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Poison resistant catalysis with microporous catalyst membranes

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Abstract

Amorphous microporous metal oxide membranes containing 1% Pt have been prepared by a modified sol–gel process. The pore diameters of these membranes range from 6 to 9 Å and the membranes show a cutoff at MW 180 in liquid phase separation. The membranes are active hydrogenation catalysts and by separating the liquid phase from the hydrogen by the membrane, poison resistant hydrogenation has been achieved. This novel approach to the processing of three phase reactions combines the unique properties of nanofiltration membranes and platinum to obtain a better control over heterogeneous catalysis.

1. Introduction

Inorganic membranes and their applications in gas and liquid separations, equilibrium shift of catalytic reactions [1], and membrane reactors are a rapidly growing area of active research [2]. Corrosion resistance and chemical and thermal stability are important advantages of inorganic compared with organic membranes. Armor suggested that there may be a real opportunity for dramatic growth in membrane catalysis [3]. Catalytic membranes combine the permselectivity of a membrane with catalytic activity. Catalytic membranes can be distinguished [4] as dense and porous membranes. Dense membranes are mainly pure metal membranes [5] and solid-electrolyte membranes [6]. Porous membranes can be divided into amorphous glass membranes [3] and crystalline zeolite membranes [7]. Potential applications of catalytic inorganic membranes are mainly related to conversions and selectivity improvements [3]. A new application of catalytic membranes is the poison resistant catalytic membrane reported here.

In heterogeneous catalysis catalyst deactivation by impurities of the liquid phase are common phenomena. Poisoning effects can be divided in inhibition, deactivation, selective, temporary and permanent poisoning [8]. Promotion of catalysis by selective poisoning is a useful aspect of catalyst deactivation [9]. For commercial applications poison resistance and catalyst lifetime are essential factors for catalyst selection. A common problem in catalyst deactivation is the presence of impurities in the feed, which compete for active sites with the substrate and thus reversibly or irreversibly deactivate the catalyst. Often, these impurities are combinations of many compounds and deactivation of the catalyst by these impurities is dependent on the compositions, which affect the reaction as well as deactivation rate. Many impurities contribute to the deactivation of the catalyst by competitive adsorption as well as by irreversible adsorption. The deactivation activity of the individual compounds correlates with the total content of the heteroatoms S, N, P, or Cl and is

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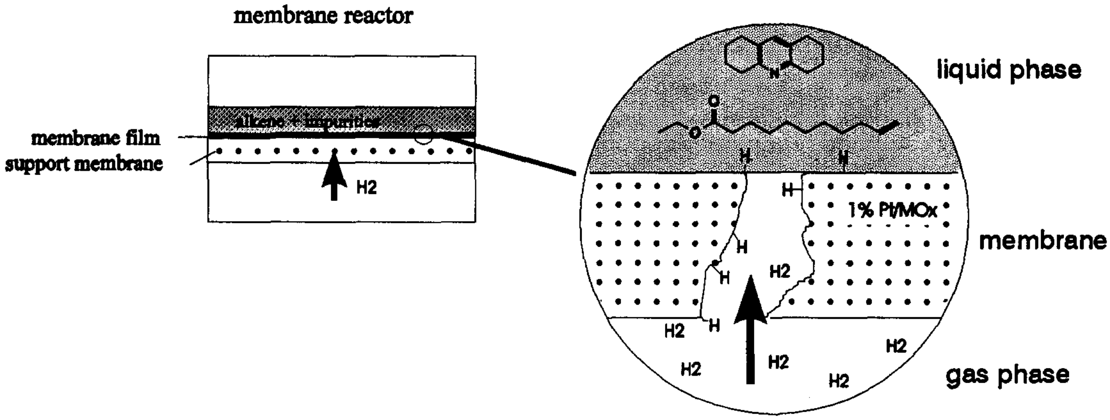


Scheme 1. Poison resistant catalysis by a size selective microporous catalyst membrane.

thus relatively insensitive to the molecular structure [10]. The poisoning problem in fat hardening is commonly overcome by using low cost nickel catalysts, utilized as additive to steel production after deactivation and/or substrate purification. Natural oils and fats contain carotinoids, phosphatidates (phospholipids), cerebrodides, steroids, vitamins, tiny fragments of plant cells and decomposition or oxidation products, which cannot be removed readily. These impurities are often of a higher molecular weight than the substrate fatty esters. This significant size difference between the organic molecules and the hydrogen can be used to design a poison resistant catalyst system. The basic concept is illustrated in Scheme 1. A membrane separates the liquid phase from the hydrogen gas. The pores in the membrane are so small that penetration can only take place by hydrogen and not by the olefin nor the poison molecules. If the membrane also contains sites capable of hydrogen activation, penetrating hydrogen can get activated and hydrogen spillover may occur. The effective rate of hydrogenation in such a membrane should be composed of the rate due to hydrogen spillover caused by noble metal sites inside the pores and an additional rate due to additional, generally accessible sites on the liquid phase side of the membrane. If the poison molecules and the selected alkenes are too large to penetrate the pores of the membrane, the rate of hydrogenation due to spillover hydrogen should not be affected by competitive adsorption. Only the rate due to the accessible sites on the upper membrane surface should be affected by the presence of poison molecules.

The conceptual use of spillover effects in catalyst development has been subject of the last conference on spillover [11]. In the past we have reported on the catalytic activity of silica films in the presence of a Pt underlayer [12], where the catalytic activity was attributed to spillover [13] effects. Hydrogen is assumed to diffuse through a microporous silica layer [14], gets activated on the Pt–silica interface and spillover hydrogen diffuses back to the surface, where it engages in the catalytic reaction with the substrates [15]. A direct demonstration of hydrogen spillover at 25°C with Pd/Al_2O_3 by ESR has just been given by Carley et al. [16].

2. Results and discussion

Prerequisite for a poison resistant catalyst membrane is the availability of catalytically active, microporous membranes capable of size selective molecular exclusion in the desired range. We have recently reported the bulk preparation of microporous metal oxide glasses with pore diameters below 1 nm and a narrow pore size distribution by a modified sol–gel procedure [17]. By dip coating of commercial support membranes in these sol–gels followed by a controlled drying and calcination procedure we have succeeded in the

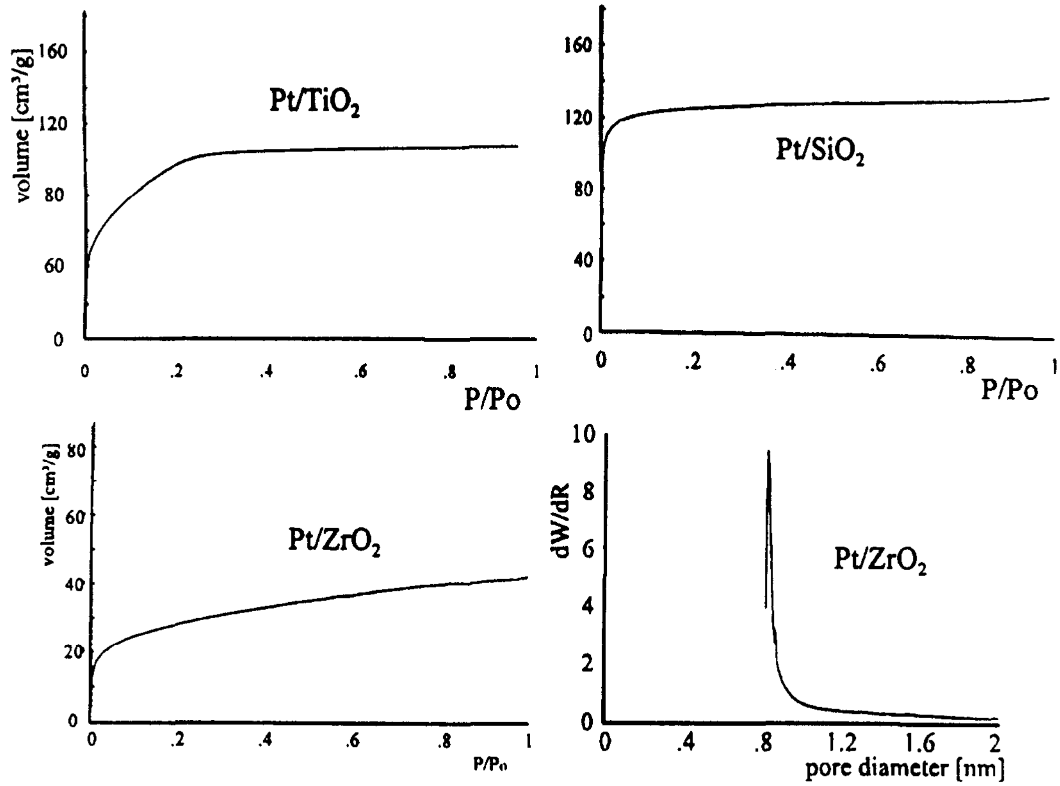


Fig. 1. N_2-adsorption isotherms of microporous 1% Pt/titania, 1% Pt/silica, 1% Pt/zirconia and a representative pore size distribution of the 1% Pt/zirconia.

preparation of nearly defect free microporous membranes, capable of molecular separation of gases [18] and liquid mixtures [19] with a cutoff at molecular weights larger 180. Membranes with such a small pore diameter and narrow pore size distribution are potential candidates to test the above concept. However, catalytically active sites had to be introduced while preserving the narrow pore size distribution. Subsequent impregnation of the membranes with noble metal solutions resulted in poor catalytic performance accompanied by pore clogging. The addition of Ni and Pd salts to the sol during the sol–gel process led to a broadening of pore size distribution accompanied by poor catalytic activity. Satisfying microporosity was obtained by the addition of sodium hexachloroplatinum derivatives to the sol. Microporous catalytically active silica, titania and zirconia containing 1% Pt have been prepared and the adsorption isotherms, shown in Fig. 1, document their microporous nature. Data treatment of the isotherms by the method of Horvath and Kawazoe [20] shows narrow pore size distributions with maxima at 0.7 nm pore diameter for the Pt/SiO_2, 0.8 nm for the Pt/TiO_2 and 0.9 nm for the Pt/ZrO_2.

X-ray diffraction with Cu K_1 from 8–88° was obtained from all materials on a Stoe Stadi II P diffractometer. The Pt/SiO_2, calcined at 250°C, is completely amorphous. Only after heating to 1023°C weak Pt-reflexes can be identified, while no indication of crystalline SiO_2 was obtained. The Pt/ZrO_2, calcined at 250°C, was amorphous, at calcination temperature of 400°C small portions of crystalline ZrO_2 can be seen while no evidence for the Pt is given. The Pt/TiO_2, calcined at 250°C was amorphous. After calcination at 400°C traces of anatase can be seen while no Pt is detectable. In the Pt/Al_2O_3, calcined at 250°C, weak reflexes of boehmit and Pt can be identified. After calcination of the powder at 400°C and 500°C the alumina reflexes disappear and only Pt particles can

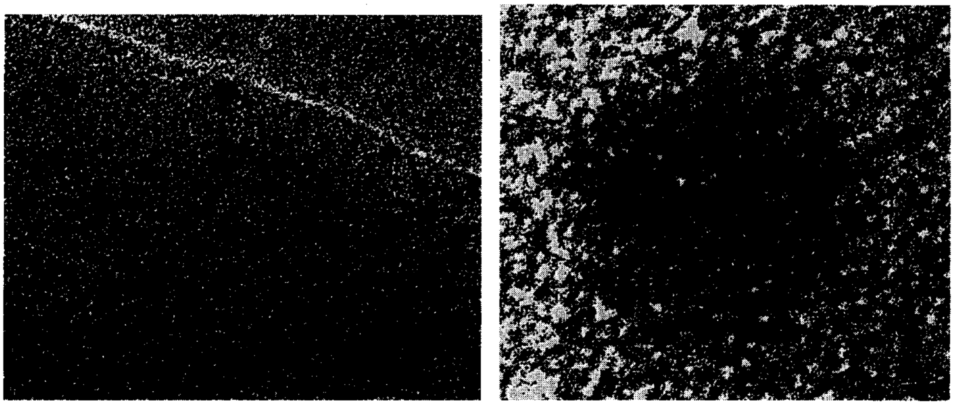
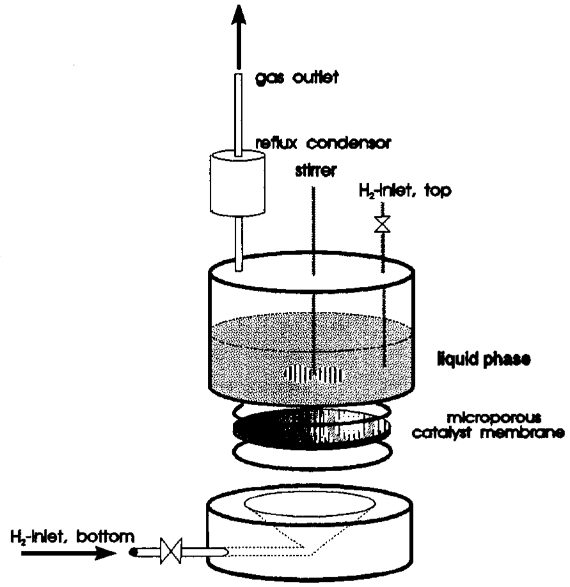


Fig. 2. High resolution transmission electron micrographs from the microporous 1% Pt/silica showing the imbedded Pt-particles of several nm in size in the silica matrix and a selected Pt-particle with lattice resolution.

be identified. High resolution transmission electron microscopy obtained on the HITACHI field emission TEM HF 2000 confirmed that all materials are highly amorphous. Pt-particles were readily detected in the silica. Fig. 2 (right-side) shows a small Pt-particle displaying its crystallinity in the otherwise amorphous silica, while Fig. 2 (left-side) is representative of a larger area of this material, displaying the differently sized Pt-particles. No Pt-particles could be detected in the titania and zirconia material, although elemental analysis confirmed the expected Pt content in all 3 materials. Both materials are amorphous. We conclude that these catalytically active materials contain Pt in a highly dispersed form with Pt particle sizes below the particle detection limit of < 1 nm.

From the sol–gel solutions used for the preparation of above described materials microporous membranes were prepared by multiple dip-coating as described earlier for the preparation of the Pt-free membranes [19]. The support membrane used for the membrane preparation was a ceramic P80 filter (20% Al_2O_3, 80 SiO_2) with pores < 1 μm. The filter diameter was 47 mm and the thickness 2–3 mm. Thinner support membranes tend to brake at the hydrogen pressure needed in the catalytic experiments described below. The film thickness of the final membranes was shown by SEM studies to be between 1 and 2 μm, which translates to a total catalyst amount of 5–10 mg/membrane. In previous studies on Pt-free microporous glasses we have shown that the pore size distribution and porosity of thin films prepared by dip coating and drying were identical to those of the bulk materials [19]. Furthermore, any significant deviation of pore size distribution would show up in the separation test of the membranes. The membranes were mounted in a filtration type steel reactor equipped with several outlets and a magnetic stirrer (see Scheme 2). The separation properties of the membranes were tested with a mixture of alkylated benzenes as described previously [19]. Figs. 2 and 3 shows the retention of alkylated benzenes, plotted against the molecular weight. The cutoff at a MW of about 180 confirms



Scheme 2. Principle construction of the stainless steel membrane reactor.

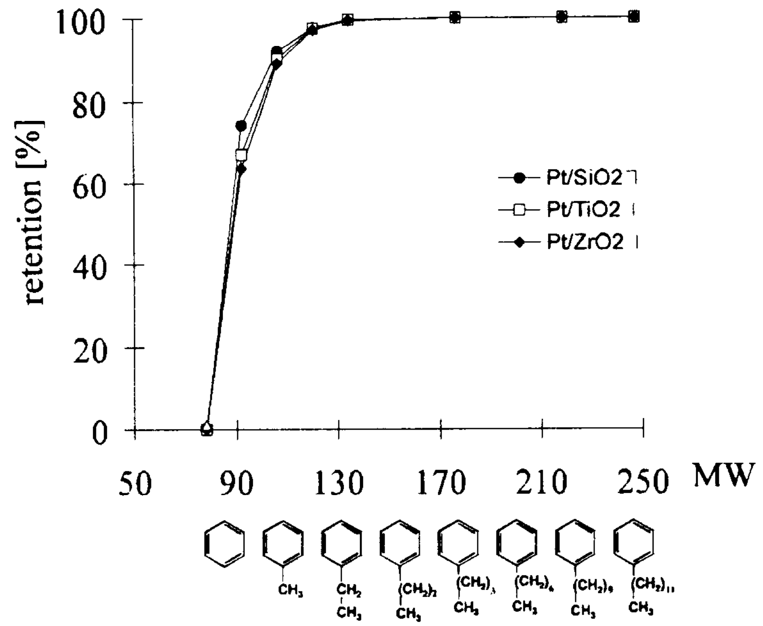


Fig. 3. Rejection of alkylated benzenes from a liquid mixture at 70°C on the membranes indicated.

that these membranes are nearly defect free and microporous.

For the hydrogenation experiments ethyl-10-undecen-1-oate (UDE) and methyl linolate (ML) were selected as alkenes and n-dodecane as solvent. Quinoline (QU), octahydroacridine (OHA) and dibenzothiophene (DBT) were used as catalyst poisons. All these molecules do not penetrate the microporous membranes to any significant extend. The reactor with the mounted membrane was first flushed with hydrogen and the catalyst membrane was activated for 10 h at 250°C with a hydrogen flow of 10 ml/min, introduced from the bottom. After the activation, the temperature was lowered to 50°C and a hydrogen flow rate through the membrane of 30 ml/min was adjusted, which required an excess pressure of 1.2 bar on the hydrogen side.

In all experiments the liquid phase side of the membrane was kept at ambient pressure. The hydrogen flow out of the reactor was monitored by a bubble counter. When the liquid phase (300 μl UDE in 7 ml n-dodecane) was introduced via syringe on the top side of the membrane the hydrogen flow out of the reactor was reduced to ca. 1 ml/min. Although hydrogenation started instantly, the observed flow reduction cannot account for hydrogen uptake by hydrogenation (<0.1 ml/min). The liquid phase seems to present a serious barrier reducing the free flow of hydrogen through the membrane. The solution was stirred with a magnetic stirrer at 800 rpm. A stirring rate study on the hydrogenation rate of UDE with a Pt/TiO_2-membrane showed that the hydrogenation rate is only affected by stirring rates below 500 rpm excluding major diffusional effects at standard conditions.

Parallel to the membrane reaction a conventional batch hydrogenation was conducted as control experiment. For this control experiment the catalyst was prepared from the remainder of the sol employed for the membrane preparation. The control catalysts were dried and calcined by the same procedure as the membrane catalyst followed by grinding in a ball mill. The characterization of these catalysts by X-ray diffraction, TEM, and adsorption isotherms was described above. At a stirring rate of 800 rpm the effect of catalyst particle size on hydrogenation rates was studied with the sieve fractions 50–1000 μm, 20–50 μm and <20 μm. While hydrogenation slowed down with the large particles, no difference in hydrogenation rate was observed with the two smaller sieve fractions. In all batch reactions the sieve fraction < 50 μm was therefore used to exclude mass transport limitations. In the batch experiments 300 μl UDE in 6 ml dodecane and 12 mg of the powdered catalyst were used. In both, the membrane and the batch experiments the amount of poison added was 20 vol.-% of the alkene. This way, the absolute weight ratio of poison/catalyst was always significantly larger than 1 and always lower in the batch reaction and the relative concentration of the poison was the same in both types of experiments.

The hydrogenation reactions of UDE, carried out at 50°C, were monitored by gas chromatographic analysis. The relative rate of the three powdered catalysts utilized for the hydrogenation of UDE under identical conditions in the batch reactor were found to be: Pt/TiO_2:Pt/ZrO_2:Pt/SiO_2 = 2.8:1.2:1, which do not correspond with the relative Pt-dispersions in the catalyst.

In all experiments, the model poison was added to the reaction solution after the unpoisoned hydrogenation was found to proceed smoothly. In the batch reaction a zero order behavior could readily be maintained by the high stirring rate, while the reaction in the membrane reactor displayed zero order behavior only at the beginning of the reaction. Fig. 4 compares a few typical examples of the effect of added model poisons on the rate of reaction in the membrane reactor and in the batch reactor. All experiments have been repeated at least once and are reproducible.

While there is no effect of the addition of OHA on the hydrogenation rate of the UDE hydrogenation in the membrane reactor with the Pt/ZrO_2, OHA-addition to the batch reaction resulted in a noticeable drop in reaction rate at the point of OHA-addition (Fig. 4). The small, but observable rate of remaining hydrogenation after the addition of the poison in the batch reactions may be attributed to spillover hydrogenation. While the poison effectively blocks all accessible Pt-sites on the external surface of the small particles, unblocked active sites must remain in the microporous inner surface of the particles. The remaining activity must therefore be caused by spillover hydrogen generated by the unblocked inner Pt particles.

In the next experiments in Fig. 4, DBT was used as a different poison on the same Pt/ZrO_2-catalyst. DBT-addition caused a recognizable drop in the rate of hydrogenation in the membrane reactor, while in the batch reactor the same catalyst material was completely poisoned. Here a second batch profile is shown in Fig. 4, which was obtained from scratching about 7 mg of material from the membrane surface of the used Pt/ZrO_2-membrane and using it as powdered catalyst in the batch reaction. This powdered membrane material shows the same poisoning behavior as the bulk reference catalyst, confirming that the observed poisoning difference between membrane and batch reactor is not due to unrecognized differences between film and bulk catalyst. A similar poison resistance as with the Pt/ZrO_2 is seen with the OHA-addition on the UDE-hydrogenation with the Pt/titania and Pt/silica catalysts (Fig. 4). While there is little effect of OHA-addition on the hydrogenation rate in the membrane reactors, the same catalysts in powdered form are effectively poisoned in the batch reactor.

Fig. 5 shows the result of the hydrogenation of methyl linoleate (ML) at a reaction temperature of 100°C on the 1%Pt/TiO_2-catalysts. ML, which is significantly larger than UDE, is even less likely to penetrate the micropores of the membrane. In the membrane reactor, the addition of OHA (20 mg) has no effect on the rate of hydrogenation, while in the batch reactor, OHA-addition (20 mg) almost terminates the hydrogenation (Fig. 5 (top)). The smaller quinoline (21 mg) has a reducing effect on ML hydrogenation in the membrane reactor, while the batch reaction is again almost terminated upon quinoline addition (Fig. 4 (bottom)). Although the major hydrogenation product is oleic acid, the selectivity drops with increasing conversion, indicating no special selectivity effects. In all cases the poison resistance of the membrane relative to the batch reaction is significant and comparable and thus seems independent of the nature of catalyst material, poison or olefin.

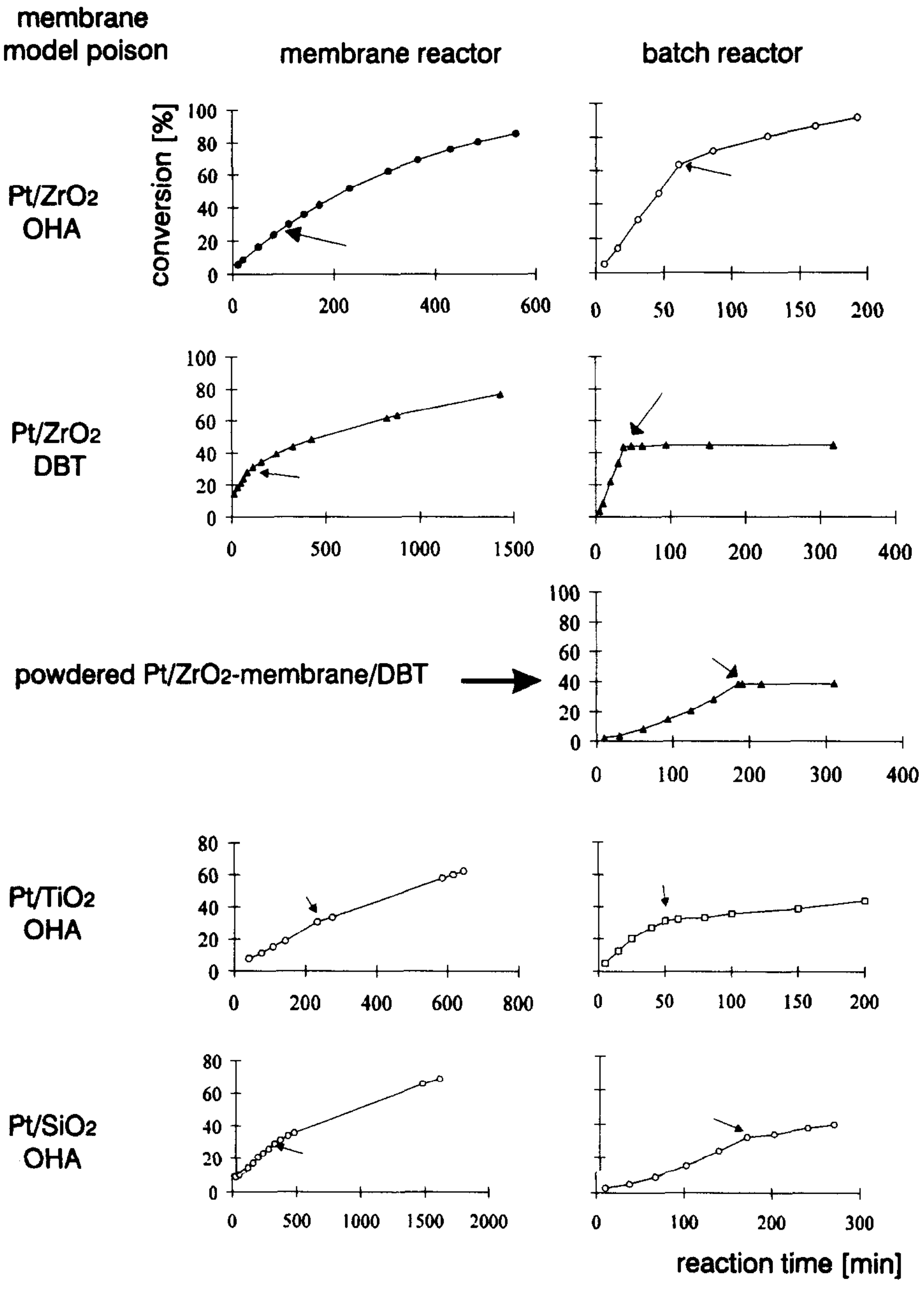


Fig. 4. Effect of model poison addition on the conversion of the UDE-hydrogenation with time in the membrane reactor and in the batch reactor on the catalysts indicated. The point of poison addition is marked by the arrow. The amount of poison was 20% of the original amount of alkene. Model poisons: octhydroacridin (OHA), dibenzothiophene (DBT).

The above results have shown that poison resistance is achieved, when the hydrogen transport to the active sites of the catalyst is mediated by size selective pores, accessible only to the hydrogen. If hydrogen addition through the microporous membrane is indeed responsible for the observed poison resistance, than hydrogen addition coming from the same side as the liquid (top inlet, see Scheme 2) should show the same poisoning as observed in the batch experiments. However, since the comparison of individual experiments may leave some doubt about truly comparable

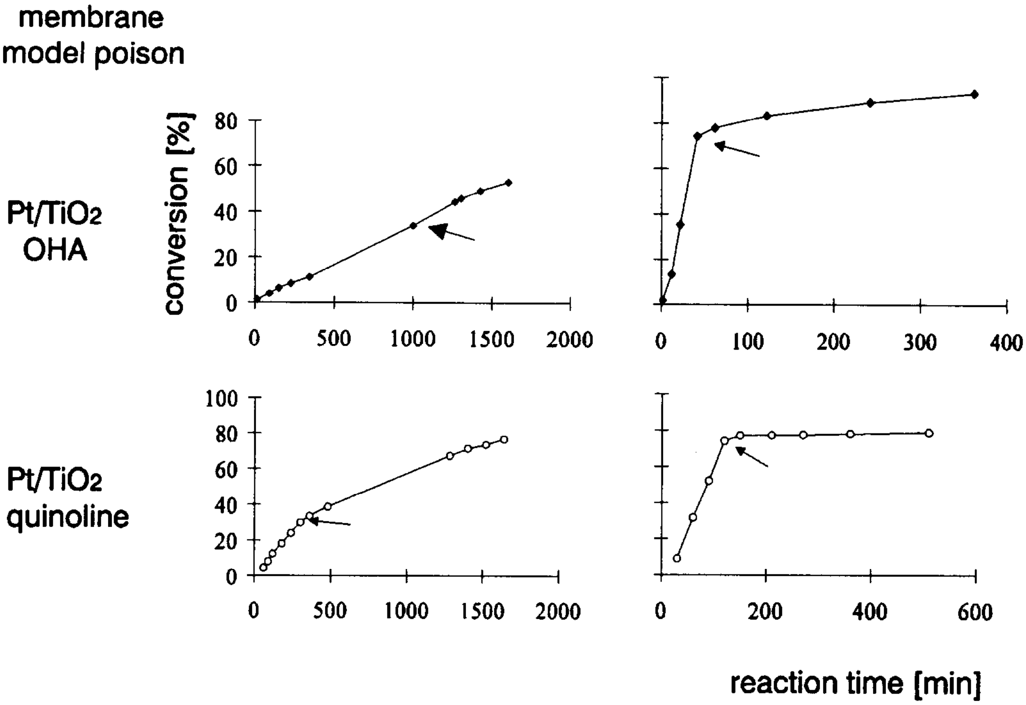


Fig. 5. Effect of model poison addition on the conversion of the LM-hydrogenation with time in the membrane reactor and in the batch reactor on the catalysts indicated. The point of poison addition is marked by the arrow. The amount of poison was 20 mg. Model poisons: octhydroacridin (OHA), quinoline (QU).

reaction conditions, the mode of hydrogen addition was switched several times during ongoing experiments.

Figs. 2 and 6 shows the hydrogenation of UDE with time in the membrane reactor at ambient temperature on the 1% Pt/zirconia membrane. After activation of the membrane the hydrogen supply was maintained at a pressure of 1.2 bar at the lower reactor part. The solution of UDE was added to the top side of the membrane. Area 1 shows steady hydrogenation with hydrogen being introduced from the bottom through the membrane — this operation is the regular membrane hydrogenation. The total rate is most likely due to the combined activity of the pores and that of the upper membrane surface, where active sites are accessible to both, the hydrogen and the organic reagents. At point 2 the hydrogen supply from the bottom was shut off and a steady flow of hydrogen of 30 ml/min was supplied from the top. This mode should be similar to the regular batch mode, where the hydrogen has to diffuse through the liquid layer before reaching the active centers. A constant rate of hydrogenation is maintained indicating that at these conditions the hydrogenation rate is not significantly affected by the mode of hydrogen addition. In this mode the rate of hydrogenation should be dominated by active centers on the top surface of the membrane. These ‘exposed’ centers should be sensitive to poison and indeed, after introduction of the model poison

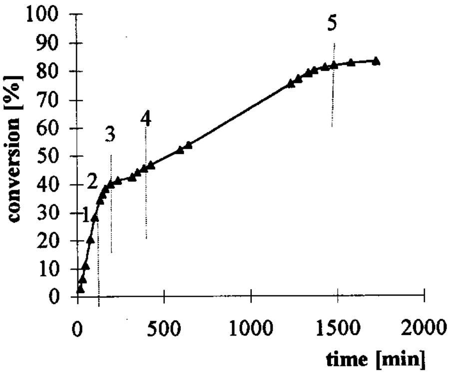


Fig. 6. Effect of DBT addition and change of hydrogen supply on the rate of hydrogenation of UDE in the membrane reactor with a Pt/ZrO$_2$-membrane at a reaction temperature of 50°C. 1: hydrogen from the bottom, 2: hydrogen from the top, 3: DBT-addition, 4: hydrogen from the bottom, 5: hydrogen from the top.

DBT (point 3) the hydrogenation comes almost to a stop in complete agreement with the observation obtained in a batch reactor with powdered catalyst of the membrane material. Assuming that the exposed active centers at the surface are now poisoned, hydrogen supply was again switched to the bottom at point 4. As expected, the rate of hydrogenation increased immediately and remained stable for a long time. It has to be assumed that the hydrogen is now activated again from the active centers in the pores and the remaining activity is the pore activity of the membrane, not accessible to the poison molecules. As can be seen in Fig. 6, this zero order hydrogenation rate is maintained in the presence of the DBT unchanged for a long time. To make sure that this activity is not the result of any unrecognized self-activation of the membrane catalyst, the mode of hydrogen addition at point 5 was again switched to addition from the top. Again, as at point 3, the rate of hydrogenation drops significantly, confirming that the hydrogenation rate from point 4 to point 5 can only be achieved by addition of hydrogen through the membrane.

From these results we conclude that our above hypothesis has been correct and we have succeeded in designing a poison resistant heterogeneous hydrogenation catalyst based on the molecular size exclusion of the substrate and the impurities by material design. It is remarkable that at a temperature of only 50°C ongoing hydrogenation in the presence of various poisons can be observed. The observed catalytic activity in the presence of the model poisons has to be attributed to spillover of activated hydrogen from the Pt particles in the pores to the inner pore surface and migration from there to the next pore opening, where the activated hydrogen can interact with the liquid and hydrogenate the alkene. There seems to be no poisoning of the spillover hydrogen confirming that poisoning is the result of interaction of the poison molecules with the active metal particles. The rather effective spillover catalysis may be a result of the very short distances of the pore openings from the next metal particles. However, the highest reaction rates with about 10 mol/h m^2 are still rather low and have to be increased significantly for technical applications.

It was demonstrated, that catalytically active microporous membranes function as poison resistant catalysts, as long as the organic substrate and the poisonous impurity are too large to penetrate the hydrogen transporting pores. This new approach of reaction control should be applicable to all heterogeneously catalyzed reactions, as long as the smaller component gets activated in the transport pores and the reactant and impurities cannot penetrate these pores. It represents a novel three phase reaction process, in which the liquid and gas reactants are separated by a permselective catalytically active membrane, penetrable only to the gas, which may lead to better control of catalytic activity and selectivity. It is hoped that by this type of reaction control a common problem of three-phase reactions, the hindered diffusion of the gas through the liquid film covering the active sites of the solid catalyst, can be overcome.

3. Experimental part

All liquids used for sol preparations were filtered through an Anopore filter with pore size 20 nm directly before use for the removal of dust, germs and other small particles.

3.1. Preparation of the aluminum containing sol

9.8 g of a solution of aluminum(III)-2-butylate in 20 ml n-butanol were added to 72 ml of water at a temperature of 90°C with stirring in a three-necked flask equipped with a reflux condenser. After 2 h a milky solution had formed which optically did not change any further. Now 8 ml of 0.16 N nitric acid where added using a pipette and the solution was boiled to reflux for 2 h where upon the solution become clear and opalescent. The solution was further heated in the open flask until the alcohol had been evaporated and the temperature of the solution had risen to 100°C. Then 20 ml of water were added and the mixture was further boiled to reflux for 24 h and cooled to room temperature. The solution was now ready for dip-coating.

3.2. *Preparation of platinum containing titanium sol*

A solution of 11.4 g of titanium(IV)-isopropylate, dissolved in 150 ml of 99% ethanol, was stirred for 30 min, followed by drop-wise addition of 0.4 ml of a 2 N nitric acid at room temperature. After 30 min, 95 mg of sodium hexachloroplatinate dissolved in 5 ml of ethanol, were added. A clear yellowish solution was obtained. If the sol is not clear, a different ethanol or higher acid concentration may have to be used. This solution was further stirred at room temperature for 4 h and then immediately used for dip-coating.

3.3. *Preparation of the platinum containing zirconium sol*

In a 250-ml polyvinyl beaker 13.7 g zirconium(IV)butylate was added dropwise with vigorous stirring to 150 ml of 99% ethanol. After 13 min, 0.75 ml of water in 45 ml of ethanol were very slowly added dropwise. Some minutes later 150 μl of 4 N nitric acid was added dropwise. After a short time the solution became clear, and then a solution of 108 mg of hexachloroplatinate in 10 ml of ethanol was added dropwise. The clear yellow solution was sealed with parafilm and after 4 h was ready to be used for coating the support membrane.

3.4. *Preparation of the platinum containing silica sol*

In a 250-ml polypropylene beaker containing 110 ml of tetraethoxysilane 85 ml of ethanol was added dropwise with stirring. 16 ml of 8 N hydrochloric acid and a solution of 739 mg of hexachloroplatinum hydroxide in 50 ml ethanol was added dropwise in sequence at an addition rate of 5 ml/min. The clear yellow solution, while further stirred, was selaed with parafilm and after 4 h was ready to be used for dip-coating.

3.5. *Preparation of control catalysts*

The sol/gel solution of the above platinum containing sols remaining after coating was loosely sealed with parafilm and further stirred for 1 d and then without stirring allowed to sit sealed for 6 d. Then the parafilm was removed and the gel was dried in a hood for another 2 weeks. Now the material was dried in the same manner as described for the manufacture of the membranes. The resulting glass particles were ground in a ball-mill and ready for use as controlled catalysts. Analytical data: SiO_2: BET 651 qm/g, pore diameter 1 nm. ZrO_2, BET 125 qm/g, pore diameter 0.9 nm. TiO_2, BET 269 qm/g, pore diameter 0.8 nm.

3.6. *Membrane preparation*

The membranes were fabricated by dip-coating a disk of ceramic filter P 80, ∅ 47 mm, thickness 2 to 3 mm, nominal pore diameter < 1 μm (Königliche Porzellanmanufaktur, Berlin). The P 80 disks were first polished with an abrasive material of grain size < 1 μm and cleaned by boiling in a 1:1 mixture of acetone and isopropanol followed by a sonic treatment in an acetone/isopropanol bath for 30 min. Then the disks were calcined in a furnace at 450°C for 4 h. The disks were submersed in the aluminum–sol solution and placed in a desiccator, which was then cautiously evacuated until bubble-formation had ceased. The beaker containing the solution was placed into a large glass vessel, which was covered with a glass plate designed with a hole. The P 80 disk, which was attached to a string passed through the hole in the glass plate and connected to a drawing motor running vibration-free, was pulled out of the solution at a drawing rate of 0.5 cm/min as much vibration-free as possible. Pulling was discontinued, once the disk had completely emerged from the solution. The disk, hanging directly over the sol-solution was then pre-dried in the closed vessel for one week. Then the disk was heated in air in a drying-oven to 60°C at a heating rate of 0.2°C/min and maintained at that temperature for 5 h. After that the disk was heated to 400°C at a heating rate of 0.1°C/min, maintained at that temperature for 5 h, and then cooled at a cooling rate of 0.5°C/min. After the disk had been cooled to room temperature, it was directly subjected to a second coating treatment as described above including desiccator treatment. The subsequent third coating treatment was carried out without evacuation in the desiccator. After this pretreatment, the large pores of the P 80 membrane had been closed to such a degree that they could now be coated with the catalytically active membrane material. Prior to the coating with the catalytically active material the atmosphere in the glass vessel was enriched with ethanol by vigorously stirring 100 ml of ethanol in a glass beaker for 10 min. Then the membrane was pulled out from the platinum containing catalyst sol in the same manner as described above, dried and calcined to a maximum temperature of 250°C.

3.7. Examination of the separation performance of the membranes

The dry membrane was heated in the reactor at 250°C under dry nitrogen in an excess pressure of 1 bar for 5 h. It was then cooled to 70°C and 8 ml of a solution of equal parts by weight of benzene, toluene, ethylbenzene, propylbenzene, butylbenzene, heptylbenzene, decylbenzene and dodecylbenzene were stirred under nitrogen for 2 h. The composition of the permeate and feed were analyzed by gas chromatography.

3.8. Hydrogenation experiments in the membrane reactor

In the membrane reactor an excess hydrogen pressure of 1 to 1.5 bar was applied to the bottom surface of the dry catalyst membrane, so that a flow-rate of 6 to 10 ml/min was observed at the gas outlet. The reactor was slowly heated to 250°C and the membrane was activated at that temperature for 2 h and then cooled to 50°C. 0.2 ml of 10-undecenoic acid ethyl ester (UDE) in 7 ml dodecane were placed on the upper surface of the membrane and hydrogen was introduced from the bottom of the membrane with an excess pressure of 1.2 bars. The reaction was monitored by taking μl-sized samples for gas chromatographic analysis. After a constant reaction rate was documented, the model poison was added at once to the reaction solution via syringe.

3.9. Control experiments in a batch reactor

12 mg of control catalyst powder were used in a batch reactor to hydrogenate 0.3 ml of UDE in 6 ml dodecane. The mixture was stirred vigorously in a hydrogen atmosphere at normal pressure. The reaction was monitored by taking samples for gas chromatographic analysis. The selected poison was added at once after a constant hydrogenation rate had been established.

Acknowledgements

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