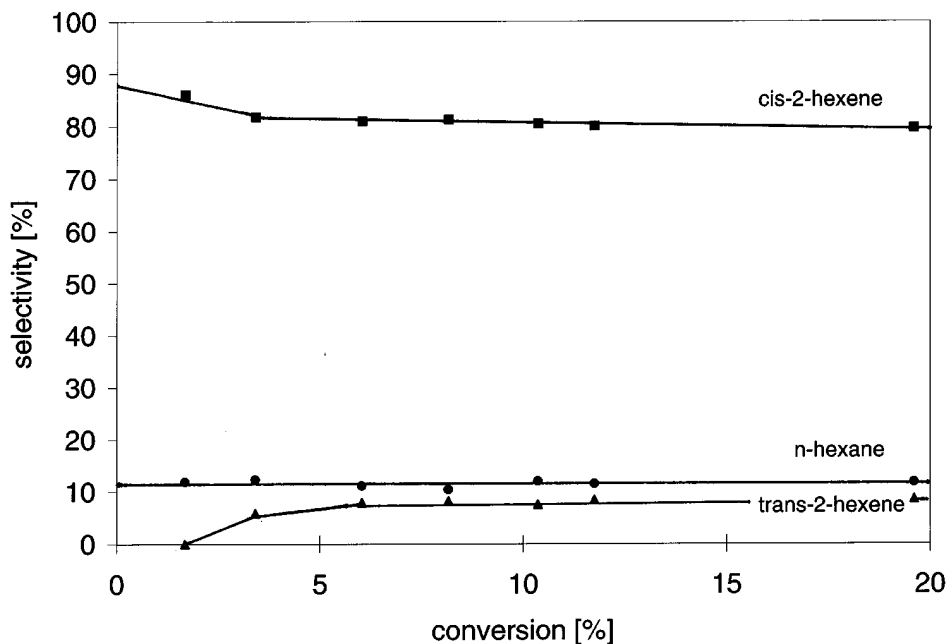


FIG. 8. Reaction profile of the hydrogenation of 2-hexyne in a conventional batch reactor at 90°C with powdered catalyst I.

accompanied by a loss in selectivity. The smaller the solvent, the larger the permeation, while the total conversion remains comparable, resulting in higher TOF with an increasing permeation rate.

To confirm that this selective catalytic behavior is due to the membrane and not just a result of the novel sol-gel catalyst, control reactions were carried out under conventional batch conditions. In the many reactions studied we have never observed the selectivity obtained with the membrane reactor. A typical reaction profile, obtained with the powdered catalyst corresponding to membrane I is shown in Fig. 8 with decane as solvent. Even at low conversions, hexane was always detectable and other hexenes are formed with increasing conversion. There is no change in *n*-hexane concentration in the product composition with decreasing conversion, indicating an intrinsic unselectivity of the catalyst. *trans*-2-Hexene, on the other hand, is clearly formed as a secondary product from the initial *cis*-component. Despite the small particle size < 10 μm and efficient stirring with a gas dispersion stirrer the TOF remained comparable to that of the membrane reactions (Table 2, entry 4). The catalyst powder corresponding to membrane III showed lower TOFs and selectivities around 90% already at conversions < 2%. This confirms that the high selectivity of the membrane is not due to the catalyst material, but must be due to the use of the catalyst in the form of the membrane. The high selectivity obtained with the membrane also proves that, even on Pt, *cis*-2-hexene is the initial product and all other products must be due to secondary reactions, even though the extrapolation of selectivity against

zero conversion at batch conditions often indicates otherwise.

Due to the novelty of these findings it was felt that another substrate should also be studied to confirm that the observed selectivity is not just restricted to 2-hexyne. 1,3-Hexadiene was therefore also hydrogenated with the membrane and the powdered catalyst. Table 4 summarizes the results obtained in decane as solvent. The membrane used here (IV) contains a very thin film, which is responsible for the low conversions observed. In contrast to 2-hexyne the selective semihydrogenation product of the diene on the membrane was found to be 1-hexene and only traces of the other products. The TOF numbers are comparable to those obtained on the previous membranes with 2-hexyne. Entry 1 in Table 4 shows the low conversion obtained at 90°C. In entry 2 the temperature had been raised to 100°C and conversion and permeation increased. At 100°C the

TABLE 4

Hydrogenation of 1,3-Hexadiene in Decane with Membrane Catalyst IV (Conc. = 0.35 mol/L; Ar/H₂, 10 mL/min)

Entry no.	Temp [°C]	Conv. [%]	[%] S ^a	TOF [h ⁻¹]	Permeation [mL/h] ^b
1	90	1	99	6	0.1
2	90-100	3	99	38	0.2
3	100	5	99	64	0.2
4	120	6	82	81	0.2

^a Selectivity to 1-hexene.

^b Liquid volume.

highest conversion with >99% selectivity and a good TOF of 60 was obtained. Temperature increase to 120°C (entry 4) resulted in considerable overhydrogenation and loss in selectivity (entry 4, product composition: 51% 1-hexene, 32% *trans*-2-hexene, 17% *n*-hexane). Astonishing to us is the high selectivity to 1-hexene, which, as a terminal olefin, is known to hydrogenate faster than the internal alkenes. It should be noted here that the reproduction of the selective hydrogenation of 1,3-hexadiene has been much more difficult than the selective hydrogenation of the 2-hexyne. So far, only two of our membranes have shown this unusual selectivity, in less selective membranes other isomers are also formed. The origin of this unusual selectivity through the membrane hydrogenation will be investigated in a separate study.

Control experiments of the hydrogenation of 1,3-hexadiene with the powdered catalyst **IV** in the batch reactor exhibit the expected lack in selectivity. Figure 9 shows the typical reaction profile, which does not indicate any selectivity comparable to that obtained with the membrane. Extrapolation of selectivity to zero conversion indicates a whole network of parallel reactions. This is strongly contradicted by the membrane experiments, where the selective formation of 1-hexene was observed.

If the selectivity is due to single-file permeation, increase in hydrogen partial pressure should result in an increase in the concentration of hydrogen in the reaction mixture as well as in the membrane pores, which eventually should re-

sult in the onset of overhydrogenation. This was tested and indeed, increase in hydrogen pressure to only 0.1 bar resulted in the formation of significant amounts in *n*-hexane (Table 2, entry 5). Reduction in hydrogen pressure led again to the exclusive formation of monoenes. An increase in reaction temperature to 120°C also results in the formation of *n*-hexane. We assume that at this temperature the “single-file” movement of the reaction mixture through the pores is already sufficiently disturbed, so that there is enough additional hydrogen transported through the pores to cause overhydrogenation. These results also suggest that in our reactions we have tailored the reaction conditions to provide an optimal composition of reactants in the pores. Due to the large size difference between hydrogen and the C₆-hydrocarbons and solvent molecules and the thermal vibrations, perfect single-file diffusion is unlikely to occur. The high dilution of >10 solvent molecules per 2-hexyne molecules together with a maximum conversion of about 33% indicates a lower limit of the molar ratio of hydrogen to hydrocarbon of 0.03 in the pores. As with decane, the solubility of hydrogen in heptane (4.6×10^{-3} mol/L) (25) accounts only for about half the conversions observed, indicating that hydrogen either permeates preferentially through the pores or that there is still limited effective diffusional transport. Since perfect single file diffusion is unlikely here, the reduction in permeation of hydrogen by the hydrocarbons in the pores (8) is the most likely explanation for the observed selectivities.

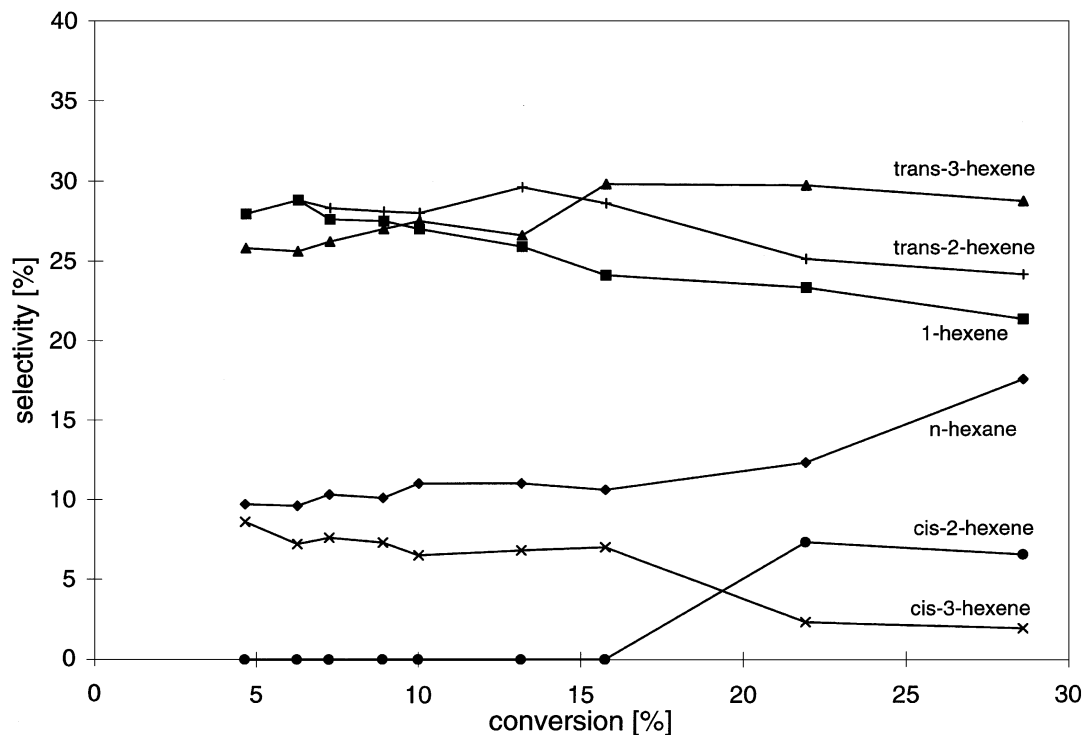


FIG. 9. Hydrogenation of 1,3-hexadiene in a conventional batch reactor at 90°C with powdered catalyst **IV**.

SUMMARY AND CONCLUSION

We have shown that overhydrogenation can be avoided by the use of catalytic membranes. The selectivity is achieved in the absence of modifiers or poisons and is solely the effect of the membrane as shown in control experiments under conventional reaction conditions. The selectivities found on the Pt-containing membranes have never been observed with unmodified conventional Pt catalysts. We attribute the membrane selectivity to a blocking of hydrogen permeation by the hydrocarbons in the pores. This study provides the first evidence that reactors based on microporous catalytically active membranes can be used to prevent secondary reactions by combining the advantages of heterogeneous catalysts with the separation properties of microporous membranes. This study opens the entry to a new reactor technology with new means to control selectivity and activity of heterogeneously catalyzed reactions. However, before practical applications can be discussed, the general nature of the proposed technique has to be demonstrated with reactions other than hydrogenations. The permeability of the membranes has to be increased drastically. Little is known about the life time and regenerability of such membranes. These and other aspects of membrane catalysis are the subject of on-going investigations in numerous research groups.

ACKNOWLEDGMENTS

We thank U. Bongard for the SEM analyses, J. A. Dalmon for discussions, J. Kóhler for assistance with hydrogen solubility measurements, and H. Verweij and R. M. De Vos for assistance with the preparation of membrane **IV** and the use of their clean room at the University of Twente.

REFERENCES

1. Wheeler, A., "Advances in Catalysis" (W. G. Frankenburg, V. I. Komarewsky, and E. K. Rideal, Eds.), Vol. 3, p. 313. Academic Press Inc., New York, 1951.
2. Hsieh, H. P., *Catal. Rev.-Sci. Eng.* **33**, 1 (1997).
3. Gryaznov, V. M., *Platinum Met. Rev.* **30**, 86 (1986).
4. Falconer, J. L., Noble, R. D., and Sperry, D. P., in "Membrane Separations Technology. Principles and Applications" (R. D. Noble and S. A. Stern, Eds.), p. 669. Elsevier Science B.V., Amsterdam, 1995.
5. Peureux, J., Torres, M., Mozzanega, H., Giroir-Fendler, A., and Dalmon, J.-A., *Catal. Today* **25**, 409 (1995).
6. Staude, E., "Membranen und Membranprozesse." Verlag Chemie, Weinheim, 1992.
7. Kukla, V., Kornatowski, J., Demuth, D., Girnus, I., Pfeifer, H., Rees, L. V. C., Schunk, S., Unger, K. K., and Kärger, J., *Science* **272**, 702 (1996).
8. Bakker, W. J. W., Kapteijn, F., Poppe, J., and Moulijn, J. A., *J. Membr. Sci.* **117**, 57 (1996).
9. Maier, W. F., Tilgner, I.-C., Wiedorn, M., and Ko, H.-C., *Adv. Mater.* **5**, 726 (1993).
10. Geus, E. R., van Bekkum, H., Bakker, W. J. W., and Moulijn, J. A., *Microporous Mater.* **1**, 131 (1993).
11. Maier, W. F., Tilgner, I.-C., Wiedorn, M., Ko, H.-C., Ziehfrennd, A., and Sell, R., *Adv. Mater.* **5**, 730 (1993).
12. Uhlhorn, R. J., Keizer, K., and Burggraaf, A. J., *J. Mater. Sci.* **66**, 271 (1992); Zaspalis, V. T., Van Praag, W., Keizer, K., Ross, J. R. H., and Burggraaf, A. J., *J. Mater. Sci.* **27**, 1023 (1992).
13. Maier, W. F., and Ko, Hee-Chan, *Catal. Today* **25**, 429 (1995).
14. Klein, S., and Maier, W. F., *Angew. Chem.* **108**, 2376 (1996); *Angew. Chem., Int. Ed. Engl.* **35**, 2330 (1996).
15. Bartók, M., Czombos, J., Felföldi, K., Gera, L., Göndös, G., Molnár, Á., Notheisz, F., Pálkó, I., Wittmann, G., and Zsigmond, A.G., "Stereochemistry of Heterogeneous Metal Catalysis." J. Wiley & Sons, New York, 1985.
16. Ulan, J. G., Maier, W. F., Rai, R. S., and Thomas, G., *J. Org. Chem.* **52**, 3126 (1987).
17. Ulan, J. G., Maier, W. F., and Smith, D. A., *J. Org. Chem.* **52**, 3132 (1987).
18. Ulan, J. G. and Maier, W. F., *J. Mol. Catal.* **54**, 243 (1989).
19. Bates, A. J., Leszczynski, Z. K., Phillipson, J. J., Wells, P. B., and Wilson, G. R., *Inorg. Phys. Theor.*, 2435 (1970).
20. Bond, G. C., Webb, G., Wells, P. B., and Winterbottom, J. M., *J. Chem. Soc.*, 3218 (1965).
21. Wells, P. B., and Wilson, G. R., *J. Chem. Soc. A*, 2442 (1970).
22. Leenaars, A. F. M., and Burggraaf, A. J., *J. Colloid Interface Sci.* **105**, 27 (1985).
23. Tilgner, I.-C., Lange, C., Schmidt, H.-W., and Maier, W. F., *Chem. Ing. Tech.* **69**, 1776 (1997).
24. Maier, W. F., Tilgner, I.-C., Wiedorn, M., Ko, H.-C., Ziehfrennd, A., and Sell, R., *Adv. Mater.* **5**, 730 (1993).
25. Fogg, P. G. T., and Gerrard, W., "Solubility of Gases in Liquids." John Wiley & Sons, New York, 1991.