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Development of catalytically reactive porous membranes for the selective hydrogenation of sunflower oil

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Abstract

The main objective of this contribution was to develop and validate new catalytically reactive porous membranes for hydrogenation of edible oil in a membrane reactor. High flux polymer membranes from polyethersulfone and polyamideimide with and without inorganic alumina filler were produced on a technical membrane casting machine. These porous membranes show water fluxes of about 30,000 L/m^2 h bar and oil fluxes of 900–2000 L/m^2 h bar at 60 °C. The pore volumes are in the range of 5–7 mL/100 cm^2 of membrane area. Large pores at high porosity were received by addition of a water soluble ethyleneoxide-propyleneoxide-*b*-copolymer (Pluronic® F127), that forms distinctive globules in the solution when cooled below 10 °C. The catalytic activity was obtained by two different methods: by wet impregnation of the membrane in a catalyst precursor solution (palladium acetate or hexachloroplatinate) followed by calcination, respectively, chemical reduction or by addition of ready-made supported catalysts to the membrane casting solutions. Catalytically activated membranes with different Pt-contents (0.1–1 g/m^2) were applied in first membrane reactor tests to hydrogenate refined sunflower oil. Within 6 h the iodine value decreased considerably and about a half of the linoleic acid was hydrogenated, which is the major compound in sunflower oil triglycerides. The overall trans-content of the fatty acids was about 25%. Membrane performance was verified in up to 5 days of discontinuous operation.

Keywords: Membrane reactor; Edible oil; Hydrogenation; Polymer membranes; Platinum; Palladium; Isomerization

1. Introduction

Up to now the standard in edible oil hydrogenation is still based on supported nickel catalysts in slurry reactors [1–3]. The most common catalyst supports in use are silica (Kieselguhr or synthetic silica) or alumina. Owing to the toxicity of the heavy metal catalyst the removal of the catalyst from the product must be almost complete and that causes high costs for the separation. A very recent tendency is to substitute nickel by palladium or platinum [4,5]. The motivation for this development is to reduce the overall formation of trans-isomers during hydrogenation. The much higher price of the noble metal catalyst has to be compensated by the repeated use of the catalyst and efficient recycling of the metal from the used supported catalyst. In any case, supported metal catalysts have to be separated very efficiently from the product. Different reactor technologies, such as fixed bed reactors, were also suggested [2] but are rarely in use because of a significant pressure drop over the reactor length and the generally higher costs. The high pressure drop results mainly from the viscosity of the oil. To reduce the viscosity and to provide high reactivity with Ni, temperatures of 170–200 °C are generally applied. However, higher temperature significantly promotes the unwanted trans-isomerization of the unsaturated fatty acids. A decrease in the required temperature is expected by improvement of the mixing of the components in this three-phase chemical reaction (hydrogen, catalyst, oil). Three-phase chemical reactions can be accomplished very efficiently by using membrane reactor technology. However, only two papers [6,7] are found regarding edible oil hydrogenation using different approaches to tackle the problem. Veldsink [6] impregnated a tubular porous membrane with palladium on one side to provide a reactive interphase between the gaseous hydrogen and the oil. The hydrogen was fed from the inactive opposite side of the tube to the palladium activated surface to get into contact with the oil. With this membrane reactor setup the pressure drop problem was solved and the reaction ran under kinetic control. However, the proportion of active

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catalyst sites to oil volume was very low and cannot be enhanced considerably using this setup. In addition, the catalyst deactivated with time. This approach may be classified as distributor/contactor mode [8]. Very intensive mixing for three-phase reactions is reported for membrane reactors using the contactor mode in the flow-through configuration [8,9]. Ilinitch et al. [7] used this approach by fixation of palladium catalysts in the pores of a polymeric nylon-6 membrane. He compared the membrane reactor results with a conventional slurry reactor operating with palladium on charcoal catalyst. He found a decrease in generating trans-isomers for the membrane reactor at comparable hydrogenation levels expressed in IV (iodine value). No detailed information was given about the operating conditions of the membrane reactor such as flow, pressure drop and total operating time. The nylon-6 membrane was activated using carcinogenic benzene as solvent for palladium dichloride or palladium acetate. The pressure drop of this setup was not reported. However, his work showed a decrease in trans-isomers and still has the advantage of eliminating the step of catalyst separation from the product in the slurry reactor.

In the following we present the development of temperature stable polymer membranes with exceptional high oil fluxes to offer low pressure drop and design a route to activate these membranes by palladium and platinum catalysts by applying a simple procedure. The catalytic membranes are designated to work in the flow-through contactor mode without any loss of catalyst metal.

2. Experimental

2.1. Polymers and casting solutions

Polyethersulfone (Radel® PXM 3000, Solvay) was dissolved in dimethylacetamide (DMAc, Merck) and polyamideimide (Vylomax®, Toyobo) in *N*-methylpyrrolidone (NMP, Merck). Ethyleneoxide-propyleneoxide-*b*-copolymer (Pluronic® F127, BASF), the additive polyvinylpyrrolidone (PVP K30, Fluka) and detergent Tego 700 (Degussa) were added as modifier to the polymer solution.

2.2. Catalyst supports (inorganic filler) and catalyst precursors

Alumina (Martoxid MR 70, Martinswerk) with BET surface 8 g/m^2 and average particle size of 0.7 μm) was used as catalyst support (inorganic filler) and kindly provided by the manufacturer. Catalyst precursors: palladium acetate ($PdAc_2$), palladium chloride ($PdCl_2$) and hexachloroplatinate ($H_2PtCl_6{\cdot}6H_2O$) (all Chempur).

2.3. Supported catalyst preparation

Catalyst preparation is by wet impregnation of alumina by a metal precursor solution in tetrahydrofurane (THF, Merck). After solvent evaporation the residue was calcinated in air at 450 °C for 10 h.

2.4. Membrane preparation

All membranes were fabricated on a technical casting machine to several square-meters. A nonwoven fabric (polyester or polyphenylenesulfide) was used to support the membranes. Three types of membranes were prepared: (a) with PVP additive, without catalyst support (filler), (b) with catalyst support (filler) and with or without PVP, (c) with active supported catalyst either Pd or Pt and with or without PVP. All casting solutions contained Pluronic® as pore modifier and Tego 700 to help degassing of the casting solution. A shortcut for membrane designation is used: polymer/filler/PVP/No. For filler containing casting solutions the filler was dispersed in pure solvent under the agitation of ultrasound using a bath type sonicator and added to the already finished casting solution. Cooling of the casting solution was accomplished under stirring and final evacuation for degassing of the solution. No filler sedimentation was observed for some hours on account of the high viscosity of the cold solution.

2.5. Catalytic activation of the membranes

Either single stamps were activated by dipping in a solution of catalyst precursor or a dip-coating machine was used to fill the pores. Two catalyst precursor solutions were applied consisting of 3 wt.% palladium acetate in ethanol/ethyl acetate (1/1) mixture or of 3 wt.% hexachloroplatinate solutions in water with the addition of about 20 wt.% of citric acid. The catalyst–precursor loaded membranes were dried at 105 °C/6 h. *Chemical reduction* was done by immersing the membrane in 1% $NaBH_4$ solution in H_2O/methanol (1:1) for several minutes, followed by washing in water. That reduction takes place immediately is shown by the instant color change from tawny to brown or black. Sometimes a few black particles leaked from the membrane, showing unbound noble metal. *Reduction by heat treatment* (calcination) was performed in a convection oven at temperatures of 175–200 °C in air for 2–8 h.

2.6. Membrane reactor conditions

Membrane reactor tests were done in the flow-through mode with permeate recirculation at 100 °C and 4 bar hydrogen-pressure. Membrane area was 100 cm^2. A pressure drop of about 2 bar was observed at a through flow of 500–800 mL/min. A geared pump with electronically controlled revolution speed was applied. In each run 500 mL sunflower oil (refined, from a local supermarket) was treated for 6–8 h. Samples were taken regularly.

2.7. Analytics

Reaction progress was analyzed by **gas chromatography** (GC) after saponification of the oil samples with methanolic KOH. GC: HP5890 with FID and auto sampler, 100 m Supelco SP 2560 capillary column, carrier gas helium. About 56 min were required for one chromatogram. **Differential scanning calorimetry** (DSC) was performed on a Netzsch DSC 204.

About 30 mg samples were sealed in a DSC pan, cooled to −30 °C, held the temperature for 40 min and heated by 10 °C per min to 100 °C, cooled to −30 °C and measured in a second cycle. **Pore sizes** were determined with a Porometer 4.900 from Porous Materials Inc. (PMI). The membrane stamps were immersed in the wetting fluid Porewick® from PMI (surface tension = 16×10^{-5} J/cm (16 dyn/cm)) for at least 15 min and then placed in the test cell with an effective area of 4.9 cm^2. For the determination of the **pore volume**, membrane stamps of 7.4 cm diameter were weighed in the dry state. Afterwards these stamps were immersed in the wetting fluid Galwick® from PMI (ρ = 1.8212 g/cm^3) for 1 h. The stamps were taken out and wiped with tissues to dab off excessive Galwick®. The pore volume is calculated to mL/100 cm^2 to make it comparable to the applied membrane area in the membrane reactor tests. As the membrane partly intrudes the nonwoven, the calculated pore volume contains some percentage of the nonwoven ''porosity''. **Scanning electron microscopy** (SEM): the morphology of the membranes was observed using a LEO 1550VP instrument (Carl Zeiss, Germany), which utilizes Gemini field emission column. The samples were fractured in liquid nitrogen and a cryopreparation (CRYO) was accomplished by a Penny sputter coater (PSC) to yield high resolution images (50,000 times) without morphological changes of the sample. For lower magnification the membrane samples were sputtered with a 2 nm Au/Pd layer using a Turbo sputter coater Emitech K575. To show the filler or catalyst with better contrast the back scattering mode (BSE) of the microscope was used in some cases.

3. Results and discussion

3.1. Membrane preparation

Microporous membranes were prepared from polyamideimide (PAI) and polyethersulfone (PES) because of the stability of these polymers in hot sunflower oil.

Fillers for polymers consist of inorganic particles such as silica, alumina, titania, zirconia or carbon. Those fillers are also the typical catalyst supports [9]. By incorporation into the membrane casting solution fillers do not influence the membrane properties as much with respect to the flux and separation properties [10]. Therefore, it is possible to activate polymer membranes catalytically by the addition of supported catalysts to the casting solution. A catalyst support with low porosity to give an egg shell type catalyst or with very large pores to show no mass transport hindrance is preferred for oil hydrogenation. For membrane requirements the particle size of the filler should not exceed the size of the membrane thickness and is typically the 5th to the 10th part of the thickness. Very small, nanoscale filler particles would be preferred to generate large surface areas inside the pores of the membrane; however, its effect of sharply increasing the viscosity of the casting solution limits the diminution of particle size. We selected a commercial alumina filler suited both as catalyst support and membrane filler.

3.2. Membrane casting and characterization

Standard membrane casting solutions for Radel® and Vylomax® applied at ambient temperature resulted in dense membranes with low nitrogen permeability and no measurable oil flux. The addition of alumina filler to the casting solution did not change the permeability. The pores are too small to allow for oil penetration. To generate hydrophilic membrane surfaces and large pores with very high water fluxes the use of additives like polyethylene glycol was reported [11–13]. We added a less hydrophilic ethyleneoxide-propyleneoxide-*b*-copolymer (Pluronic F127) with a molecular mass of 12,000 g/mol, consisting of EO_{98}–PO_{67}–EO_{98} blocks to the casting solution. Such polymers are known to form globular structures in water and can crystallize on surfaces [14]. The addition of Pluronic® to the casting solution of Radel® of about 30 wt.% in relation to Radel® did not improve the oil permeability (see Table 1). However, when cooling the casting solution to temperatures below 9 °C a dramatic change occurred in the membrane properties. The N_2 flux increased by an order of magnitude from 100 to 200 m^3/m^2 h bar to 1200–3000 m^3/m^2 h bar and a high oil flux of 400–1300 L/m^2 h bar was measured (Table 1). This effect was also observed in casting with Vylomax® (Table 1). The melting point of Pluronic® F127 is at 56 °C. To understand the influence of temperature on this additive, we

Table 1
Radel® membranes prepared with different amounts of Pluronic®, respectively, filler and detergent

Membrane no.	Casting temperature (°C)	Ra, Vy (g)	Pluronic (g)	Al_2O_3/detergent (g/g)	Concentration of Ra, Vy (%)	Bubble point (μm)	N_2 flux (m^3/m^2 h bar)	H_2O flux (L/m^2 h bar)	Oil flux (L/m^2 h bar)
Ra-1	20	50	25	–/–	10	<0.015	105	–	–
Ra-2	20	60	24	–/–	14	<0.015	220	–	–
Ra/Al-1	7	60	24	30/2.5	11	4.4	3000	27000	1300
Ra/Al-2	9	65	24	30/–	12	4.5	1200	800	400
Ra/Al-3	9	65	24	30/0.25	12	4.4	1300	500	400
Vy/Al/-/21 °C	21	120	48	70/1.1	11	2.5	25	5	0
Vy/Al/-/16 °C	16	120	48	70/1.1	11	2.5	40	30	0
Vy/Al/-/12 °C	12	120	48	70/1.1	11	8.8	2800	36000	1370
Vy/Al/-/9 °C	9	120	48	70/1.1	11	9.0	3000	33000	1600
Vy/Al/-/5 °C	5	120	48	70/1.1	11	3.9	2700	–	1380

Solvent: DMAc/GBL (5/1). Vylomax® membranes with alumina filler prepared from identical casting solution at different temperatures. Composition: 50% Vylomax®, 29.5% Al_2O_3, 20% Pluronic® and 0.5% detergent. Solvent: NMP, total concentration: 22%. Oil flux measured at 60 °C, other fluxes at RT.

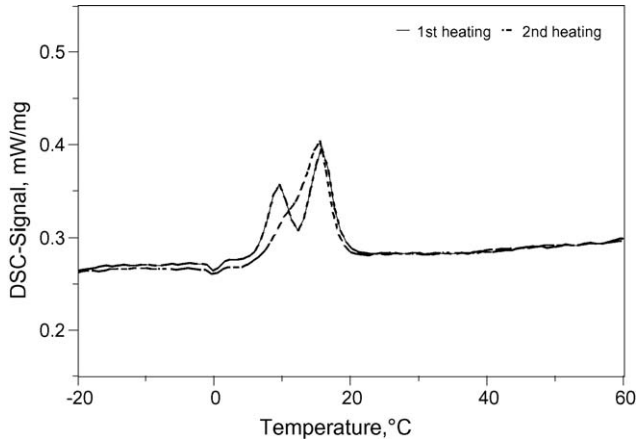

Fig. 1. DSC scans of a Vylomax® casting solution. Composition: 46% Vylomax, 27% alumina, 18.5% Pluronic® F127, 7.7% PVP, 0.8% Tego; concentration in NMP: 24%.

analyzed the membrane casting solution by differential scanning calorimetry (DSC). A typical DSC scan of a casting solution with filler is shown in Fig. 1. Two melting peaks are visible in the region of around 10 °C. During the first heating of the sample two separated peaks at 9.4 and 15.6 °C are found, whereas in the second heating the first peak is seen only as shoulder but the second peak is maintained. Without filler and lower overall concentration again two peaks were detected but both peaks appeared at slightly higher temperatures of 12.7 and 16.9 °C. The melting peaks were detected only in presence of Pluronic®. We assume the forming of clusters of Pluronic® in the casting solution below about 10 °C. These water soluble agglomerates are the reason for the forming of large pores in the top layer of the membranes and thus generating the exceptional high oil flux. To apply catalytically reactive membranes in the flow-through contactor mode a high oil flux is required to provide a low pressure drop. In Fig. 2 are shown SEM pictures of two different membranes from Table 1. Casting at 21 °C resulted in a rough surface without any pores in this low magnification (Fig. 2a). In Fig. 2b the membrane cast at 12 °C exhibits evenly distributed large pores. In the cross-section (Fig. 2c and d) using the BSE mode, a uniform distribution of the alumina filler is identified as white spots. The alumina particles are arranged at the interface of the inner membrane pores and, therefore, are highly accessible to the permeate.

In the final membrane reactor operation it is expected that the oil would have to pass through the membrane pores several times to result in high conversion. To increase the conversion in one pass a higher membrane thickness should enhance the number of catalytic sites installed in the membrane and consequently the turnover rate. Membranes with a steady increase in final membrane thickness (130, 230 and 330 μm (without nonwoven) and pore volume (5.6, 6.3 and 8.1 mL/100 cm^2) were prepared. The membranes containing no filler (Vy/-/PVP) became impermeable to oil at a thickness of 330 μm, the other fluxes decreased drastically. This effect was

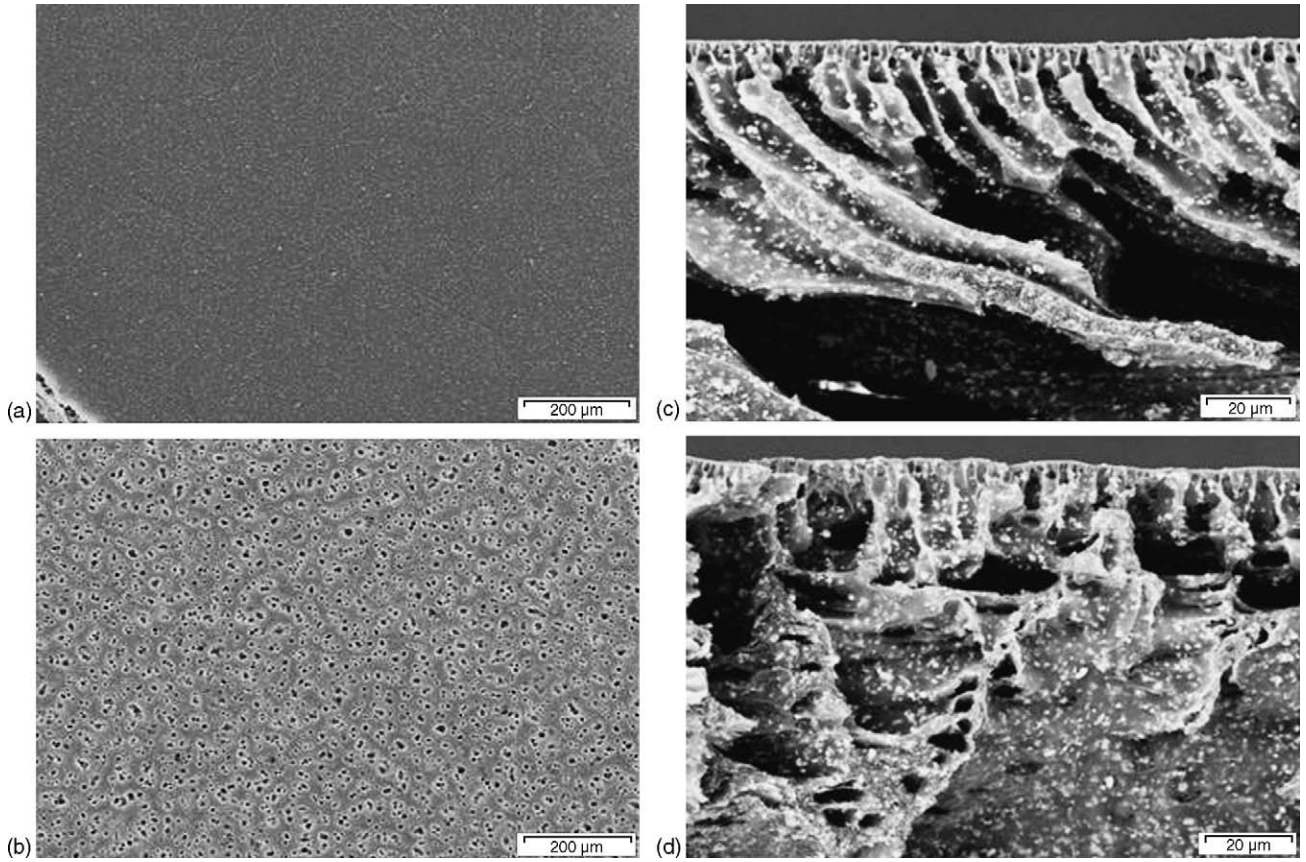

Fig. 2. SEM micrographs of membranes Vy/Al/-/*x* °C (Table 1). Surfaces, cast at 21 °C (a) and 12 °C (b). Cross-sections (in BSE mode), cast at 21 °C (c) and 12 °C (d).

Table 2
Vylomax® membranes prepared from NMP solutions of different composition with: PVP/no filler, PVP/filler, and no PVP/filler

Membrane no.	Membrane support	Vylomax® (%)	Pluronic® (%)	Alumina (%)	PVP (%)	Concentration of the casting solution (%)	N_2 flux (m^3/m^2 h bar)	Oil flux (L/m^2 h bar)	Bubble point (μm)	Pore volume (mL/100 cm^2)
Vy/-/PVP/2	PES	64	25	–	11	18.7	2300	1490	4.7	5.4
Vy/Al/-/1	PES	48	19	33	–	22.7	2700	2200	9.5	5.9
Vy/Al/-/2	PES	50	20	30	–	21.8	2900	1870	7.6	5.6
Vy/Al/-/3	PPS	50	20	30	–	21.9	1240	980	6.6	5.6
Vy/Al-Pt/-/1	PES	49	19	32	–	22.5	2750	1860	9.6	5.1
Vy/Al-Pt/PVP/1	PES	46	19	27	8	23.7	1900	900	8.9	7.0

The temperature of the casting solution was set to 9 °C. Membrane support: polyester (PES), polyphenylensulfide (PPS). PVP: polyvinylpyrrolidone. Detergent: ca. 1% of all solids.

less pronounced with the filler containing membranes (Vy/Al). It turned out, however, that with increasing membrane thickness the contact between nonwoven and membrane degraded, the membranes were mechanically less stable. Therefore, we focused on lower thickness (130–230 μm).

The effect of PVP on membrane casting solutions [15] was studied by several researchers, e.g. in detail by Wienk et al. [16]. Besides changes in pore structure by adding this additive, some amounts of the water soluble PVP are trapped irreversibly in the membrane and influences the hydrophilicity of nonpolar polymers. Additionally, PVP is known to bind metal nanoclusters [17] and that could be an advantage for the catalytic activation described later. Several membranes with or without PVP were prepared at similar casting conditions (Table 2). Oil fluxes were in all cases rather high (1500–2200 L/m^2 h bar) and were reduced only in case of higher thickness (230 μm, last entry Table 2) or PPS nonwoven (Vy/Al/-/3). From these data no influence of PVP on membrane properties was detectable.

PPS as nonwoven is preferred at temperatures up to 200 °C, because PES nonwoven becomes very soft above 120 °C.

3.3. Catalytic activation of the membranes

Catalytic activation of the membranes was performed on two routes:

(A) The membrane was impregnated by wet impregnation of the precious metal precursor $PdCl_2$ or H_2PtCl_6 in a suited solvent. The solvent has to be indifferent towards the membrane polymer (e.g. water or alcohol). Different concentrations should result in different loadings of the catalyst. After drying of the impregnated membrane, the metal was fixed to the membrane in two ways: (i) chemical reduction by borohydride and (ii) calcination of the membrane at temperatures of 175 or 200 °C. However, way (i) did not bind the catalyst permanently to the membrane, in hydrogenation reactions the metal was partially washed out. Activation by calcination at these low temperatures was found to be more effective in the presence of citric acid in the impregnation solution. Citric acid acts two-fold: improving the dispersion by serving as anion and by creating a reducing atmosphere during calcination. Examination of an impregnation solution with 20% citric acid by thermogravimetry up to 175 °C (10 K/min) revealed that after 10 min the catalyst precursor was completely reduced to the metal. The catalytically reactive membranes obtained by procedure (A) are of light to dark brown color. Metal contents in the range of 0.1–2 g/m^2 were obtained (measured by X-ray total reflection (TXRF) [18] after dissolution of the metal in aqua-regia). Calcinated membranes did not bleach during repeated membrane reactor runs.

(B) A pre-prepared supported catalyst was added to the casting solution instead of plain filler. The two membranes Vy/Al-Pt/-/1 and Vy/Al-Pt/PVP/1 (Table 2) were prepared by this method. Catalysts of 2 wt.% of Pd or Pt were prepared by wet impregnation of alumina by dissolved $PdCl_2$ or H_2PtCl_6. After calcination in air the catalyst is in the stable oxidic form and was added to the casting solution. Well-distributed catalyst suspensions were achieved by sonification (see Section 2) and sufficient stirring for 1–2 days. The membrane formation was not influenced by the presence of the metal. In Fig. 3a a cross-section of membrane Vy-Al/Pt-1 is displayed in BSE-mode showing the regular distribution of the supported catalyst over the membrane structure. At high magnification (50,000) the catalytic Pt-metal could be detected as nanosized white spots on the (grey) alumina particles inside the porous membrane structure (Fig. 3b). However, the overall catalyst contents of the membranes obtained by this method were rather low (0.07 g/m^2). A ready-made catalyst with higher metal content, however, may be less active because of a lower dispersion and larger metal cluster sizes. Additionally, the overall addition of active filler to the casting solution is limited to about 50 wt.% in relation to the Vylomax® and the metal content therefore will not exceed 0.3 g/m^2 of membrane area.

3.4. Membrane reactor tests: hydrogenation of sunflower oil

Triglycerides in sunflower oil contain in average about 58–65% linoleic acid (C18:2), 20–28% oleic acid (C18:1), 6% palmitic acid (C16:0) and 3–4% stearic acid (C18:0). A sum parameter for determination of the double bonds is the iodine

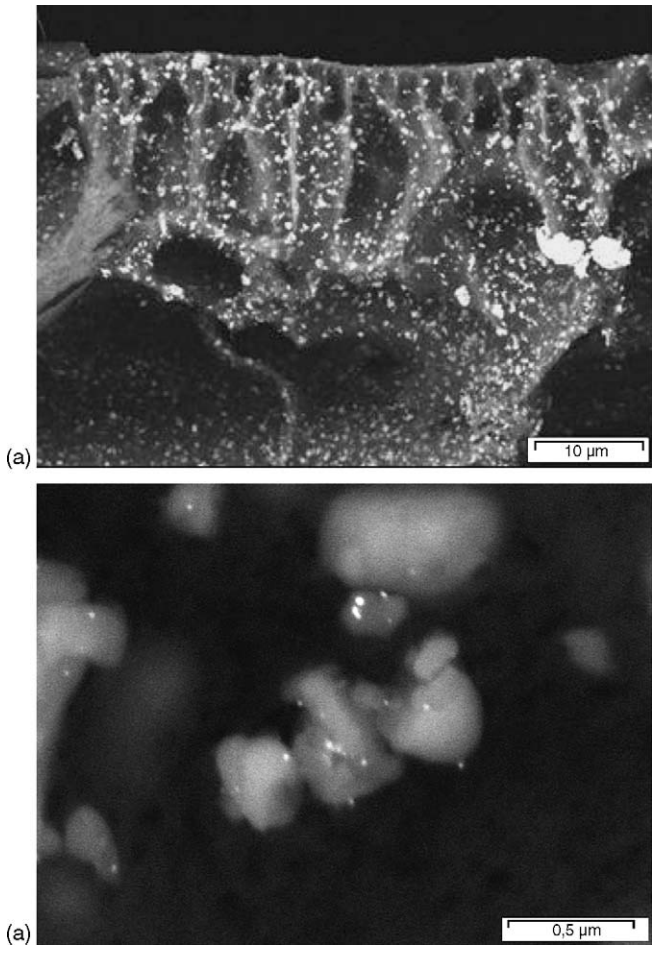

Fig. 3. SEM micrographs of membranes with catalyst. (a) Cross-section of membrane Vy/Al-Pt/-/1 in BSE mode. (b) Nanosized Pt on the alumina support (magnification 50,000).

value (IV), measured either by the iodometric titration of the oil or by calculation from the composition measured by GC. Typical sunflower oil has an IV of 130–134 and the IV is decreasing gradually with the hydrogenation.

The flow-through membrane reactor setup consists of a heated container that is connected to the membrane test cell by insulated tubes. The container is pressurized by hydrogen gas to 4 bar and the permeate recirculated. The catalytic membrane is pre-activated for hydrogenation in the reactor with 2 bar H_2 at ambient temperature overnight to remove the oxidic layer of the catalyst. After this treatment the membrane is so active that it would ignite in air. A low pressure drop of about 2 bar at an optimum reactivity was detected at an oil flux of 600–700 mL/min. In this case all of the oil was pumped through the pores of the membrane in less than 1 min. At lower fluxes the activity of hydrogenation was reduced considerably. At the end of the run the membrane was deactivated by flushing with nitrogen.

In the following are presented two selected hydrogenation experiments to demonstrate the membrane reactor process. Two membranes from Table 2, Vy/Al/-/1 activated and calcinated by (A) and Vy/Al-Pt/-/1 activated by method (B) were chosen. In both examples the catalytic metal was platinum because this catalyst is reported to produce a lower

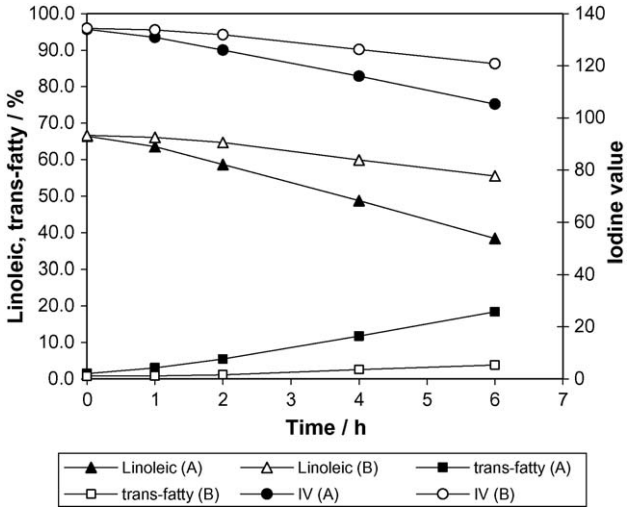

Fig. 4. Product distribution in membrane reactor hydrogenation of sunflower oil. *Conditions*: 100 °C, 4 bar H_2, 500 mL oil, 100 cm^2 membrane area. Filled symbols: VyAl/-/1 (A), catalyst content: 0.87 g Pt/m^2; open symbols: Vy(Al-Pt/-/1 (B), catalyst content: 0.07 g Pt/m^2.

amount of trans-fatty acids at a certain IV compared to palladium and nickel [4].

The hydrogenation results are presented in Fig. 4. The membrane Vy/Al/-/1 (filled symbols) contained 0.87 g Pt/m^2 and was calcinated at 175 °C. The IV dropped reproducible to 90 within 8 h, linoleic acid (C18:2) to 25%. The increase of stearic acid (C18:0) was from 4 to 10%. The trans-isomers reached 25% after 8 h reaction time.

In the other example an already fixed to the support platinum catalyst (2 wt.% Pt on alumina) was incorporated in the membrane. The final metal concentration of the membrane (Vy/Al-Pt/-/1, open symbols) was rather low (0.07 g Pt/m^2). The membrane showed less activity in accordance with its low catalyst content. The IV dropped to 116, C18:2 to 50%. Nevertheless, the formation of C18:0 per time was comparable (10% in 8 h). The trans-fatty acid content (5%), however, was low compared to the first example: at IV = 116 the trans-fatty acids in Example 1 had reached already 15%. Using the same membrane for additional runs without further activation in hydrogen it was found, that with lowering activity the membrane produced a relatively decreasing amount of trans-fatty acids but an increasing percentage of fully hydrogenated stearic acid.

4. Conclusions

Catalytic membranes with exceptional high oil fluxes and reasonable reactivity at only 100 °C and 4 bar H_2-pressure were developed and successfully tested in selective hydrogenation of sunflower oil. The addition of a water soluble co-polymer to the casting solution and a casting temperature below 10 °C led to highly porous membranes. Catalytic activation of these membranes was achieved by two different methods: (A) by wet impregnation of the membranes in metal precursor solution or (B) by the addition of ready-made supported catalyst to the casting solution. The latter resulted in membranes with a low

catalyst content and a corresponding low activity in hydrogenation reactions. Catalytic membranes prepared by method (A) were reduced either with sodium borohydride or by calcination in the presence of high amounts of citric acid. Only the latter procedure provided durable, well-fixed catalysts inside the membrane pores. By the addition of citric acid, the calcination temperature could be reduced to 175–200 °C and, therefore, applied to polymer membranes. The catalysts Pt or Pd attached in this way were not washed out even during prolonged reaction times.

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