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Application of a forced-flow catalytic membrane reactor for the dimerisation of isobutene

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Abstract

A forced-flow catalytic membrane reactor was applied for dimerisation of isobutene to isooctene. Several catalysts, such as silica supported Nafion® (Nafion® SAC-13), Nafion® NR50, Amberlyst™ 15, and silica supported phosphotungstic acid were mixed in solution with a polymeric binder. Teflon® AF, Hyflon® AD, polytrimethylsilylpropyne, and polydimethylsiloxane (PDMS) were applied as binder to form a porous, reactive layer on top of a porous, polymeric, supporting membrane. An optional intermediate PDMS film acted as flow regulator and enabled selective product removal. Isobutene was fed to the reactive membrane, the reaction started immediately and a pressure of around 4 bar built-up on the feed side. Liquid product was collected on the permeate side in an iced trap. Depending on the type of binder high conversions up to 98% at 22% selectivity to isooctene (binder = Hyflon® AD) and space velocity of 530 g_{i-C4}/g_{cat} h, or high selectivities of >80% at 45% conversion of isobutene and space velocity of 275 g_{i-C4}/g_{cat} h (binder = Teflon® AF) were achieved. Catalyst poisoning was not observed during operation for at least 1 week.

Keywords: Catalytic membrane reactor; Dimerisation; Isobutene; Forced-flow

1. Introduction

The excess from C_4 raffinate of isobutene in refineries is used for long time to produce branched hydrocarbon (b-HC) with high octane number, perfect for blending to fuel or react it with methanol to yield methyl-*t*-butylether (MTBE) also for improving the octane number of gasoline. However, MTBE is suspected of ground water pollution and may be banned as fuel additive. Therefore, less isobutene will go for MTBE syntheses and increasing amounts of isobutene are available. Two routes are established to refine isobutene to higher molecular weight b-HC: dimerisation and alkylation. Both reactions are somewhat similar, different only in reactivity of the intermediate carbon cation. Usually, the process is run in homogeneous phase with liquid acid catalysts such as H_2SO_4 or HF. A major drawback of these catalysts is their environmental and health risk, when used in large amounts such as in known batch processes. Fluorinated sulfonic acids are also efficient alkylation catalysts [1] but even with immobilisation of the acid onto a support and applying a moveable fixed-bed process excess of the acid needs to be removed from the product. Another well-known process, the Bayer process [2], uses acid ion exchangers for dimerisation of isobutene. The process is run at 100 °C and ca. 20 bar in the liquid phase and yields nearly quantitative conversion with dimer to trimer proportion of about 75/25. Recently, a membrane reactor approach was reported to improve the selectivity to the dimer by extraction of preferentially the dimer through the channels of a tubular zeolite membrane filled by the acid resin Amberlyst™ 15 [3]. Compared to a fixed-bed reactor, the continuous removal of the product increased conversion and selectivity considerably. Besides the application of Amberlyst type ion exchangers [4–6], other liquid, supported liquid or solid acid catalysts are also reported for alkylation or dimerisation [7]. Perfluorosulfonic acid based catalysts are also applied successfully in alkylation and dimerisation [8–10]. We recently introduced another membrane based approach to dimerisation of isobutene as an example for dimerisation and

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alkylation by a membrane reactor. Based on known problems of sometimes low selectivity, conversion, and of catalyst poisoning in real C_4 raffinate streams caused by, e.g., by-products such as diolefines or acetylene, we located an acid catalyst in the porous layer of a composite membrane and generated a pressure difference of 400–900 mbar by a vacuum pump on the permeate side. Therefore, a forced-flow through the acid catalyst layer is generated, accompanied by short, scalable contact time. Because in this set-up the contact to the acid catalyst sites is no longer controlled by diffusion, no poisoning by generation of oligomers and polymers is expected. Up to 10% conversion at a selectivity of about 90% to the dimer was observed without poisoning during the runs for about 2 weeks [11,12]. We extended this approach and simplified the experimental set-up to a pure forced-flow membrane reactor without any retentate stream and no use of vacuum pumps to generate the driving force through the membrane. We report here on the results using polymer based composite membranes with Nafion® SAC-13 and other solid acids in various compositions. Recently, Torres et al. [13] reported a similar approach applying inorganic membranes with a beta-zeolite film as catalyst supported on a tubular Al_2O_3 membrane. The concept of forced-flow membrane reactors with catalyst located inside the membrane pores is reported barely in the literature [14–16], however, the results were promising and may be applied as an easy to handle new technology. Total combustion of volatiles from air in the ppm range with huge space velocities was also reported to work efficiently with flow through catalytic membranes in the Knudsen-diffusion regime [18–20].

2. Experimental

2.1. Materials

Nafion® SAC-13 and Nafion® NR-50 were by courtesy of Engelhard (Ohio, USA), and Amberlyst™ 15 was purchased from Aldrich. Two catalysts were made by impregnation of phosphotungstic acid $H_3PW_{12}O_{40}{\cdot}nH_2O$ (Fluka, Germany) or Nafion® solution (Du Pont, USA) on silica – Aerosil OX-50 (Degussa, Germany). Another type of a catalyst was made by loading on silica matrix during a sol–gel process similar to Nafion® SAC production.

Four different polymers were used as binder: Teflon® AF 2400 (Du Pont, USA), Hyflon® AD 80X (Ausimont, Italy), Elastosil® E-43 (Wacker-Chemie, Germany) and polytrimethylsilyl propyne (PTMSP), by courtesy of Benny Freeman from The University of Texas (USA). In-house fabricated membranes were used as a microporous support, made from polyacrylonitrile (PAN) or Torlon®, a polyamideimide (PAI). They were used uncoated or coated with a thin, non-porous polydimethylsiloxane (PDMS) film.

Teflon® AF 2400 and Hyflon® AD 80X are polymers soluble in commercial solvent FC 77 that was supplied from 3M™ (Fluorinert™, USA), whereas Elastosil® E-43 was solved in isooctane and PTMSP in tetrahydrofuran (THF).

Isobutene 2.8 (>99.8 vol.% purity) was purchased from Messer Griesheim (Germany) and propane 2.5 (>99.5 vol.% purity) from Linde AG (Germany).

2.2. Catalyst and membrane preparation

Nafion® SAC-13, in the physical form of 1 mm extruded particles, was milled using a ball mill over night, sieved with a 32 μm pore size sieve and stored in a desiccator. Amberlyst™ 15 could not be ball-milled due to elasticity of the beads. It was ground manually in a mortar. Nafion® NR-50 in the form of 60× 100 mesh powder was used as received.

Supported acid catalysts were prepared from a mixture of ethanol and water in volumetric ratio 1:1 and $H_3PW_{12}O_{40}{\cdot}nH_2O$ (HPW) or Nafion® solution. The impregnation was performed at room temperature in a flask containing 2 g of silica powder (Aerosil OX-50), suspended in 8 cm^3 of ethanol–water mixture with 0.4 g HPW or 8 g 5% Nafion® solution (20% in relation to silica) under continuous stirring for 72 h [17]. The suspension was dehydrated slowly at 50 °C for 1.5 h in vaccuo using a rotavapor (Büchi, Germany). The resulting silica–heteropolyacid powder was dried at 120 °C for 4 h and 2.2 g of the final supported catalyst was obtained.

Silicon dioxide particles derived from a sol–gel process [21] loaded with Nafion® served as another type of a catalyst. A mixture of 6 g water, 2.4 g 1-butanol and 16.1 g 5% Nafion® solution (13 wt.% to silica) was added to 6.94 g tetraethyl orthosilicate (TEOS), and stirred at 80 °C for 5 h. Obtained gel was dehydrated slowly at 80 °C for 2 h in vaccuo, and dried at 120 °C for 6 h to give a silica-supported Nafion® (Nafion® SAC is produced similarly).

The final acid, porous membranes were obtained as composite membranes by a casting process. The casting solution consisted of supported catalyst particles mixed with the polymeric binder. Thus: in 0.533 g of a 0.6% binder solution 0.04 g of the grounded catalyst was suspended by stirring to obtain the casting solution. Catalyst to binder mass ratios of 1:0.08 and 1:0.25 were mostly applied. The suspension was further homogenised by an ultrasonic bath (Bandelin-Sonorex, Germany) for 30 min. A 19 mm diameter metal ring was centred and placed over a 20 mm diameter supporting membrane. Uniform suspension was cast in the ring and left over night at RT to evaporate the solvent. A porous catalyst layer was formed on top of the membrane support. The final composite membrane was dried in an oven at 105 °C for 1 h and then installed immediately in the membrane reactor.

2.3. Characterisation methods

2.3.1. Gas permeation

Gas permeation was measured applying the membrane reactor set-up. The feed pressure was recorded and the permeate gas flow rate per time was measured by a soap bubble meter.

2.3.2. Porosity and pore size distribution

Membrane porosity was determined by filling the pores with 1-propanol or methanol (for PTMSP membranes) as an inert fluid for all membrane components. The weight difference between the dry and the wet membrane was measured and the porosity was calculated as the weight fraction of the medium that occupies the void space. The dry and wet membrane with the catalytic layer were weighted and compared. Porosity was calculated according to:

$$\text{porosity} = \frac{(m_{\text{w}} - m_{\text{d}}) - (m_{\text{ws}} - m_{\text{ds}})}{m_{\text{w}} - m_{\text{ws}}} \times 100$$

where m_{d} designates dry membrane, m_{w} is wetted membrane and m_{ds} and m_{ws} are dry and wet support, respectively.

The porometry tests to determine pore size distribution were performed using an automated capillary flow porometer (PMI, USA). Galwick® was used to wet the pores completely. The fully wetted sample was placed in the sample sealed chamber and nitrogen was used as measuring gas.

2.3.3. Determination of acidity

The acidity was determined by potentiometric titration with 0.1N NaOH. The titration was performed with a 716 DMS Titrino (Metrohm, Swiss) at room temperature. The catalyst (0.2 g) was added into the vessel with 20 cm^3 water and a magnetic stirrer. The titrant was added automatically in very small volume increments to avoid sample over-titrating.

2.3.4. Scanning electron microscopy (SEM)

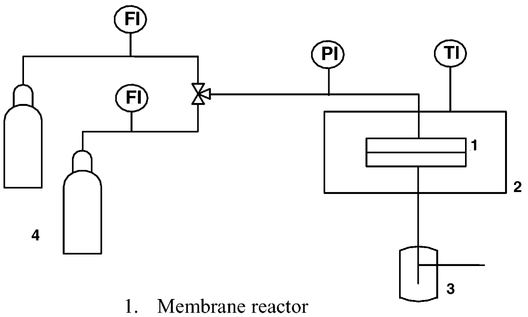
The morphology of the membranes was observed using a scanning electron microscope type LEO 1550VP (Carl Zeiss, Germany), which utilises Gemini field emission column. The samples were fractured in liquid nitrogen and a cryopreparation was accomplished by a Penny sputter coater (PSC). Due to the catalyst layers brittle structure some samples were scanned separately from the PAN/PDMS support.

2.4. Isobutene dimerisation experiments

Experiments were carried out in a membrane reactor with 2.54 cm^2 membrane area. The so called flow through membrane reactor was designed this way that the gas feed line is centred over the membrane holder, thus a permeating fluid or gas is equally distributed on the membrane surface. The membrane reactor was placed in a thermostated water bath with a magnetic stirrer to maintain a constant temperature and ensure a uniform temperature distribution among the reactor. A Voltcraft® 306 (Taiwan) sensor fixed on the outer reactor surface was used to monitor the temperature. Isobutene and propane gas flows were set by a mass-flow controller (MKS Instruments – Multi Gas controller 147), which was calibrated for isobutene (0–145 cm^3/min) and propane (0–180 cm^3/min). The pressure, built-up by the incoming gas stream on the feed side, was measured by a pressure sensor (MKS Instrument) calibrated in the range of 0–5000 mbar. The membrane reactor outlet line was immersed in an ice bath. The liquid products dimer, trimer and tetramer, with some dissolved isobutene, were collected in a U-shaped cooling trap. Output mass was measured by a Mettler AT 2000 microbalance. For the set temperature and gas flow, the obtained built-up pressure, experiment time and product mass were noted. The membrane reactor normally operated in the range from 1.2 to 4.7 bar, which was the limit of the pressure of isobutene at RT supplied from the gas cylinder. The space velocities were in range from 40 to 3200 ($g_{i\text{-butene}}/g_{\text{catalyst}}$ h), at temperatures ranging from 30 to 50 °C and with *i*-butene inlet flow rate from 10 to 270 cm^3/min. The scheme of the apparatus is presented in Fig. 1. After reaching steady state conditions, the condensed products were sampled and analysed by a gas chromatograph (CE Instruments GC8000, Italy) using a flame ionisation detector (FID), type FID 80. The capillary column used was of the type J&W 30 m × 0.53 mm. The GC carrier gas was Ar. The following temperature program for GC was used:

- start at 100 °C for 0.8 min;
- heating to 150 °C at a temperature ramp of 70 °C/min and holding at 150 °C for 0.7 min;
- heating to 200 °C at a temperature ramp of 70 °C/min and holding at 200 °C for 4.5 min.

This program ensures to find all products developed during the reaction. The GC outgoing signal gives the mass ratio of the condensate composition. Knowing isobutene inlet flow rate and also mass and composition of the condensate, the molar balance was established.



1. Membrane reactor
2. Water bath
3. Cooling trap
4. Gas bottles (isobutene, inert gas)

Fig. 1. Scheme of the catalytic membrane reactor.

3. Results and discussion

3.1. Membrane preparation and characterisation

Various composite membranes were prepared according to the description in the experimental part. The membranes are composed of a porous support and the porous, reactive layer. The catalytic active layer is built-up by an immobilised acid, supported on silica, and is hold together by a polymeric binder. Additionally, a thin intermediate layer of a pore-free PDMS film is placed between the support membrane and reactive layer. Depending on the thickness of this PDMS thin film, the overall gas flow through the composite membrane can be regulated as reported in Table 1. Thus, the propane gas flow of the supporting membrane is reduced from 110 to 10 m^3/m^2 h bar (PDMS 0.26 μm) or 0.9 m^3/m^2 h bar (PDMS 3.8 μm). Without intermediate layer of PDMS the porous, reactive layer reduces the gas flow to about 18 m^3/m^2 h bar (Table 1, no. 7–9 (PAN/Naf. SAC-various binders)). With reactive layer and intermediate thin PDMS film (0.26 μm) the flow of propane is only slightly reduced to about 9 m^3/m^2 h bar (Table 1), thus demonstrating a negligible resistance of the reactive, porous layer to gas flow. Accordingly, the intermediate PDMS layer may act as a flow regulator, independent on the pore sizes and porosity of the reactive layer in some range.

The porosity and the pore sizes of the reactive layer should be closely related to its reactivity by theoretical considerations. The pores should be ‘‘large’’ enough to allow for free passage of dimer and possible side products trimer and tetramer, and ‘‘small’’ to provide close contact to the acid surface for high reaction rates. The porosity of the active layer depended mainly on the catalyst/binder weight ratio, e.g., the porosity decreased from ~44% (weight ration 1:0.08) to ~33% (weight ration 1:0.25) with increasing amount of binder (see Table 1). The use of non-uniform catalyst particles results in higher porosity of 53% (Table 1, no. 1 (PAN/Naf. SAC–Teflon, non-sieved)). The membrane with Amberlyst (no. 11, Table 1) showed lowest porosity of 17% at all.

For membranes with PDMS intermediate layer the porometry test to determine mean pore sizes is not applicable. Only membranes without intermediate PDMS film could be measured. The detected mean pore size did not depend on the type of binder (0.6 μm, nos. 3, 4 (PDMS or Teflon AF), Table 1), but on the catalyst/binder weight ratio. Increasing amount of binder (1:0.08–1:0.25) reduces the mean pore size to 0.4 μm (no. 8 (PAN/Naf. SAC–Hyflon), Table 1). Also, the pattern of pore size distribution was narrow from 0.3 to 0.6 μm (mean: 0.4 μm) compared to 0.3–0.9 μm (mean: 0.6 μm).

Microscopic methods, such as SEM are perfect to visualise porous layers within the micrometer range. The cross-section of four membranes is represented in Fig. 2a–d. In Fig. 2a the top layer of the supporting membrane, the 3.8 μm PDMS film, and the reactive layer of membrane no. 6 (PAN/PDMS/Nafion® SAC–Teflon, Table 1) is pictured. A close packing density is obvious together with a slight asymmetry in packing of the catalyst particles. The visible

Table 1
Catalytic membranes and their basic properties

No.	Membrane	Catalyst	Catalyst (mg)	Catalyst/ binder weight ratio	PDMS thickness (μm)	Ar permeability (m^3/m^2 h bar)	C_3H_8 permeability (m^3/m^2 h bar)	Porosity (%)	Mean pore size (μm)
A	Torlon					123	124	68	
B	PAN					108	110	69	
C	PAN/PDMS				0.26	5.4	10.4		
D	PAN/PDMS				3.8	0.48	0.91		
1	PAN/PDMS/Naf. SAC–Teflon[a]	Nafion® SAC	8.7	1:0.08	0.26			53	
2	Torlon/Naf. SAC–Teflon	Nafion® SAC	21.7	1:0.08	0.26			45	
3	PAN/Naf. SAC–Teflon	Nafion® SAC		1:0.08					0.61
4	PAN/Naf. SAC–PDMS	Nafion® SAC		1:0.08					0.60
5	PAN/PDMS/Naf. SAC–Teflon	Nafion® SAC	16.3	1:0.08	0.26			44	
6	PAN/PDMS/Naf. SAC–Teflon	Nafion® SAC	38.3	1:0.08	3.8			44	
7	PAN/Naf. SAC-PTMSP	Nafion® SAC	20.6	1:0.25	–	14.9	18.5	34	
8	PAN/Naf. SAC–Hyflon	Nafion® SAC	25.3	1:0.25	–	13.5	17.4		0.41
9	PAN/ Naf. SAC–PDMS	Nafion® SAC	15.7	1:0.25	–	13.6	18.1		
10	PAN/PDMS/Naf. SAC–Hyflon	Nafion® SAC	28.5	1:0.25	0.26	4.4	8.1	34	
11	PAN/PDMS/Amb. 15-Hyflon	Amberlyst 15	12.5	1:0.25	0.26	6.3	9.5	17	
12	PAN/PDMS/Naf. NR–Hyflon	Nafion® NR	23.1	1:0.25	0.26	5.9	9.2	31	
13	PAN/PDMS/OX-50 + HPW–Hyflon	HPW[b]	23.9	1:0.25	0.26	4.7	9.4	35	
14	PAN/PDMS/OX-50 + Nafion®–Hyflon	Nafion®	19.7	1:0.25	0.26	4.5	9.3		
15	PAN/PDMS/ (SiO_2/Nafion®)-Hyflon	Nafion®	19.7	1:0.25	0.26	5.6	10.2	31	

[a] Catalyst not sieved.

[b] Phosphotungstic acid.

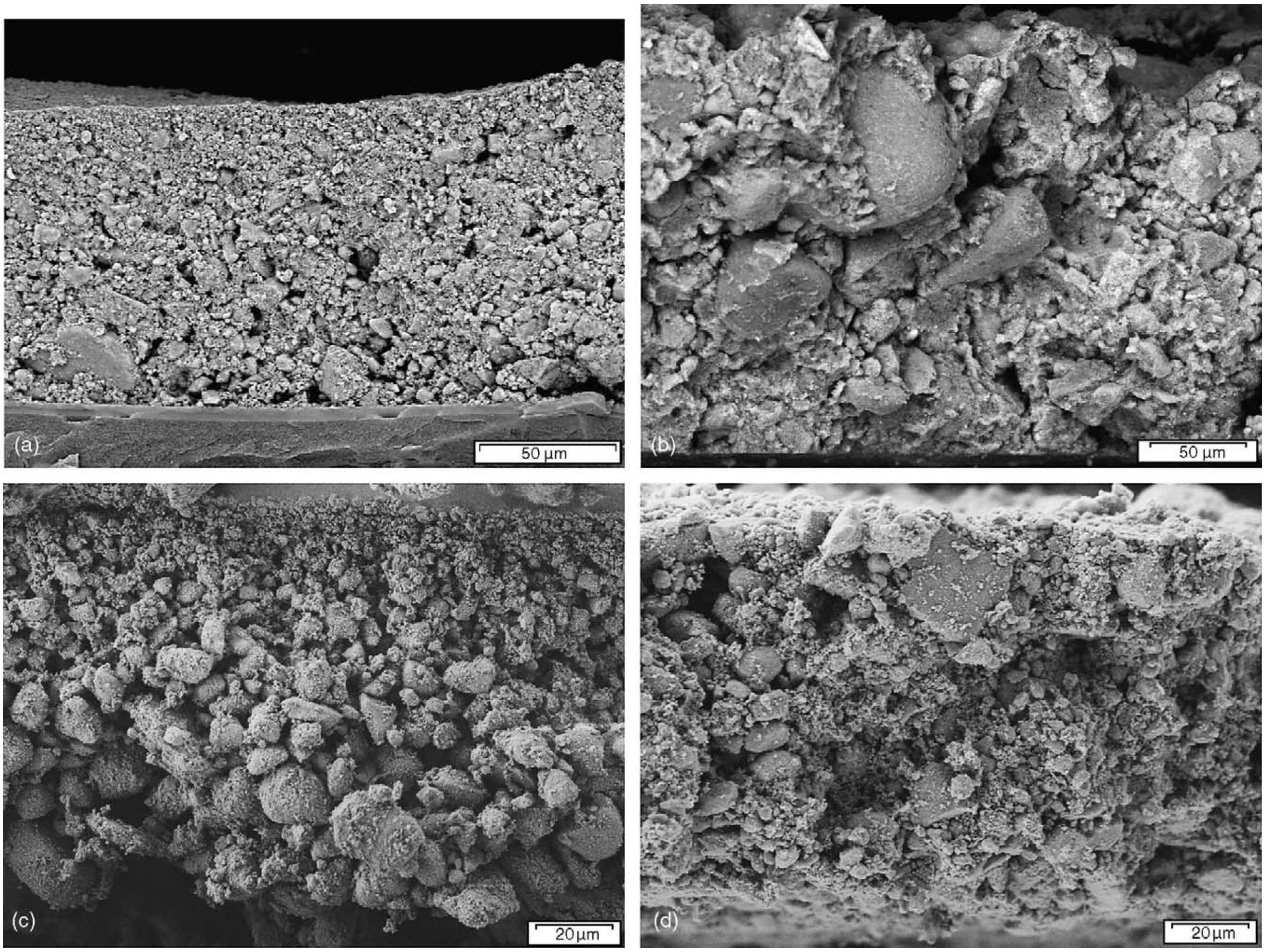


Fig. 2. Scanning electron micrographs of the cross-section of four membranes: nomenclature according to Table 1; no. 6 (PAN/PDMS/Naf. SAC-Teflon) no. 13 (PAN/PDMS/OX-50 + HPW–Hyflon) no. 9 (PAN/Naf. SAC-PDMS) no. 10 (PAN/PDMS/Naf. SAC-Hyflon).

cavities are most probably due to artefacts whilst fracturing in liquid nitrogen for sample preparation. The asymmetry can be seen more clearly in Fig. 2c with PDMS as binder. With the binder Hyflon AD a rather symmetric structure is obtained (Fig. 2d). Membranes made from Aerosil OX-50 as catalyst support showed the larger particle size of the catalyst support in Fig. 2b. The catalysts Amberlyst™ 15 and Nafion® NR were available even after grinding only in sizes of about 20–50 μm (Amberlyst™ 15) or 50–100 μm (Nafion® NR). The structure of the reactive layer, therefore, reflected this inconsistency and resulted in a non-uniform thickness of Amberlyst type membranes. With Nafion® NR no porous structures could be obtained.

Structure, porosity, catalyst partition, and catalyst accessibility are all important for the final reactivity of the membrane. From the reaction scheme (Fig. 3) can be deduced that proton abstraction from the catalyst surface starts and supports further reaction. The H^+ active sites must be obtainable to the educts. Simple titration with 0.1N NaOH was applied to measure acidity of pure catalyst and catalyst encased by the binders Teflon AF and Hyflon AD (Table 2). The values of measured acidity of pure catalyst corresponding to the data are given in the literature (see Table 2). Highest acidity is provided by Nafion® NR, however, the binding of the particles with Hyflon AD reduces the available H^+ sites drastically from 0.64 to 0.12 mmol_{H+}/g_{cat}. Similar effect is found for Amberlyst at higher binder content. Also, reactive membranes from both catalysts did not produce defined porous layers (see previously). The acidity of Nafion® SAC is strongly influenced by the type of binder. With Teflon AF addition of only 10% of the binder reduces the measured acidity from 0.14 to 0.02 mmol_{H+}/g_{cat}. Hyflon AD, on the other hand, only slightly decreases the acidity to 0.12 mmol_{H+}/g_{cat} even with 20% of binder added. Moreover, the acid strength of the catalyst correlates with its reactivity towards dimerisation, i.e., on the ability of a site to activate a certain reaction by providing the protons effortless [24]. The major difference between perfluorinated sulfonic acids and styrene based acids is in acid strength. Corma et al. [25] found a similar correlation between the catalyst acidity and activity for another pair of catalysts in isobutane/2-butene alkylation. A

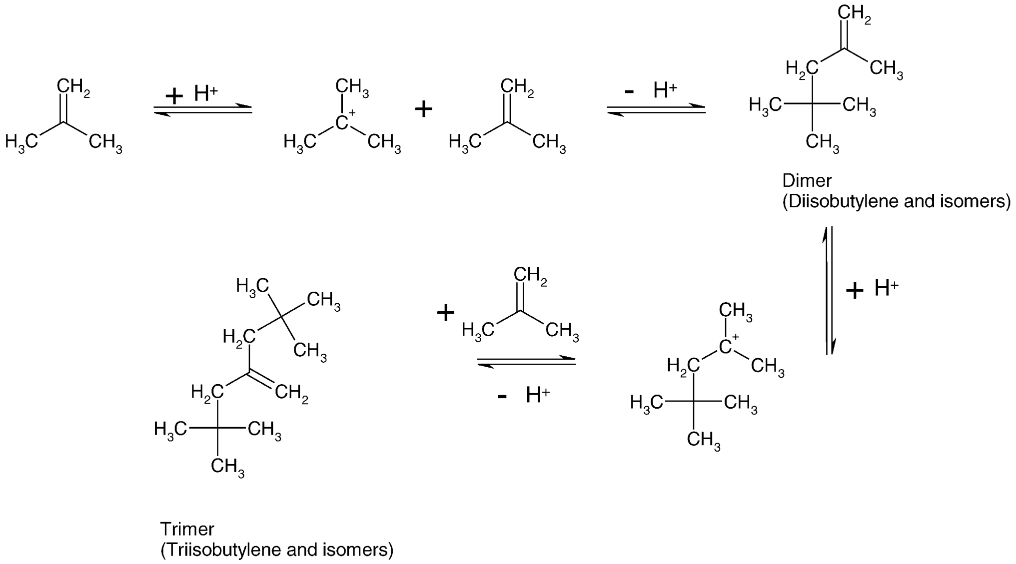


Fig. 3. Reaction scheme of acid catalysed isobutene oligomerisation.

binder, present in a catalytically active layer, effects acidic properties of the catalyst by changing its proton exchange efficiency and also blocking some of the catalysts inner surface, i.e., the active sites that are placed inside the catalyst pore system.

3.2. Performance of isobutene dimerisation in the flow through membrane reactor

The forced-flow membrane reactor was operated as described in Fig. 1. In the reaction experiments a steady flow through the membrane is generated, driven by the set flow rate and the resulting built-up pressure difference. Normal pressure was at the reactor outlet. The main interesting results are conversion, selectivity and space velocity of the reactor runs.

The conversion of isobutene that passed through the membrane reactor, was calculated according to (Eq. (1)):

$$C_{i\text{-C4}} = \frac{m_{\text{cond}} \sum_i m_{\%,i}}{m_{f\text{-C4}}} \tag{1}$$

The selectivity (Eq. (2)) of isooctene is defined as:

$$S_{i\text{-C8}} = \frac{m_{\%,i\text{-C8}}/M_{i\text{-C8}}}{\sum_i m_{\%,i}/M_i} \times 100 \tag{2}$$

where m_{cond} designates mass of the trapped condensate, $\sum m_{\%,i}$ sum of products percentages in the condensate, $m_{f\text{-C4}}$ the mass of isobutene in the feed, $m_{\%,\, i\text{-C8}}$ the percentage of isooctene in the output and M_i the molecular mass of the components.

Space velocity (Eq. (3)) is defined as the rate of feed of the given reactant per unit mass of the catalyst:

$$\text{SV} = \frac{\dot{m}_{i\text{-C4}}}{m_{\text{cat}}} \tag{3}$$

where $\dot{m}_{i\text{-C4}}$ is isobutene mass-flow rate and m_{cat} is the mass of catalyst.

3.2.1. Influence of the conversion on space velocity and feed pressure

With the mass-flow controller the reactor input can be set within some limits. By means of the membrane area an

Table 2
Acidity of the active catalytic layer

Binder	Catalyst: binder, weight fraction	Catalyst fraction (%)	Acidity ($\text{mmol}_{\text{H+}}/\text{g}_{\text{cat}}$)		
			Nafion SAC	Nafion NR	Amberlyst 15
Literature		100	0.14–0.16[a]	0.85[b]	4.8[c]
Measured		100	0.139	0.638	4.81
Teflon AF	1:0.08	90	0.024		3.64
	1:0.25	80			0.18
	1:0.40	70	0.008		
Hyflon AD	1:0.08	90	0.135	0.154	4.04
	1:0.25	80	0.123	0.121	0.23

[a] Engelhardt, product data sheet Nafion® SAC-13.

[b] [22,23].

[c] [5].

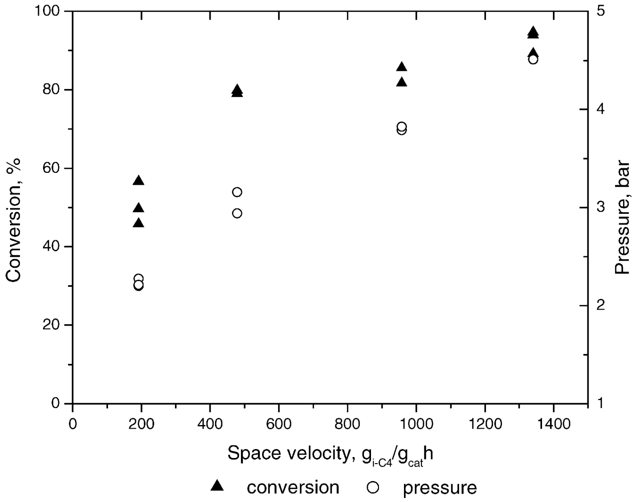


Fig. 4. Isobutene conversion and built-up pressure as a function of space velocity. Membrane no. 9 (Naf. SAC-PDMS), 50 °C, 140–20 ml/min, total time 380 min.

isobutene input flow between 10 and 200 ml/min could be realised with the membranes. Owing to the membrane resistance, depending on the membrane quality and the reaction conditions with the set of an input flow a certain pressure will build up and after reaching equilibrium results in a stable flow and permeate composition out of the reactor. In Fig. 4 is presented the typical behavior of a membrane without intermediate PDMS layer (no. 9 (PAN/Nafion® SAC–PDMS), see Table 1). Input flow was varied stepwise from 140 to 20 ml/min within 380 min. With decreasing space velocity the conversion decreased from 90 to 80% and dropped at the lowest SV of 190 $g_i g_{i-C4C4}/g_{cat}$ h down to 45% at the end of the experiment. The selectivity to the dimer did not change significantly. A maximum of 14.5 was found at SV = 480 g_{i-C4}/g_{cat} h. The feed pressure lowers with decreasing SV from 4.5 to 4 bar and finally to 1.5 bar. At the lowest SV of 200 g_{i-C4}/g_{cat} h (=20 ml/min I–C4 input) the generated driving force of 1.5 bar is too low to generate stable reaction conditions. On the other hand, the process is fully reversible and initial SV could be recovered. During the reaction it is reasonable that the pores will be filled by the liquid products and a certain flow (pressure) is required to purge the filled pores fast enough from product and possible oligomers.

3.3. Performance of the different built-in catalysts with Hyflon AD as binder

The various prepared membranes are different in porosity, acidity and activity. To detect the best suited membrane catalyst at forced-flow reaction conditions, various catalysts were investigated under the same operating conditions. The catalyst particles were interconnected by Hyflon AD in 1:0.25 weight ratio and placed as reactive, porous layer on top of a PAN/PDMS support membrane. The catalysts Nafion® SAC, Nafion® NR, SiO_2 + Nafion®, Amberlyst, and OX-50 + HPW were applied.

3.3.1. Effect of the temperature

Increasing temperature influences conversion and selectivity. The tendency of increasing conversion with temperature is identified in Fig. 5a. The input flow was set to 100 ml/min with the exceptions indicated in Fig. 5a. The resulting SV varied from 130 (no. 12, PAN/PDMS/Naf. NR-Hyflon) to 1200 g_{i-C4}/g_{cat} h (no. 11, PAN/PDMS/Amb. 15-Hyflon). The highest conversion was established for the Nafion® SAC catalyst at a notable high SV of 530 g_{i-C4}/g_{cat} h. Also the silica supported phosphotungstic acid catalyst (no. 13, PAN/PDMS/OX-50 + HPW–Hyflon) converted isobutene up to 45% but only at about half of the SV of the Nafion® SAC catalyst. We contribute this lower conversion and the even lower conversions of the other catalysts given in Fig. 5a mainly to the imperfect pore structure of the reactive layer. An optimised pore structure of these membranes is expected to result in higher conversion rates even for these catalysts.

In Fig. 5b is displayed the effect of temperature on the selectivity to the dimer. Generally, the highest selectivity is found at lowest temperature. The membrane with the best conversion (Nafion® SAC catalyst) showed lowest selectivity of about 40% to the dimer. A compromise between high conversion and acceptable selectivity yielded the membrane no. 13 with the silica impregnated phosphotungstic acid (PAN/PDMS/OX-50 + HPW–Hyflon). At 30 °C a conversion of ~30% was accompanied by a selectivity to the dimer of ~70%.

3.3.2. Effect of space velocity

Isobutene conversion and isooctene selectivity dependence on space velocity is shown in Fig. 6a and b. The inlet flow rate, the parameter that exerts direct influence on the space velocity, changed in the range from 270 to 20 ml/min, from high to low, and the measurements were performed at 50 °C.

The membrane with highest conversion (no. 10, PAN/PDMS/Nafion® SAC–Hyflon) showed a slight maximum at medium SV = 500 g_{i-C4}/g_{cat} h of 90% and about 80% conversion at SV of 250 and 1000 g_{i-C4}/g_{cat} h. At the lowest SV of 100 g_{i-C4}/g_{cat} h the conversion significantly dropped to (30%). At this low SV most probably the reaction conditions at the catalyst inside the pores changed from forced-flow to more diffusion controlled flow. We assume, that the pores are filled at all SV with liquid (i–C4 and products). At the lowest SV and the low conversion of (30%) the reaction mixture inside the pores is “diluted” by i–C4. Therefore, also a change in selectivity to the dimer is observed in this flow regime. The accompanied selectivity (Fig. 6b) changed with SV from 40% (SV = 1000 g_{i-C4}/g_{cat} h) to a minimum of 37% (SV = 500 g_{i-C4}/g_{cat} h), and finally increased sharply to 70% (SV = 100 g_{i-C4}/g_{cat} h). The two other membranes, more imperfect in respect to their pore system, showed increasing

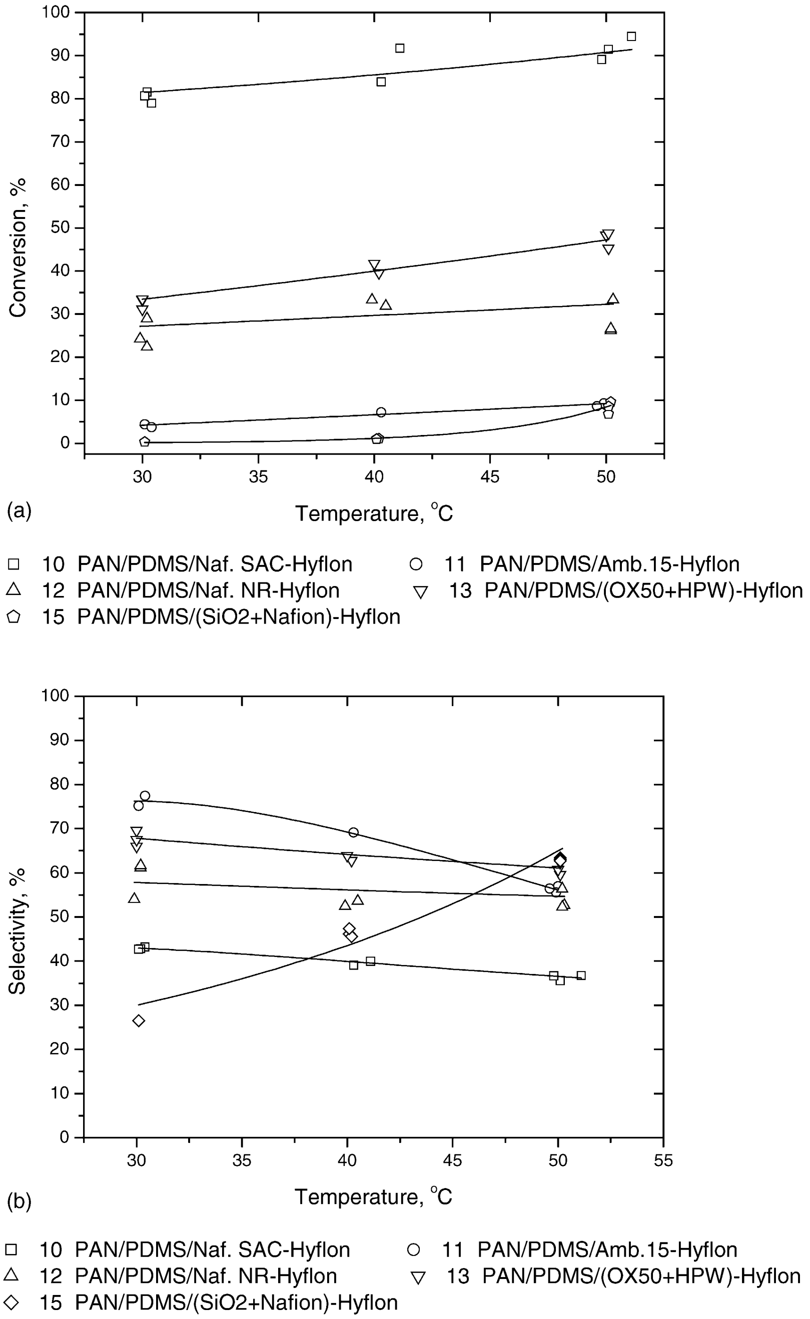


Fig. 5. Conversion (a) and selectivity (b) of isobutene dimerisation as a function of temperature for membranes with various catalysts and Hyflon AD as binder (flow rate = 100 ml/min, nos. 10, 11, 15; 20 ml/min, no. 12; 40 ml/min, no. 13).

conversion (no. 15, PAN/PDMS/SiO_2 + Nafion®) or decreasing conversion with increasing SV (no. 11, PAN/PDMS/Amberlyst). The selectivity change with increasing SV is in the opposite direction to the conversion for these two membranes.

3.4. *Effect of binder*

The influence of binder type on the product composition of isobutene dimerisation is further analysed. The most promising catalyst, Nafion® SAC, was selected to test the binder influence on the membrane reactor performance. Four different polymers were utilised as the binder. No flow regulating, intermediate PDMS layer was present.

3.4.1. *Effect of temperature to various binders*

Isobutene conversion and isooctene selectivity dependence on temperature is depicted in Fig. 7a and b. The conversion increases steadily with temperature starting from

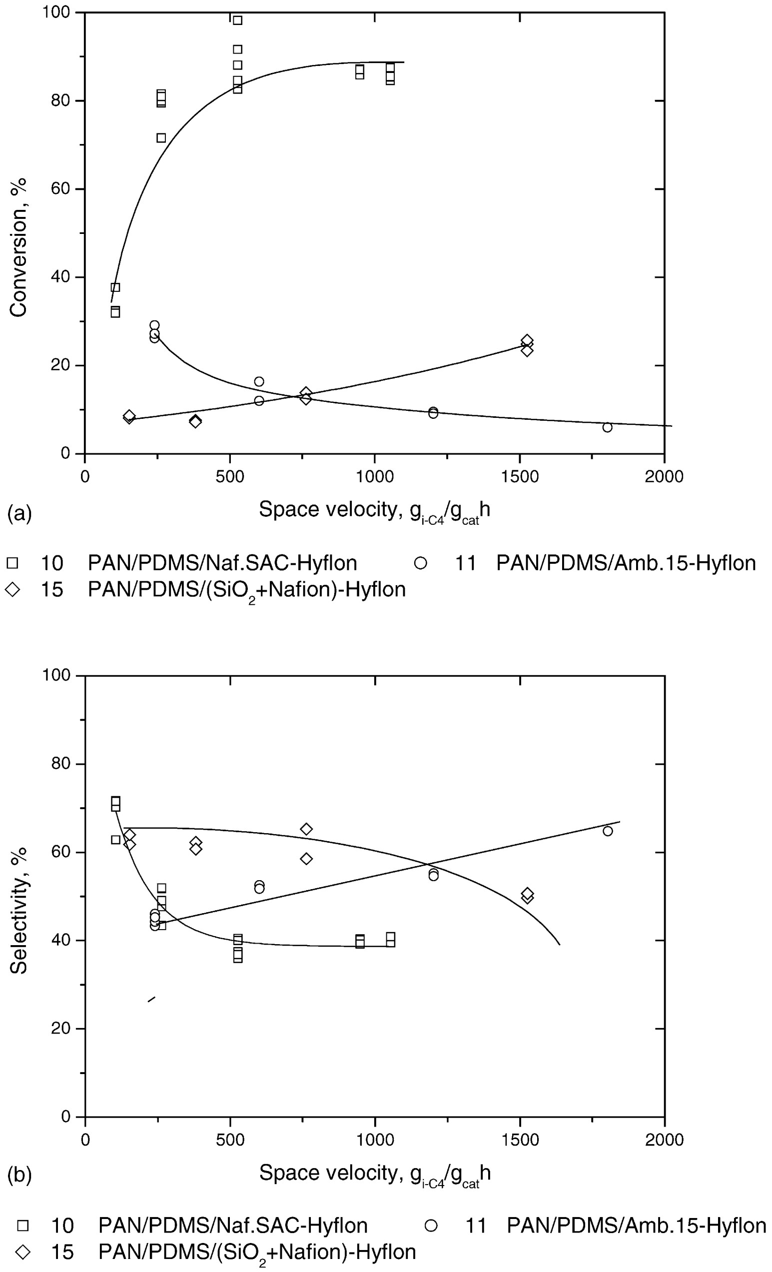


Fig. 6. Influence of space velocity on conversion (a) and selectivity (b) of isobutene dimerisation for membranes with various catalysts and Hyflon AD as binder at 50 °C.

different levels. For the membrane with the catalyst particles bound by Hyflon AD the conversion increases from 70 to 85%, with PTMSP from 25 to 40% and PDMS from 65 to 80%. The membrane with Teflon AF as binder, compared to the other membranes, has much lower conversion of 5% at 30 °C but increased to 45% at 50 °C. The selectivity decreased in all cases with temperature (Fig. 7b). Hyflon AD and PDMS as binder of the membrane have very similar selectivity decreasing from 55 to 45%. The highest selectivity exhibits the PTMSP bound membrane that is about 90% at 30 °C and about 80% at 50 °C. Teflon AF as a binder yielded 85% selectivity at 30 °C and only 60% at 50 °C.

3.4.2. Effect of space velocity to various binders

The influence of space velocity change on both isobutene conversion and isooctene selectivity was investigated. The space velocities were increased by increasing isobutene feed flow rate from 10 to 150 ml/min. The dependencies are plotted in Fig. 8a and b for the conversion and selectivity, respectively.

A similar behavior was found for the binders Hyflon AD and PDMS (Fig. 8a). With decreasing SV (∼500 g_{i-C4}/g_{cat} h) the conversion decreased sharply from ∼85–90 to 45%. Teflon AF as binder resulted in no change in conversion (SV could only be varied from 360 to 80 g_{i-C4}/g_{cat} h). Due to membrane properties, the SV of the

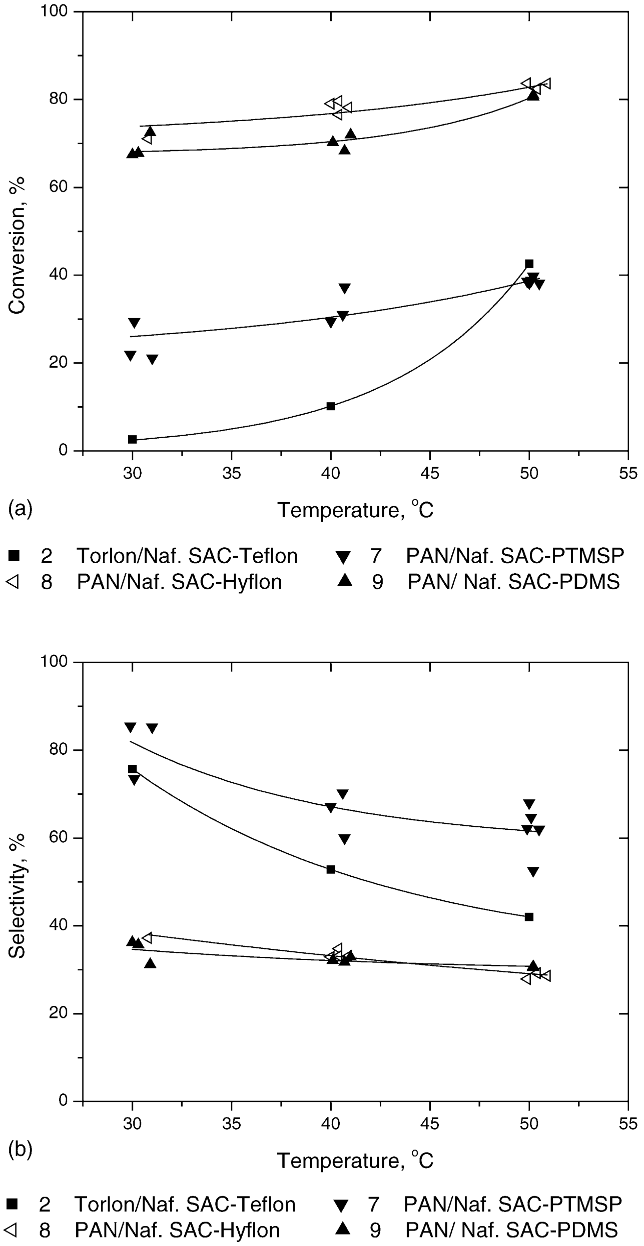


Fig. 7. Conversion (a) and selectivity (b) of isobutene dimerisation as a function of temperature for Nafion® SAC based membranes (flow rate = 100 ml/min, no. 8, 9; 50 ml/min, no. 2; 24 ml/min, no. 7).

PTMSP bound membrane could not be changed. The accompanied change in selectivity to the dimer (Fig. 6b) was increasing with decreasing SV for the Teflon AF (up to 80% at SV ~80 g_{i-C4}/g_{cat} h) and Hyflon AD (up to 60% at SV ~80 g_{i-C4}/g_{cat} h) bound membrane. The PDMS integrated catalytic membrane showed similar selectivities at all SV (~22%) with a slight maximum at SV ~500 g_{i-C4}/g_{cat} h, at which conversion decreased (see Fig. 8a). PDMS, in contrast to the other binders, is able to solve hydrocarbons to a high amount. We assume, that this solving/swelling balances the reaction conditions inside the pore system and reduces the conversion at low SV.

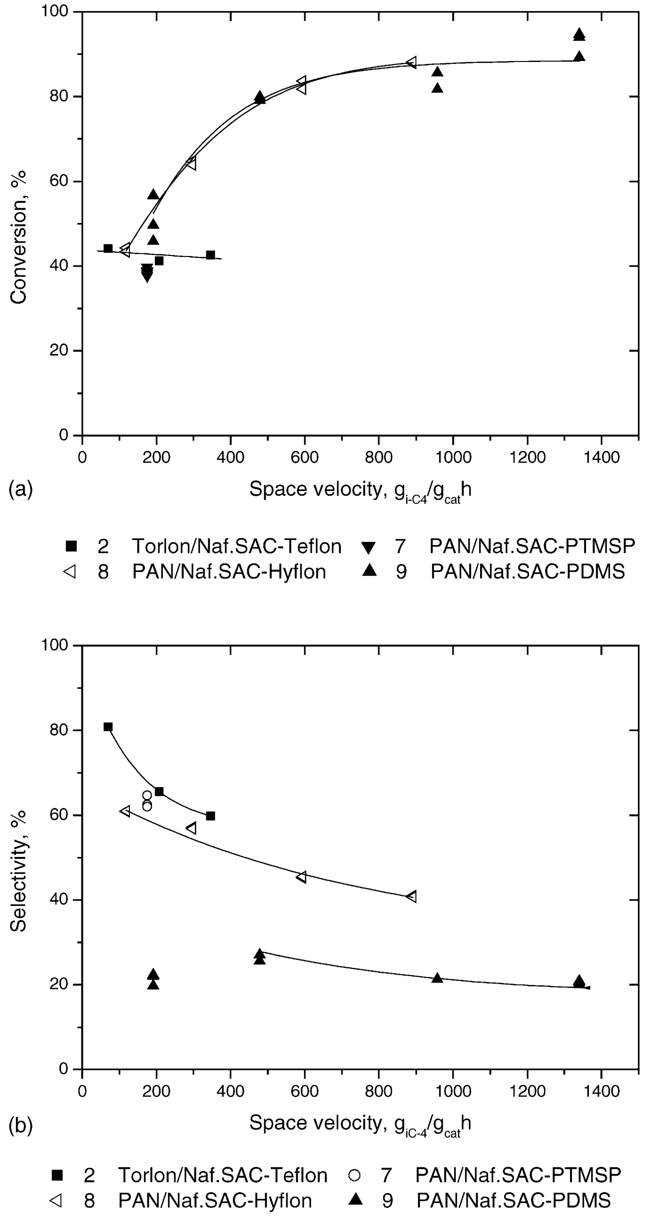


Fig. 8. Influence of space velocity on conversion (a) and selectivity (b) of isobutene dimerisation for Nafion® SAC based membranes at 50 °C.

3.4.3. Effect of an intermediate thin PDMS film

The influence of an intermediate PDMS film on the isobutene dimerisation product composition was investigated. The effect of a PDMS film was different on membranes with low and with high isobutene conversion at similar input flow of 100 ml/min and comparable SV. Low conversion was obtained with Teflon AF binder and high conversion with Hyflon AD binder.

In Fig. 9a and b is shown the influence of an intermediate PDMS film on the membrane properties at low conversion. From the graph it can be seen that a PDMS film placed between a low active catalytic layer and a substrate slightly improves both isobutene conversion and isooctene selectivity. Fig. 10a and b depict the effect of an intermediate PDMS

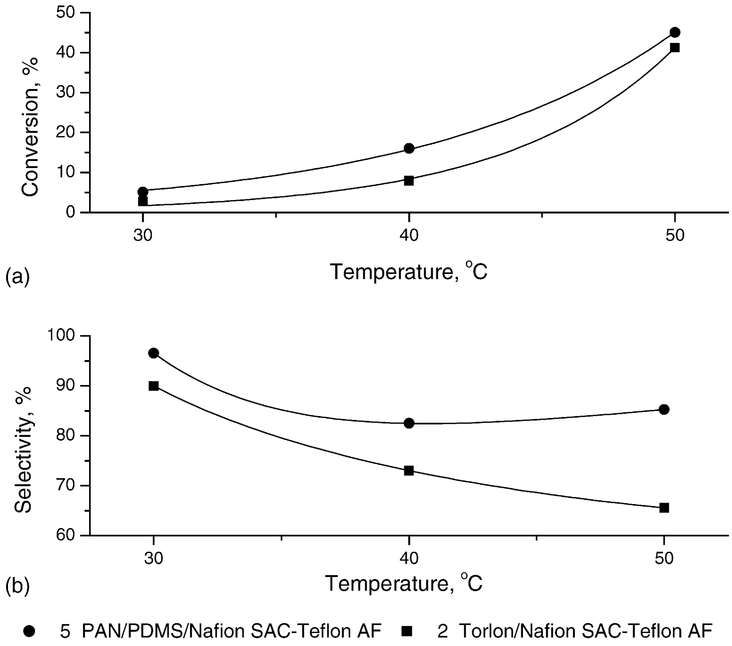


Fig. 9. Influence of an intermediate PDMS film on conversion (a) and selectivity (b) of isobutene dimerisation at low conversions (flow rate = 100 ml/min).

film at high conversion. The PDMS film placed between a highly active, catalytic layer and a substrate improves the isobutene conversion further but downgrades the selectivity to the dimer isooctene. The membrane no. 8 without PDMS intermediate film produced isobutene conversion increase from 70% at 30 °C to 80% at 50 °C, whereas the membrane no. 10 with PDMS film has increased conversion from 80 to 90% at the same temperature range. The slopes of the conversion and also the selectivity increase/decrease with temperature were similar.

Comparing Figs. 9a, b and 10a, b the applied membranes differ in binder and are utilised with or without intermediate PDMS film. The binder mainly provides high (Hyflon AD) or low (Teflon AF) conversion (Figs. 9a and 10a). A PDMS intermediate layer, however, affects the reactive membrane properties differently. With PDMS film at high or low

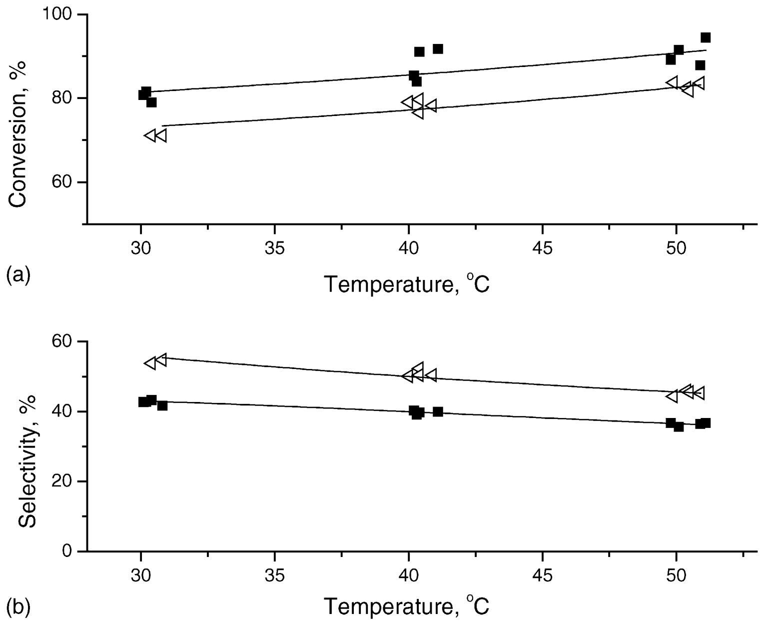


Fig. 10. Influence of an intermediate PDMS film on conversion (a) and selectivity (b) of isobutene dimerisation at high conversions (flow rate = 100 ml/min).

conversion an increase in conversion (Figs. 9a and 10a) was detected. However, with low conversion (Fig. 9a) the PDMS film improved selectivity, whereas with high conversion the PDMS film decreased selectivity (Fig. 10a). Because similar input flows of isobutene and SV were applied and also the pore system is equal the reason may be found in the PDMS properties. The filtration of a mixture of isobutene, dimer, trimer, and tetramer through a thin film composite membrane (PAN support, 1 μm PDMS) results in a preferential permeation of dimer, trimer (at similar rates) and tetramer in relation to isobutene which is enriched in the retentate [26]. We conclude, therefore, that the preferential transport of products produces a retroaction in the liquid reaction mixture inside the reactive pores. For membranes with already low conversion the selective product withdrawal results in an improved conversion (Fig. 9a) and selectivity (Fig. 9b). In case of already high conversion this effect cannot work, however, the flow inside the reactive pores of different sizes is equalised by the dense PDMS film and selectivity decreases.

3.4.4. Effect of particle size and uniformity of pores

Nafion® SAC-13 was received in the form of 1 mm extruded particles. The higher catalyst surface area was obtained by grinding the product using a ball mill over night and sieving with a sieve of 32 μm mesh size. In order to investigate the influence of catalyst size on the final catalytic membrane properties, two types of membrane were produced. One was prepared with ground Nafion® SAC-13, ground and sieved and the other was only ground. The catalytically active layer on the first type of membrane consisted of smaller, more homogeneous catalyst particles. The same amount of smaller particles has higher surface area than that of bigger ones. Additionally, the resulting pore system is more uniform with small, uniform catalyst particles. The conversion increases with temperature for the membrane with the sieved catalyst from 5 to 45% and for the non-sieved one from 1 to 20% at the temperatures from 30 to 50 °C. This result can be understood in the way that the smaller, more uniform pores of the reactive layer facilitate the overall reaction rate and result in improved conversion.

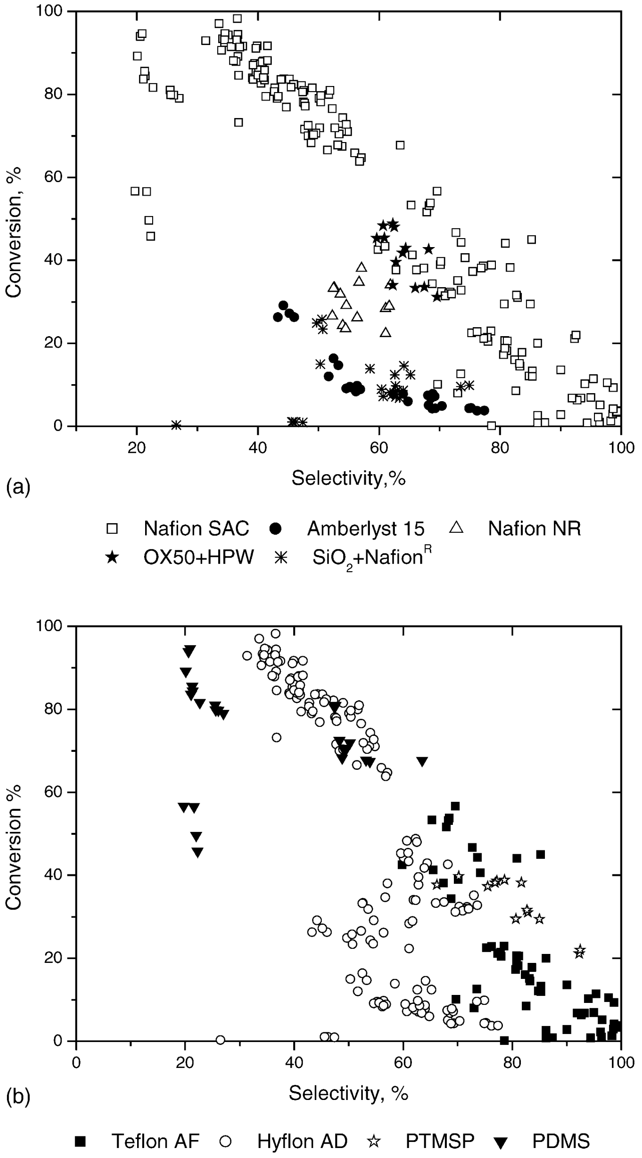


Fig. 11. Summarising graphs of catalyst (a) and binder (b) effect on conversion in relation to selectivity of isobutene dimerisation.

3.5. Summary of the catalyst and binder effects of various reactive membranes

An overview plot of the measured data in respect to selectivity and conversion is given in Fig. 11a and b. In Fig. 11a the selectivity to the dimer is plotted versus the overall conversion of isobutene for the applied catalysts. It is obvious, that the Nafion® SAC catalyst may deliver high selectivity at low conversion, or the reversed case, and additionally data in between. This can be adjusted by the parameters: catalyst particle size, type of binder, intermediate PDMS film, thickness of the reactive layer and of the PDMS film. Further on, the process parameters such as input flow and temperature also contribute significantly to the process performance. In the similar plot (Fig. 11b) the different catalysts were encased by four different binders to form the reactive layer. Here, the optimal binder can be selected from the graph, e.g., for high selectivity Teflon AF is most suited and allows acceptable conversion in one pass. If high conversion is required, then Hyflon AD may be selected but lower selectivity must be accepted.

3.6. Comparison of membrane reactor concept

Besides the numerous existing common and specifically developed reactor types membrane reactors may be regarded as another, however, specialised reactor. A direct comparison of membrane reactors to state of the art reactors is often difficult to perform. van de Graaf et al. [27] discussed the possibility of industrial application of zeolite membrane

Table 3
Summary of the results

Membrane no.	Catalyst	Polymeric binder	Pressure (bar)	Temperature (°C)	Conversion (%)	Selectivity (mol%)	SV[a] (g_{i-C4}/g_{cat} h)
10	Nafion SAC	Hyflon AD	3.5	50	90–98	34–43	500
9	Nafion SAC	PDMS	4.5	50	90–94	20	1300
9	Nafion SAC	PDMS	4.0	50	70	50	1000
13	SiO_2/HPW[b]	Hyflon AD	4.4	50	50	60	250
7	Nafion SAC	PTMSP[c]	3.7	30	22	86	175
5	Nafion SAC	Teflon AF	3.9	50	45	80	275

[a] Space velocity.

[b] Phosphotungstic acid.

[c] Poly(trimethylsilylpropine).

reactors and concluded, that in case of membrane reactors space time yield should be divided by the areal time yield (same as permeation flux) to obtain the area-to-volume ratio of the membrane reactor. This should give a realistic value to be compared to industrial reactors.

Piera et al. [3] compared a fixed-bed reactor and a zeolite membrane reactor. Both reactors worked at 15 bar in the liquid phase. The zeolite tube membrane reactor was filled with Amberlyst™ 15 catalyst and the zeolite tube was used for selective product removal. The membrane reactor was more efficient in respect to $i{-}C_4$ conversion and dimer selectivity. At 58 °C and space velocity of 53 g_{i-C4}/g_{cat} h the membrane reactor gave 95% conversion and 59% $i{-}C_8$ yield. A sweep gas of 90 L_N/h is necessary to selective product removal.

Torres et al. [13] used a tubular zeolite membrane with an area of 51 cm^2, an input olefin feed from 20 to 60 ml/min and calculated a WHSV of about 1 min^{-1}. The conversion increased from 15% at 50 °C to about 60% at 100 °C at a selectivity around 60%. With increasing reactant flow rate, a decrease in isobutene selectivity from 65% (20 ml/min) to <30% (60 ml/min) was found. The membrane reactor did not show deactivation compared to rapid deactivation of experiments with the same catalyst operating in a fixed-bed reactor.

In Table 3 are summarised our main results. The pressure drop is always around 3 bar, only. High conversions with lower or low selectivity, and lower but feasible conversions with selectivities up to 86% were achieved. The experiments could be performed in all cases at high to very high space velocities. These space velocities were achieved with a membrane area of 2.5 cm^2 only. Thus, also very high area-to-volume ratios were realised.

4. Conclusions

In this study was investigated the isobutene dimerisation utilising a forced-flow catalytic membrane reactor. Porous, catalytically reactive membranes were developed and characterised. Various catalysts and binders were employed to make an active, porous layer on the top of porous supporting membranes. Reactive, thin film composite membranes were achieved from these materials with a wide range of reactivity and product selectivity.

Scanning electron microscopy of the catalytic membranes showed the structure of a highly porous catalyst layer. Porosities of around 30–45% were detected. Although sieved, Nafion® SAC-13 particles were not of uniform size, which caused asymmetric structure when it was bound with Teflon AF, PTMSP and PDMS. In contrast, with Hyflon AD as a binder, symmetric structures result by applying the same catalysts. Also, the effect of binder on the acidity decrease is very low for Hyflon AD compared to Teflon AF and results in higher reactivity (conversion) of this type of catalysts. The dimerisation carried out in the membrane reactor, performed utilising various catalysts bound with Hyflon AD, showed the highest reactant conversion for Nafion® SAC-13 of 90% and the lowest for Amberlyst™ 15 based membrane of 10% at 50 °C and 100 cm^3/min flow rate. Nafion® SAC-13 provided much higher isobutene conversion, although its total acidity of 0.14 $mmol_{H+}/g_{cat}$ is much lower compared to that of Amberlyst™ 15 (3.8 $mmol_{H+}/g_{cat}$). Satisfactory results were obtained also with Aerosil OX-50 + HPW based catalytic membrane showing 50% conversion at the same reaction conditions. For all membrane types conversion increased and selectivity decreased with increasing temperature. Amberlyst™ 15 as a promising and already in use catalyst for dimerisation could not manufactured into membranes with a defined pore system and results are therefore hard to compare. The composite catalytic membranes used for isobutene dimerisation provide removal of the desired intermediate product isooctene, thus inhibiting secondary reactions to give trimer and oligomer compounds. In the membrane forced-flow reactor the by-products are purged from the catalysts active sites by the non-diffusive flow of educts and products before the reaction proceeds further. Therefore, catalyst deactivation by building up of higher oligomers cannot result and no catalyst deactivation is expected and not found within operation for 1 week.

In this work it is shown that attractive, new and simple to operate technologies can be designed in the field of isobutene dimerisation and are also expected to run for similar dimerisation or alkylation reactions. High to very high space velocities could be generated with these membranes. These are prerequisites for economically viable processes.

Acknowledgements

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