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Porous, catalytically active ceramic membranes for gas–liquid reactions: a comparison between catalytic diffuser and forced through flow concept

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Abstract

Catalytically active membranes can be applied for three-phase reactions (liquid, gas and solid catalyst) and have advantages over conventional particle catalysts. Catalytically active components are deposited in the thin fine-porous membrane layer of an asymmetrical ceramic membrane. One reactant is dissolved in the liquid and diffuses through the porous structure of the membrane to the active inner surface, the other reactant is fed through the support to the catalytic layer from the other side of the membrane. Thereby, an effective contact between the two reactants and the solid catalyst is established. Under these conditions catalytically active membranes can typically be applied for hydrogenation or oxidation processes. Alternatively, if pore diffusion needs to be eliminated the dissolved reactants can be pumped through an asymmetric ceramic membrane or just a ceramic support coated with catalytically active metals. Thus, a very short contact time can be achieved. The following paper compares these two concepts—the catalytic diffuser and the forced through flow concept—and discusses their application for hydrogenation processes, like the catalytic nitrate/nitrite reduction in water and the dechlorination of chlorinated hydrocarbons. The developed catalytic membranes are not limited to these reactions, but are applicable for a number of multiphase reactions. A preparation method in order to make ceramic membranes catalytically active and different characterization methods will be described.

Keywords: Catalytic membrane reactor; Catalytic diffuser; Forced through flow; Multiphase reactions; Catalytic nitrate reduction; Dechlorination of chlorinated hydrocarbons

1. Introduction

1.1. Catalytic diffuser concept

Catalytically active ceramic membranes can be applied for three-phase reactions (one liquid reactant, one gaseous reactant, and solid catalyst). The catalytically active components are deposited on the pore walls of the thin fine-porous membrane layer of an asymmetrical ceramic membrane that is commercially available and normally used for micro- or ultrafiltration processes. One reactant is dissolved in the liquid phase and is sucked into the fine-porous catalytic layer by capillary forces. The reactant diffuses through the porous structure of the membrane to the catalytic sites. The gaseous reactant is fed through the support to the catalytic layer from the other side of the membrane. Thus, the two reactants approach the catalytic layer from opposite sides. The gas–liquid phase boundary is determined by the pressure difference between the gas and the liquid side. The pressure on the liquid side can

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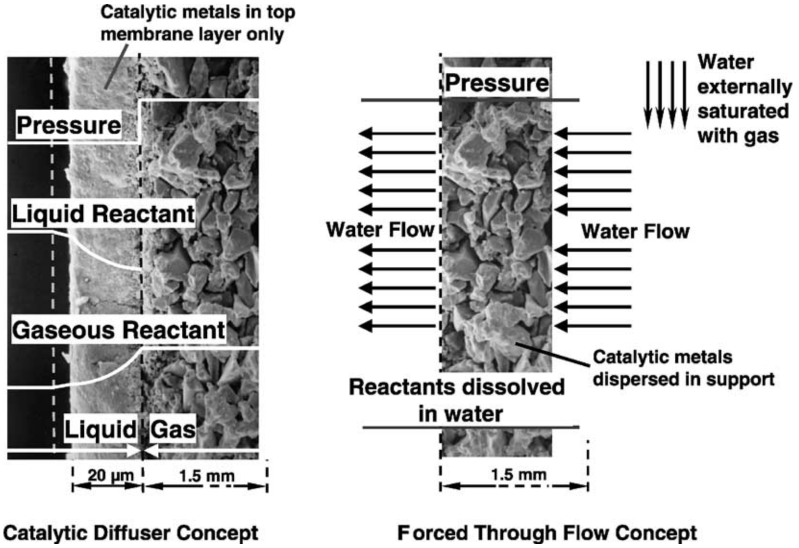

Catalytic Diffuser Concept

Forced Through Flow Concept

Fig. 1. Working principle of the catalytic diffuser and the forced through flow concept and concentration/pressure gradients in the membrane.

be atmospheric pressure, on the gas side there is an elevated pressure. The gas pressure is above the bubble point of the support so that water in there would be forced out, but does not exceed the bubble point of the fine-porous membrane layer. This membrane reactor concept for gas–liquid reactions is called “catalytic diffuser”. Fig. 1 (left) shows an SEM picture of an asymmetric ceramic (α-Al_2O_3) membrane with a coarse-porous support and a fine-porous membrane layer on top and demonstrates the working principle of the catalytic diffuser. In contrast to a conventional catalyst particle, where the two reactants (gas and liquid) have analogous concentration profiles, the concentration profiles in the catalytic diffuser are reverse. The pressure in the membrane changes from high pressure on the gas side including the support to low or atmospheric pressure in the fine-porous catalytic layer and reactor.

The limiting value of 50 mg/l for nitrate in ground water is exceeded in many regions of Europe. The increasing content of nitrate in drinking water involves health risks and is mainly caused by agricultural over-fertilization and emissions of nitrogen oxides. Nitrate and nitrite can be removed from drinking water by the so called “catalytic nitrate reduction”. This process was first described by Vorlop and Tacke in 1989 [2]. Nitrite is an intermediate product in the nitrate reduction process to nitrogen. Nitrite is reduced to nitrogen on a supported noble metal catalysts with hydrogen as reducing agent. As an undesired byproduct ammonium is formed. For the catalytic nitrite reduction supported palladium as catalyst is preferably used. For the reduction of nitrate to nitrite a second metal, preferably tin, copper or indium is essential. Eqs. (1)–(3) illustrate the stoichiometry of these reactions:

$$NO_3{}^- + H_2 \rightarrow NO_2{}^- + H_2O \qquad (1)$$

$$2NO_2{}^- + 3H_2 \rightarrow N_2 + 2OH^- + 2H_2O \quad \text{(desired)} \qquad (2)$$

$$2NO_2{}^- + 6H_2 \rightarrow 2NH_4{}^+ + 4OH^- \quad \text{(undesired)} \qquad (3)$$

An optimized catalyst for the catalytic nitrate reduction should have bimetallic clusters (e.g. Pd/Sn) and monometallic palladium clusters side by side on a supporting material [3,4]. The activity and selectivity is highly dependent on the reaction conditions, mainly on the pH-value of the reaction solution. A high pH-value leads to a low activity and a high ammonium formation. In a more acidic medium the activity is higher and less ammonium is produced, thus, the selectivity towards nitrogen is higher. Different materials like alumina, zirconia, silica, etc. can be used as support for the catalytic metals. The support must provide a large inner surface for the deposition of the catalytically active metals and should be stable against attrition and hydrolysis [1]. Furthermore, experiments by several different research groups have shown that activity and selectivity is also strongly influenced by the particle size of the catalyst [5–7]. The particle size must be small enough to enable short diffusion pathways. If the diffusion inside the catalyst particle is too slow in comparison to the reaction, the produced hydroxyl ions are not neutralized or transported away from the catalytic sites fast enough. As a consequence, there can be a local pH-increase in the catalyst particle which again results in poor catalyst activity and an increased ammonium formation. This can be avoided by using an extremely fine catalyst powder of a few microns. But in a technical process it is very difficult to handle and recover such a fine powder catalyst.

The catalytic diffuser concept was initially developed to solve this problem. On an asymmetric ceramic membrane the catalytic metals can be deposited in the thin fine-porous top layer of the membrane. Thus, the catalyst is immobilized and no separating process for the catalyst from the reaction solution is necessary.

On the one hand, the membrane is the catalyst support, on the other hand it also functions as a dosing device for hydrogen. The hydrogen is dosed directly to the catalyst, where it is consumed, and does not need to be fed to the reaction solution in an additional hydrogen saturator. This is especially advantageous because the hydrogen solubility in water is very low. The two reactants approach the catalytic membrane layer from opposite sides. Thereby, an effective contacting between the reactants and the catalyst is achieved.

If tubular membranes with an inorganic membrane layer (Al_2O_3, ZrO_2, TiO_2, carbon) on the outside are used, it is possible to work with a high gas pressure inside the membrane, while the reactor itself can be operated at atmospheric pressure. This leads to a simplified process design, and overall, to a safer and cheaper process.

By varying the gas pressure inside the membrane it is also possible to control the gas–liquid transition, i.e. the gas uptake into the liquid and the transfer to the catalyst and to some extent the position of the gas–liquid phase boundary. Thereby, the catalyst activity can be adjusted to the varying needs of the reaction with the H_2-pressure in the membrane.

The membrane enables very short diffusion pathways, similar to the condition in a powder catalyst, as the catalytically active metals are deposited in a thin fine-porous membrane layer of about 20 μm or less. In the case of the catalytic nitrate reduction this is favorable for a high activity and a high selectivity towards nitrogen.

Into the membrane a mixture of hydrogen and another gas, for example, carbon dioxide, can be fed. The carbon dioxide dissolves physically in water and some part of the carbon dioxide reacts with water to carbonic acid. The carbonic acid functions as a buffer and is able to neutralize hydroxyl ions formed during reaction, pH-gradients in the catalytic membrane layer can thereby be further suppressed.

1.2. *Forced through flow concept*

In the catalytic diffuser, even with a very thin catalytic membrane layer on top of a ceramic support, mass transport limitation by pore diffusion can occur if the reaction is very fast. Furthermore, the addition of carbon dioxide can only decrease pH-gradients in the membrane layer, but does not change the concentration gradients of the reactants (nitrate, nitrite, ammonium, hydrogen). By using a very fine catalyst powder it is possible to minimize these concentration gradients, but such fine powders are difficult to be separated and recovered on a technical scale. Another way to minimize the pore diffusion is to pump the whole reaction solution through an asymmetric ceramic membrane or a ceramic support coated with catalytically active metals. This idea was also suggested by Ilinitch et al. [8,9] and Lüdtke [10]. By adjusting the flow rate of the pump the contact time at the catalyst can be varied and very short contact times can be achieved.

If the reaction solution is pumped through the membrane fast enough, pore diffusion can be totally eliminated, so that there are no concentration gradients in the pore system of the catalytic layer. This is illustrated in Fig. 1 (right).

As the reaction is not fast enough to achieve a total conversion with one pass through the membrane a product recycle is necessary, i.e. the reaction solution must be pumped through the membrane several times. As the reactants are transported to the catalyst again and again, a very effective contacting between reactants dissolved in the reaction solution and the solid catalyst on the pore walls is accomplished.

A ceramic membrane or a support coated with catalytically active metals behave like a microreactor with very small channel diameters and thereby relatively high contact surface. Moreover, compared to conventional microreactors no expensive microstructuring techniques are needed as the membrane or the membrane support already contain small channels.

2. Experimental

2.1. Preparation of catalytically active ceramic membranes

2.1.1. Palladium-chemical vapor deposition

Commercially available ceramic ultra- and microfiltration membranes made of different ceramic materials were used as starting material. In our lab experiments we mainly used tubular ceramic membranes with an outer diameter of 10 mm, an inner diameter of 7 mm and a length of about 10 cm, and with the membrane layer on the outside of the membrane. The support is usually made of α-alumina and has pores in the range of 3 μm in diameter. The membrane layer consists of α-Al_2O_3, γ-Al_2O_3, ZrO_2 or TiO_2, and the pore diameters of the membrane layer vary between 5 and 400 nm depending on the material. The membranes were obtained from HITK e.V., Hermsdorf (Germany). For hydrogenation processes we coated these membranes with palladium.

For this purpose we developed a special metal-organic chemical vapor deposition (MOCVD) process with palladium(II)-hexafluoroacetylacetonate (Aldrich 401471) as palladium precursor. With this new technique it is possible to achieve a uniform deposition of palladium in the form of highly dispersed metal clusters on inert ceramic surfaces that contain no active sites. The penetration depth of the palladium into a ceramic membrane can be controlled, thus it is possible to coat the top layer of a membrane only. Also ceramic supports without any top membrane layer can be coated by this method. The bonding between support and metal clusters is very stable, thereby any loss of the expensive noble metal palladium by abrasion can be avoided. A more detailed description of the developed palladium MOCVD preparation technique will be disclosed soon in a German patent application which is currently in progress.

2.2. Characterization of catalytically active ceramic membranes

Various catalyst characterization methods are applicable for the characterization of catalytically active membranes. The pore sizes of the membrane layer are measured with mercury porosimetry and capillary flow porometry. The cluster sizes of the deposited catalytic metals can be determined with XRD, CO-pulse-chemisorption and TEM. SEM, TEM and AFM methods are used to analyze pore and membrane structure. EPMA (electron probe microanalysis)/WDX (wavelength-based detection) is used to determine the metal distribution over the membrane length and into the membrane layer. Typical results of TEM and EPMA/WDX characterization will be demonstrated here as example.

2.2.1. TEM-characterization

By TEM-characterization of the coated membranes it is possible to obtain an impression how the deposited metals, especially palladium deposited with our CVD-method, are present on the ceramic membrane. Thus, we can make a statement about the quality of the developed CVD-technique. For the analysis the top membrane layer needs to be scratched off. It is suspended in an organic solvent, e.g. ethanol or acetone, and then ground in an ultrasonic bath to a particle size suitable for the investigation in the transmission electron microscope. Thereafter, one drop of this suspension is given on a copper net that has a carbon film on one side. The organic solvent evaporates off and the sample can be investigated in the microscope. For the TEM-characterization we used a Philips EM420 transmission electron microscope. If the ceramic particles are in the range of 50–100 nm the electron beam is still able to pass through the ceramic material. Fig. 2 shows palladium clusters on an α-Al_2O_3 particle. The particle was taken from the top membrane layer of an asymmetric α-Al_2O_3-membrane that was coated with Pd according to the description in Section 2.1.1. We can see that the palladium clusters sit on the alumina in the form of hemispheres. The clusters are connected with the ceramic and the bond seems to be very strong. No loose particles can be found in the TEM picture.

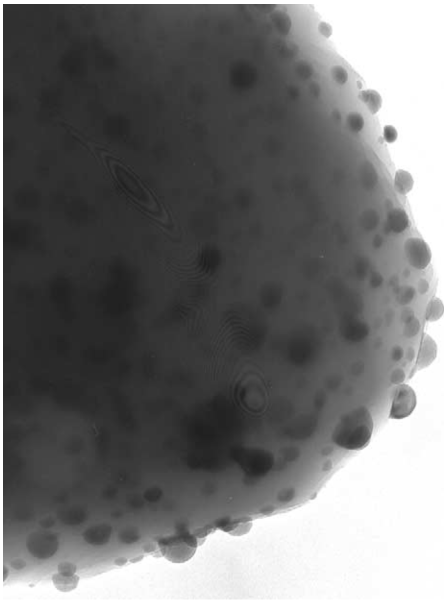

Fig. 2. TEM-photograph of palladium clusters on an α-Al_2O_3-particle. The top membrane layer of an asymmetric membrane was coated with Pd (MOCVD-process), the layer was scraped off from the membrane and prepared for TEM-characterization. Pd-clusters are firmly attached to the α-Al_2O_3 particle.

In the catalytic experiments in our reactor no abrasion of palladium was observed and no leaching of the palladium should occur during the reaction.

TEM-characterization can also be used to determine the size of the palladium clusters. Fig. 3 shows a TEM-photograph of a powder sample scraped off from a top layer made of zirconia that was CVD-coated with palladium. The average pore diameter of the ZrO_2 membrane layer was 110 nm. The larger chunks in the TEM-photograph are ZrO_2 particles and the small black dots are palladium clusters. A picture analysis of the TEM-photograph leads to a cluster size distribution of the Pd-clusters. As a conclusion it can be said that the MOCVD process described in Section 2.1.1 can produce palladium clusters with an average cluster size of about 7 nm on a zirconia layer.

2.2.2. *Electron probe microanalysis*

The distribution of deposited palladium over the membrane is determined by EPMA (Cameca SX50) with WDX. Cross-sectional cuts of the membrane were prepared by metallographic methods. The distribution of the catalytic metal is very important as it strongly influences the catalytic properties of the catalytically active membrane. For the catalytic diffuser

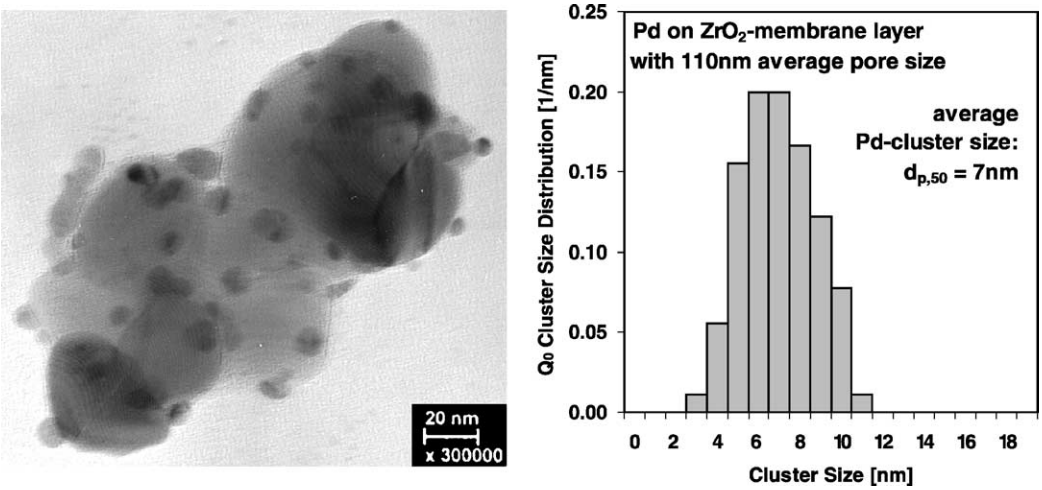

Fig. 3. TEM-photograph of Pd-clusters on ZrO_2-top membrane layer and appendant cluster size distribution of Pd-clusters. Deposition technique: Pd-MOCVD. Pore size of the top ZrO_2-layer: 110 nm. Thickness of the top layer: 20 μm. Small particles represent Pd-clusters. Large particles represent ZrO_2 from top layer. Average palladium cluster size: 7 nm.

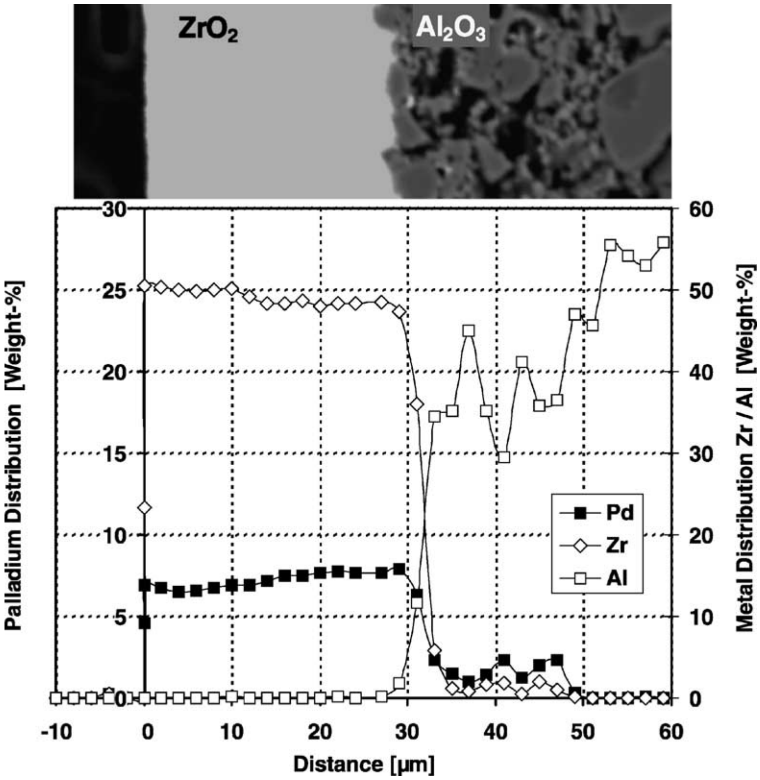

Fig. 4. BSE picture of an asymmetric membrane. Top layer: ZrO_2 with 110 nm average pore size. Thickness 30 µm. Intermediate layer and support: α-Al_2O_3. EPMA gives the metal distribution for Zr, Al, and Pd. Pd was deposited into membrane layer with MOCVD. Pd is mainly deposited in the top ZrO_2-layer. Deposition of Pd into the ceramic support can be avoided and the Pd-concentration is relatively constant over the whole ZrO_2-layer.

concept palladium should be deposited only in the top membrane layer, not in the support. The concentration over the whole top layer should be constant. Fig. 4 shows an EPMA for an asymmetric ceramic membrane consisting of an α-Al_2O_3-support, an intermediate α-Al_2O_3-layer with some smaller particles and a ZrO_2-top layer with an average pore size of 110 nm. This structure can also be seen in the back scattered electron (BSE) photograph in Fig. 4. The metal distribution for zirconium and aluminum shows where the top zirconia layer and the intermediate and support α-alumina layer are located. Palladium is almost only located in the ZrO_2-layer. Only small concentrations of Pd can be found in the intermediate layer. The Pd-concentration over the top layer is relatively constant except for a slight rise towards the ZrO_2/Al_2O_3 transition.

2.3. Catalytic membrane and reactor: experimental setup

For our experiments we use asymmetric tubular ceramic membranes with an outer diameter of 10 mm and an inner diameter of 7 mm and a length of about 10 cm. The fine-porous membrane layer is on the outside of the membrane. Thus, the outer membrane area available in a typical experiment is about 31.4 cm^2. The ends of the coated catalytically active membrane are glued with epoxy resin. It is then built into a membrane holder, where the membrane is clamped between two silicon rubbers. The epoxy resin is necessary in order to harden the ends of the membrane, otherwise parts of the membrane layer would come off when the membrane is pressed between the two silicon rubbers. The membrane holder has a 6 mm connector for gas

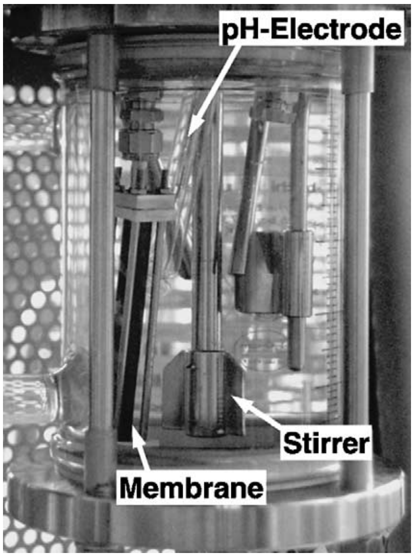

Fig. 5. Double-walled glass reactor with catalytically active ceramic membrane. The tubular membrane is built into a membrane holder clamped between two silicon rubbers.

supply. If the membrane is immersed in water and is free of defects, a pressure up to 15 bar is possible inside the membrane with no gas bubbles being visible.

The catalytic properties were tested in a stirred-tank membrane reactor in a batchwise mode. Fig. 5 shows a photograph of the membrane in the reactor. The membrane in the membrane holder is immersed in the reaction solution ($V_R = 750$ ml) which is stirred by a magnetically coupled blade stirrer. Reaction solutions were made with pure deionized water. Hydrogen and carbon dioxide are fed to the membrane with two thermal mass flow controllers allowing the H_2:CO_2-ratio to be set. An electronic upstream pressure controller keeps the pressure in the membrane constant. For a typical experiment we have atmospheric pressure in the reactor and an overpressure of 5 bar in the membrane. The reaction scheme for the catalytic diffuser concept can be seen in Fig. 6 (left).

The reactor vessel consists of a double-walled glass jacket fixed between two metal flanges (Buechi glasuster). By a temperature-controlled shell-side liquid the temperature in the reactor is regulated. The reactor is equipped with electrochemical hydrogen and carbon dioxide sensors to detect the concentration of dissolved hydrogen and carbon dioxide in the liquid. The pH of the solution can be measured with a pH-electrode or can be kept constant during the reaction by a pH-controller with a hydrochloric acid dosing unit. A small bypass stream is pumped continuously through the injection valves of two ion chromatographs (Metrohm IC 732/733 with column Metrosep Anion Dual 1 and IC690 with column Metrosep Cation 1-2) to analyze the anions (nitrate, nitrite) and the cations (ammonium) in the solution. An analysis is made automatically every 20 min.

As this paper wants to make a comparison between the two introduced concepts—catalytic diffuser and forced through flow—we decided to take the reduction of nitrite as test reaction. For the reduction of nitrite only palladium as catalytic metal is necessary. No bimetallic Pd/Sn sites next to monometallic sites in a certain ratio and in a certain arrangement on the

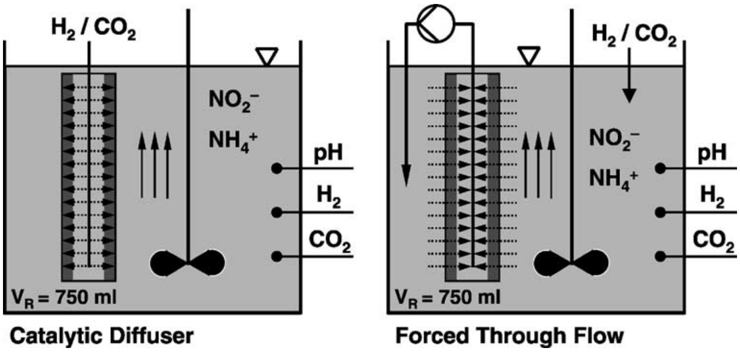

Fig. 6. Experimental setup for the catalytic diffuser and the forced through flow concept. In the catalytic diffuser setup hydrogen and carbon dioxide are fed into the membrane at an elevated pressure. In the forced through flow setup the reaction solution is pumped through the membrane support and the gases are dosed into the reaction solution. The concentrations of H_3O^+, H_2 and CO_2 are measured with electrochemical sensors. With an ion chromatograph the concentration of the dissolved ions, NO_2^- and NH_4^+, is determined.

membrane surface are needed. Thus, all influences that come from the preparation of bimetallic Pd/Sn are eliminated. To characterize the catalytic performance of the membranes we will display the concentration of nitrite over time as a measure for the catalyst activity and the molar selectivity towards ammonium (Eq. (6), index “0” denotes the start of the reaction):

$$S_{NH_4^+} = \frac{c_{NH_4^+} - c_{NH_4^+,0}}{c_{NO_2^-,0} - c_{NO_2^-}} \tag{6}$$

The unwanted byproduct ammonium is measured, since it is very difficult to determine the concentration of the desired product nitrogen dissolved in water. Assuming that no other products are generated the nitrogen selectivity can be calculated ($S_{N_2} = 1 - S_{NH_4^+}$). Several experiments showed that N_2O can be found as intermediate product but it will finally react to N_2.

For the evaluation of the forced through flow concept the reaction solution was pumped through the membrane using a gear pump with variable flow rate (Ismatec MS-Z with pump head 181; gear material: graphite). The flow rate through the membrane was determined with a conventional rotameter. Hydrogen and carbon dioxide are dosed to the reaction solution through a sintered metal filter. Fig. 6 (right) shows the schematic reaction setup for the forced through flow concept.

Besides the catalytic nitrite reduction the two membrane reactor concepts are also compared for the catalytic dechlorination of chlorinated hydrocarbons in this publication. In order to investigate the dechlorination of chlorinated hydrocarbons on catalytically active membranes we chose chloroform reduction as a test reaction. To measure the concentration of chloroform in water we take a 5 ml sample out of the reactor at certain time intervals; the chloroform is extracted with 5 ml pentane and then an analysis is made in a gas chromatograph (Carlo Erba GC6000 with ECD; column DB624 30 m).

3. Results and discussion

3.1. Catalytic nitrite reduction—pH-dependency of the reaction

First the pH-dependency of the catalytic reduction of nitrite to nitrogen was investigated. The measurement was carried out at 20 °C. Into the membrane hydrogen was fed at an overpressure of 5 bar. During the reaction hydroxyl ions are released according to Eqs. (2) and (3), so that the pH-value would rise if no measures are taken against it. In the following experiment the pH was kept constant at certain values by automatic dosing of a 0.1 mol/l hydrochloric acid to the reaction solution. The nitrite concentration and the selectivity towards ammonium over time for three different pH-values are shown in Fig. 7. The membrane used was an asymmetric α-Al_2O_3-membrane with a fine-porous membrane layer on the outside that was coated with the described CVD-method with 23.1 mg palladium. The average pore diameter of the top membrane layer was 100 nm. Activity and selectivity are strongly dependent on the pH-value of the reaction solution. At pH 5 there is still a high selectivity to ammonium of about 64%, at pH 4 the selectivity towards ammonium is suppressed to values below 10%, consequently the selectivity towards nitrogen is above 90%. Furthermore, the reactions gets significantly faster. At the same time the reaction order seems to change. At pH 3 the reaction apparently is independent of nitrite concentration (zero-order reaction).

3.2. Buffering with carbon dioxide—dependency on H_2:CO_2-ratio

The hydroxyl ions released during nitrite reduction can be neutralized by HCl-dosing. Another way to keep the pH-value of the solution constant is to feed a mixture of hydrogen and carbon dioxide into the tubular membrane instead of pure hydrogen. The CO_2 dissolves physically in the water and reacts to carbonic acid that neutralizes the formed hydroxyl ions. Thereby, even without acid dosing the pH of the reaction solution can be kept constant. Also the nitrogen selectivity is increased with CO_2-dosing from the inside of the membrane, compared to HCl-dosing from the outside, because the carbon dioxide is fed directly to the catalytic membrane layer where hydroxyl ions are formed and buffers the solution at the catalytic sites and thus, a local pH-increase in the porous membrane layer can be better avoided.

Fig. 8 shows the results of an experiment where the H_2:CO_2 molar ratio was varied over a wide range and demonstrates what activities and selectivities can be obtained also with extreme ratios (up to H_2:CO_2 =

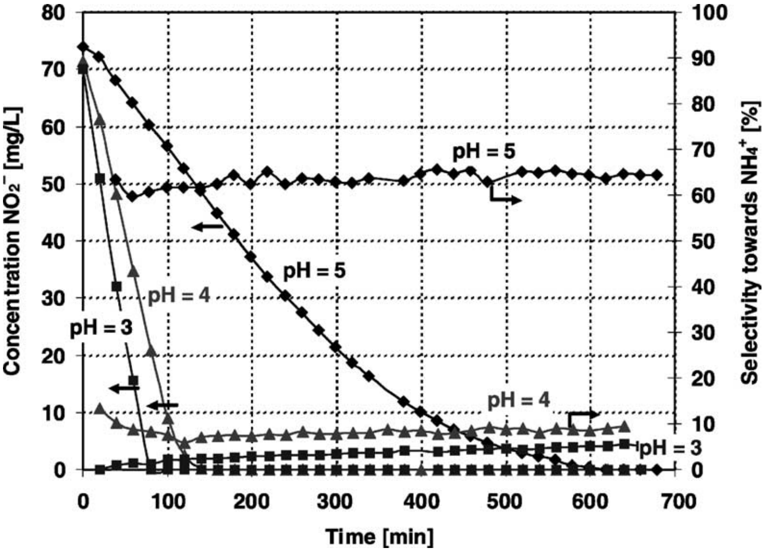

Fig. 7. pH-dependency of catalytic nitrite reduction. Activity and selectivity is strongly dependent on the pH-value of the reaction solution. Membrane: asymmetric, tubular, ceramic α-Al_2O_3-membrane with membrane layer on the outside. Average pore diameter of membrane layer: 100 nm. Palladium (23.1 mg) deposited (CVD-method) into top membrane layer. Hydrogen in membrane at 5 bar overpressure. Reactor at atmospheric pressure. Temperature of reaction solution: 20 °C. pH kept constant by automatic hydrochloric acid dosing. Reaction volume: 750 ml.

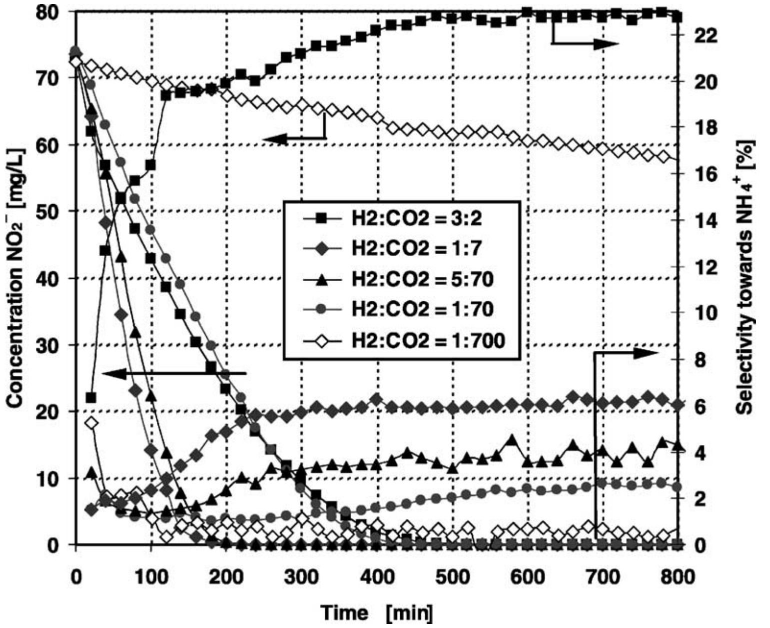

Fig. 8. Dependency of catalytic nitrite reduction on H_2:CO_2-molar ratio inside membrane. Membrane: asymmetric, tubular, ceramic membrane. Support: α-Al_2O_3 (3 μm average pore diameter). Membrane layer: ZrO_2 (110 nm average pore diameter) with 18.6 mg Pd; 5 bar overpressure in membrane. Temperature: 20 °C. Reaction volume: 750 ml.

1:700). For this experiment an asymmetric, tubular, ceramic membrane with a top membrane layer made of ZrO_2 (110 nm average pore diameter) was used. Experiments showed that zirconia as membrane material gives slightly higher activity and N_2-selectivity for the catalytic nitrite/nitrate reduction in comparison with alumina. Palladium (18.6 mg) was deposited in the top membrane layer. The gas inside the membrane was at 5 bar overpressure and the temperature of the reaction solution was 20 °C. On the left side of the graph in Fig. 6 the nitrite concentration, on the right side the ammonium selectivity is shown. With increased CO_2-concentration the NH_4^+-selectivity is more and more repressed. That means that the nitrogen selectivity increases with increasing CO_2-concentration fed to the membrane. Several effects might be responsible for this. With increasing CO_2-concentration also the pH-value in the bulk changes. At a H_2:CO_2-ratio of 3:2 the pH-value during the reaction stays relatively constant at 5.5 after a short initializing period. With a H_2:CO_2-ratio of 1:7 and 5:70 the pH-value proceeds between 4.8 and 4.5, at $H_2:CO_2 = 1:70$ the pH-values starts at 4 and rises to 4.5 with proceeding reaction and at $H_2:CO_2 = 1:700$ it runs near pH 4. Furthermore, the buffering within the porous membrane structure might get better with increasing CO_2-concentration. The carbon dioxide might also change the catalytic palladium surface, or the hydroxyl ions might be more quickly removed from the catalytic sites with the CO_2-transport into the reaction solution. The reduction of nitrite is at first accelerated with increasing CO_2-fraction. The activities at the H_2:CO_2-ratios 1:7 and 5:70 are almost the same (see Fig. 6). If the hydrogen concentration is further reduced, the nitrite reduction gets slower again, because not enough hydrogen is available any more for the reaction. But even with a H_2:CO_2-ratio of 1:700 nitrite is still reduced.

3.3. Forced through flow at different flow rates and comparison with catalytic diffuser

In our first forced through flow experiment, we took a regular asymmetric α-Al_2O_3-membrane with a top layer on the outside that was coated with palladium. We pumped the reaction solution from the inside to the outside of the membrane. The initial flow rate through the membrane (length: 10 cm) was 54 ml/min. After a few hours the flow decreased gradually until no water could be pumped through the membrane any more. Inside the membrane on top of the support, we found that small particles plugged the membrane support. During the reaction the filter cake grew until the pressure drop through it got too high. Repetition of this experiment showed that the pores of the membrane always get very easily plugged, if the reaction mixture is pumped from the inside to the outside of the membrane. In order to solve this problem we decided to take a ceramic support without any membrane layer on top. Thereby, we would also have a higher flow rate through the membrane. The surface of the support is still high enough to deposit 20 mg palladium in a high dispersion. Next, the flow was reversed, i.e. the water was sucked from the outside to the inside of the membrane (see Fig. 6, right). On the retentate side there was a turbulent flow from the magnetic stirrer in the reactor. Several experiments showed that the forced through flow operation can be maintained, if the water flows from the outside to the inside of the membrane and if there is a sufficient cross-flow on the retentate side. Then, no plugging of the membrane pores will occur.

Fig. 9 demonstrates the performance of the forced through flow with different flow rates through the membrane. For this experiment a ceramic α-Al_2O_3-support with 3 μm average pores in diameter was coated with 18.6 mg palladium. The stirrer in the reaction solution provided the necessary turbulent flow on the retentate side. A H_2/CO_2 gas mixture with a H_2:CO_2 molar ratio of 3:2 was bubbled into the reaction solution. Fig. 7 shows that the activity and selectivity is dependent on the flow rate through the membrane. At very low flow rates the catalyst activity is not so high. With an increased flow rate the activity gets higher until further increases of the flow do not change the activity significantly any more. In Fig. 9 it can be seen that for a flow rate of 68 and 145 ml/min through the ceramic support (length: 10 cm) almost the same activities are obtained. If we look at the selectivities we can see that also the ammonium formation is dependent on the flow rate. The shorter the contact time is in the porous support, the less ammonium is produced.

The performance of the ceramic support operated in the forced through flow mode is also compared with the catalytic diffuser in Fig. 9. For the catalytic diffuser experiment an asymmetric, tubular, ceramic

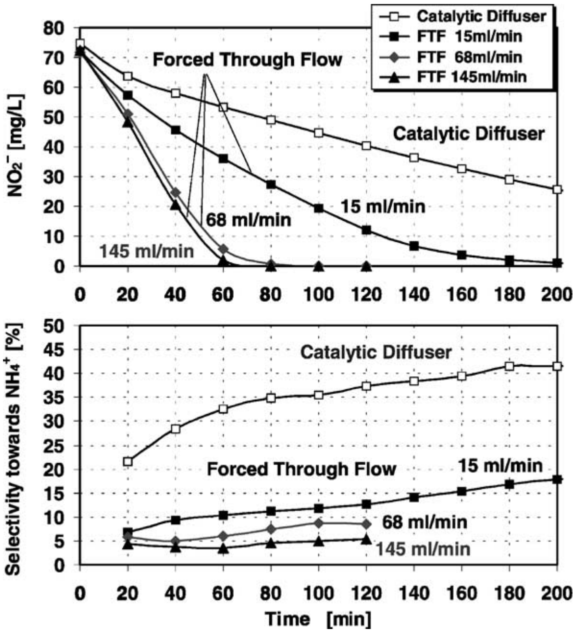

Fig. 9. Forced through flow performance at different flow rates through the membrane in comparison with catalytic diffuser for the catalytic nitrite reduction. For the forced through flow experiment a ceramic support (α-Al_2O_3) with average pore diameter of 3 μm coated with 18.6 mg Pd (MOCVD-technique) was used. Water was externally saturated with gas (H_2:CO_2-ratio = 3:2) at atmospheric pressure. For the catalytic diffuser experiment an asymmetric, tubular, ceramic membrane with a ZrO_2-top membrane layer with also 18.6 mg Pd was used; 5 bar overpressure in membrane. H_2:CO_2-ratio = 3:2. Temperature: 20 °C. Reaction volume in both experiments: 750 ml.

membrane with a ZrO_2-top membrane layer (110 nm average pore diameter) with the same amount of palladium (18.6 mg Pd) as in the forced through flow experiment was used. A H_2/CO_2 gas mixture (H_2:CO_2 = 3:2) was fed to the inside of the membrane at an overpressure of 5 bar.

By quickly passing through the membrane several times, mass transport limitation by pore diffusion can be avoided and the contact between the reactants dissolved in the reaction solution and the catalyst in the porous support is intensified. As a consequence, the forced through flow concept shows a higher catalyst activity. The forced through flow concept also shows a lower ammonium formation compared to the catalytic diffuser, because a local pH-increase and concentration gradients in the porous structure can be eliminated.

3.4. Forced through flow and catalytic diffuser in comparison for dechlorination of chlorinated hydrocarbons

Chlorinated hydrocarbons have been widely utilized in the last few decades as solvent for cleaning processes, as extraction fluid, as heat transfer fluid, as coolant, as pesticides and for many other applications. Because of their high stability towards biodegradation and the unconcerned dealing with the problem, toxic chlorinated hydrocarbons can be found nowadays in many places as contamination in soil and ground water.

Chlorinated hydrocarbons can be dechlorinated in a catalytic reaction activated with hydrogen on a supported palladium catalyst [11] in order to reduce their toxicity and their persistence in the environment.

To investigate the catalytic dechlorination of chlorinated hydrocarbons on catalytically active membranes we chose chloroform reduction as a test reaction. On the catalytic membranes coated with palladium, chloroform is reduced with hydrogen to methane according

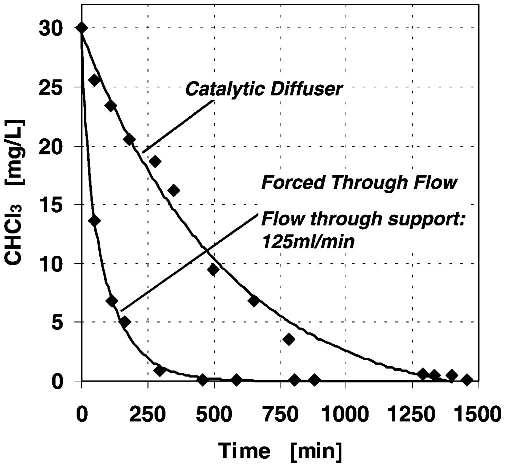

Fig. 10. Catalytic diffuser and forced through flow in comparison for the dechlorination of chloroform. Catalytic diffuser membrane: tubular, asymmetric ceramic membrane with α-Al_2O_3 top layer with 100 nm average pore diameter, 15 mg Pd. Forced through flow membrane: α-Al_2O_3-support with average pore diameter of 3 μm coated with 18.4 mg Pd. Flow of reaction solution through support: 125 ml/min. Initial concentration: 30 mg $CHCl_3$ in 1 l water, reaction volume: 750 ml.

to the following equation:

$$CHCl_3 + 3H_2 \rightarrow CH_4 + 3H^+ + 3Cl^- \quad (7)$$

Hydrochloric acid is formed as side-product.

Fig. 10 shows a comparison between the catalytic diffuser and the forced through flow for the dechlorination of chloroform. In the graph the chloroform concentration over time is displayed for the two experiments. Also here the activity for the forced through flow is significantly higher than with the catalytic diffuser, because mass transport effects are eliminated and by the pumping through the porous catalytic structure the contacting is intensified between catalyst and dissolved reactants and thereby, a process intensification is achieved.

4. Module design and conclusion

Catalytic diffuser and forced through flow are both concepts using catalytically active ceramic membranes for gas–liquid-reactions. The two concepts have advantages and disadvantages. Forced through flow operation showed a higher catalyst activity for the catalytic nitrite reduction and the dechlorination of chloroform and a higher nitrogen selectivity in the case of catalytic nitrite reduction due to the minimization of transport effects and an intensified contacting between reactants and the catalytic metal. On the other hand potential membrane blocking and a higher energy consumption of the forced through flow operation can be a problem.

With different applications the catalytic diffuser might be more advantageous. In a European research project the synthesis of hydrogen peroxide from hydrogen and oxygen with the catalytic diffuser concept is currently being studied. The hydrogen is fed to the inside of the membrane, and oxygen dissolved in water approaches the catalytic layer from the outside. Initial tests showed that with the catalytic diffuser concept H_2O_2 can be produced. The forced through flow concept in that case is not applicable, as it would probably only produce water from hydrogen and oxygen.

The process design for the catalytic diffuser is also relatively simple as no cross-flow needs to be established in order to avoid membrane blocking. For the module design commercially available ceramic multi-channel filtration elements could be used. Several of these elements can be combined to a module.

For the forced through flow concept a sufficiently high cross-flow is necessary to avoid pore blocking and maintain operation. This high turbulent flow involves a high energy consumption. A suitable module for the forced through flow concept might be designed with rotating filter disks as they provide very high cross-flow speeds at a considerably reduced energy consumption compared to conventional systems that create the necessary cross-flow by recirculating large fluid volumes.

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