

Membranes and Catalysis

NCCR SECOND ANNUAL DAY

2nd August 2008

JOINT RESEARCHFELLOWS' WORKSHOP

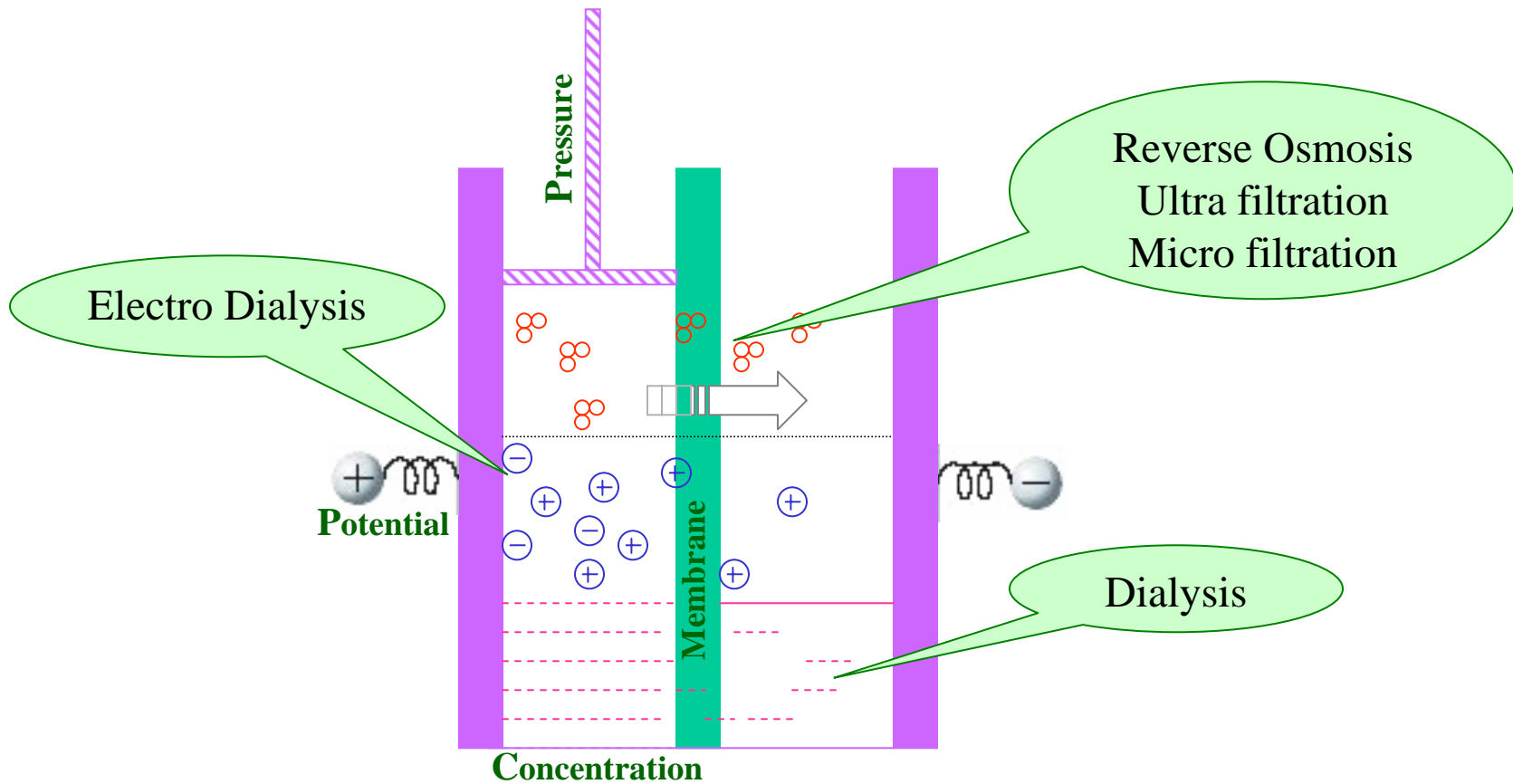


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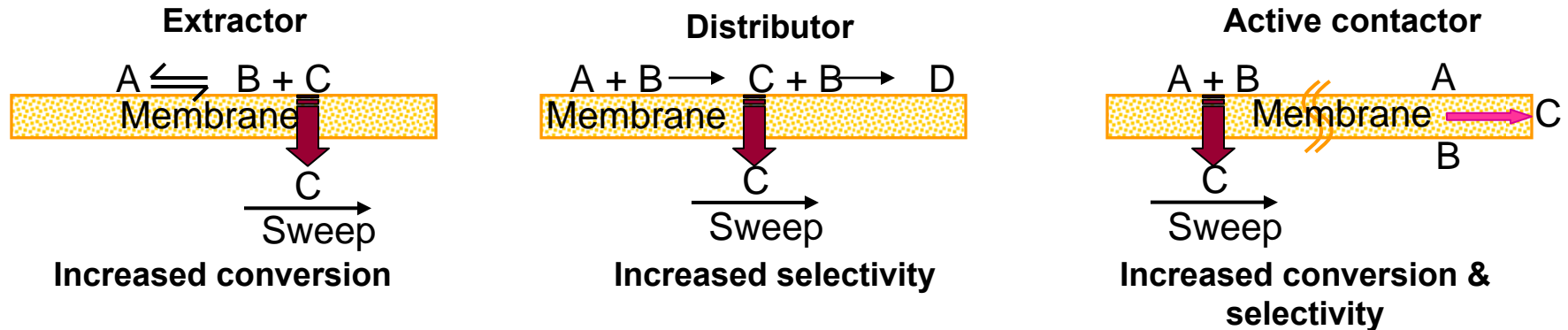


Schematic representation of membrane and processes therein





Membrane functions in a membrane reactor



Extractor mode

Alkane dehydrogenation - selectively extracts the hydrogen produced

Other H_2 producing reactions – water gas shift, steam reforming of methane & decomposition of H_2S & HI

Distributor mode

Partial oxidation
Oxy-dehydrogenation of hydrocarbons
Oxidative coupling of methane

Contactor mode - acts as a diffusion barrier & catalytically active

Forced flow-mode - Enzyme-catalyzed reactions
Oxidation of volatile organic compounds
Opposing reactant mode – Equilibrium & irreversible reactions
Partial oxidations

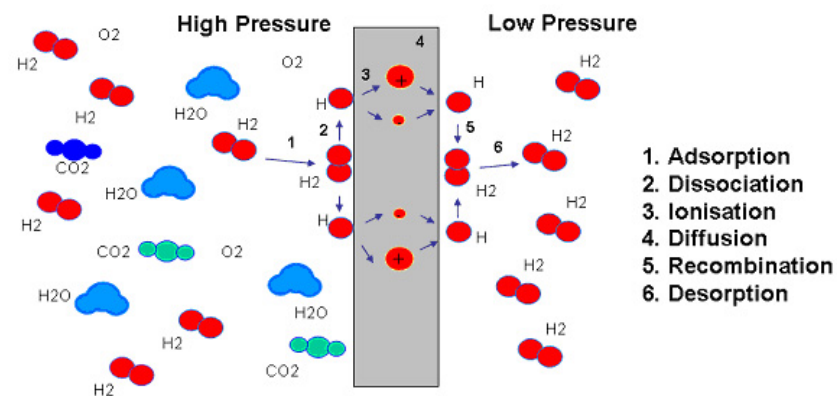
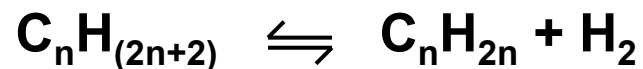


Inorganic membranes

- **Made from metals or ceramics**
- **Inert or catalytically active**
- **Either dense (Pd or Pd alloys, Ag, stabilized zirconia) or porous (Al_2O_3)**
- **Uniform in composition or composite, with a homogeneous or asymmetric porous structure**
- **Can be supported on porous glass, sintered metal, granular carbon or ceramics such as alumina**
- **Different membrane shapes can be used- flat discs, tubes (dead-end or not), hollow fibers or monolithic for ceramic membranes but also foils, spirals or helix for metallic membranes**
- **Specific surface/volume ratio for the reactor need to be maximized for industrial applications**
- **Low cost, resistant and efficient membranes for the process**
- **Membrane permeability - related to membrane structure (dense or porous) - defines the transport mechanisms through the membrane**



Dehydrogenation reaction



- Pd and Pd alloy membrane - Selective diffusion of hydrogen
Equilibrium shift
- Pd-Rh(15 wt %) membrane - Cyclohexanediol to pyrocatechol (95 % yield) & no phenol formation
- Pd-W-Ru (94:5:1) membrane - Dehydrocyclization of alkanes to olefins

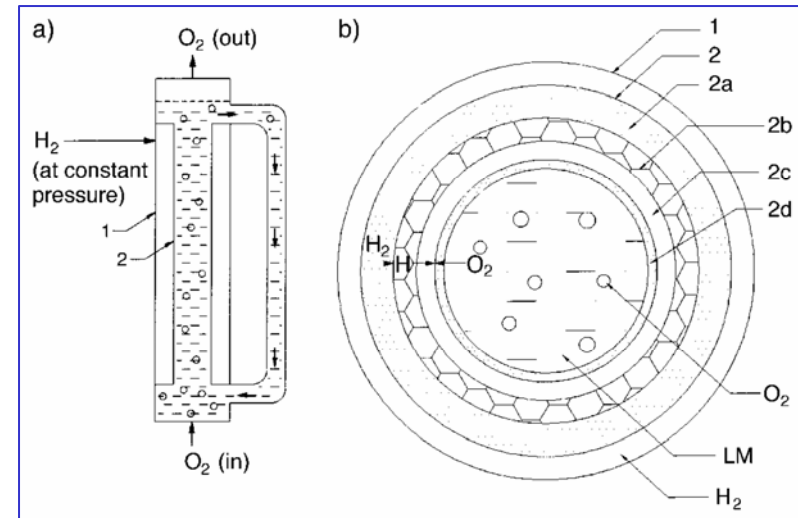
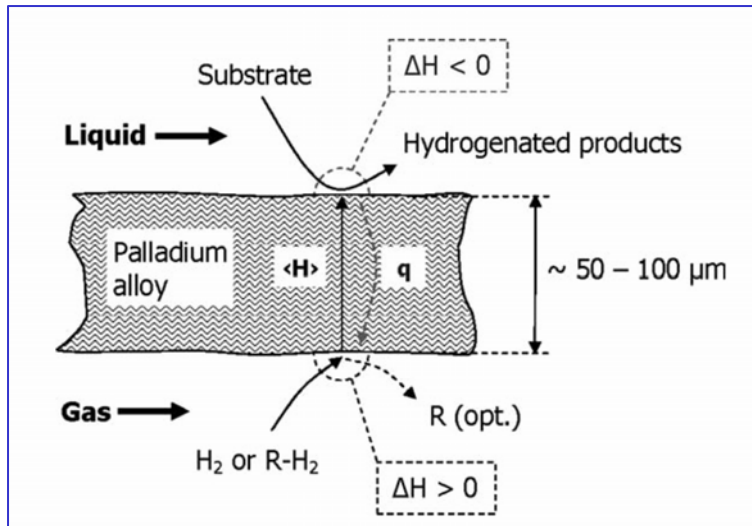
Disadvantages of Pd

- Cost, fabrication & durability
- Rate of diffusion of hydrogen relatively slow under operation conditions - very high membrane areas or very thin, and hence fragile, foils are in need
- Poisoning by impurities - Hydrogen diffusion in palladium depends palladium surface
- low melting point - low-temperature reactions

Tantalum or titanium offer some advantages over palladium



Hydrogenation reaction



- **200 spirals Pd-Ru(6%) - Linalool via the hydrogenation of dehydrolinalool**
- **100 μm Pd-Ru (90.2:9.8%) - hydrogenation of 1,3 cyclooctadiene at different hydrogen pressures (0.19 -16.2 MPa) and temperatures (626-746 °C) - yields of 83% cyclooctene with 94% selectivity**
- **100 μm Pd-Ru (92-97:8-3%) - aniline via the hydrogenation of nitrobenzene -participation of atomic hydrogen (as opposed to the dissolution of molecular hydrogen in a liquid medium) provides a 100-fold higher productivity**
- **Pd-Ag alloy/ γ - or α -alumina membrane - Oxidation of hydrogen to hydrogen Peroxide (50-70 % selectivity)**

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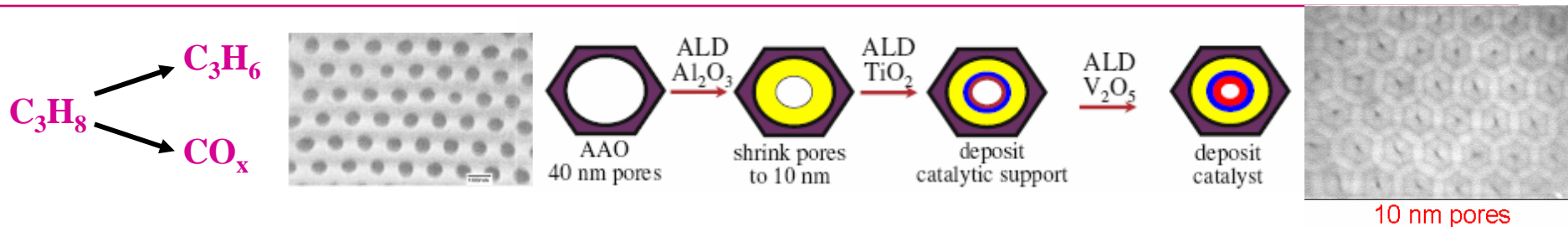
Meso- and microporous inorganic membrane materials

- **Alumina** – decomposition of methanol to formaldehyde - selectivity 15 % at 450°C 10 times higher than fixed-bed reactors
- **Vanadium modified Titania** – reduction of nitrogen oxide (side of the support) with ammonia (toplayer)-At low rates of nitric oxide, the conversion of nitric oxide – 100 % & the selectivity of nitrogen at 320°C - 75-80 %
- **V-ZSM-5 zeolite** – oxidative dehydrogenation of propane – propene (selectivity =40%)
- **LaOCl** - oxidative coupling of methane
- **RuO₂-TiO₂ and RuO₂-SiO₂** - oxidation of isopropyl alcohol
- **VMgO** - Oxidative dehydrogenation of propane
- **La based perovskites** - combustors of VOCs (toluene and methyl ethyl ketone)
- **VO_x/Al₂O₃/AAO** - Oxidative dehydrogenation of propane

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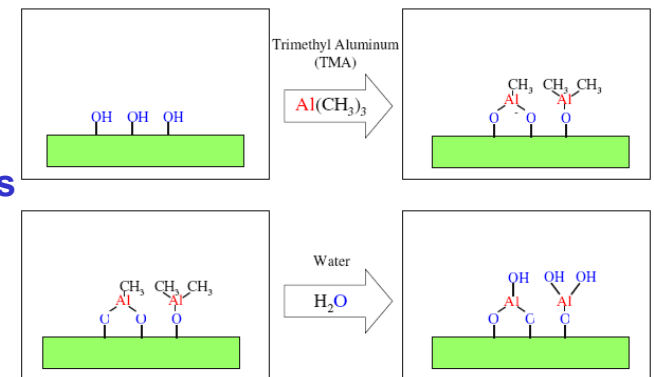
Oxidative Dehydrogenation (ODH) of propane



$VO_x/Al_2O_3/AAO$ membrane catalyst

- Higher selectivity to propylene than conventional VO_x/Al_2O_3 powder catalyst - 60 % vs. 25 %
- For membrane catalyst prepared by Atomic layer deposition
- ODH activity of propane increases as the VO_x loading increases
- Attributed to the formation of polyvanadates species (V-O-V bonds)
- The selectivity to propylene depends on

Atomic Layer Deposition (ALD)



- ✓ Amount of V- loading - 1 ML ALD (80 %) > 2 ML ALD (35 %)
- ✓ Method of Vanadium deposition - 2 ML incipient wetness impregnation (IWI) (63 %) > 2 ML ALD (35 %)
- ✓ Chemistry of the support - Al_2O_3 (80 %) > Nb_2O_5 (55 %) > TiO_2 (45 %)



Inorganic membranes

Advantages

- ✓ Long-term stability at high temperatures
- ✓ Resistance to chemicals (organic solvents, wide pH ranges, detergents, steam, etc.)
- ✓ Mechanical stability up to high pressure drops (> 30 bar)
- ✓ Stability to microbial degradation
- ✓ Long lifetime
- ✓ Easy cleanability (steam sterilization allowed, high back flushes can be used to reduce fouling)
- ✓ Catalytic activity is relatively simple to be promoted
- ✓ High throughput fluxes are attainable when operating with high pressure drops

Disadvantages

- X High capital and repair costs
- X Brittleness (special handling procedures and supporting systems are needed)
- X Low surface area to module volume ratios feasible
- X High selectivities available only on a few laboratory-scale membranes
- X Membrane sealing into modules difficult at high temperatures



Catalytic polymeric membranes

- For the membrane-assisted processes, a much wider choice of polymeric membranes is mostly available to select the most appropriate form, as compared with metallic or ceramic membranes
- The technology to manufacture polymeric membranes is generally much better developed already than the one for inorganic and metallic membranes
- The operation of the polymeric CMRs at relatively low temperatures is also associated with less stringent demands in sealing
- Nano-ordered composite materials consisting of organic polymers and inorganic compounds attracted attention for their use in creating high performance polymeric materials



Polymer Selection

- **Mechanical, thermal & chemical stability under reaction conditions**
- **Resistant to high temperature, aggressive solvents & oxidative conditions**
 - e.g) Nafion and poly-(dimethylsiloxane) (PDMS) - fine chemical synthesis or catalytic water treatment**
- **High catalytic loading without brittleness of the films**
- **Good adhesion to the filler**
- **Excellent film forming properties**
- **Good transport properties - reagents and products**



Permeability and Permselectivity of polymers

Physicochemical factors influencing

- 1) The mobility of polymer chains
- 2) The intersegmental spacing, which is taken as a measure of the mean free volume of the polymer, &
- 3) The penetrant polymer interactions

Rubbery polymers - high permeability & low selectivity

Glassy polymers - high selectivity & lower permeability- **industrial interest**

High permeability and selectivity - chain stiffness coupled with an \uparrow in interchain separation

- ✓ Bulky side groups in glassy polymers - polysulfones, polycarbonates, polyarylates & poly(2,6-dimethyl-1,4-phenylene oxide)
- ✓ Silyl-modified polysulfones and poly(phenylsulfone)s - trimethylsilyl, dimethylphenylsilyl, diphenylmethylsilyl - \uparrow in free volume and transport properties
- ✓ Aromatic polyamides - direct polycondensation with 4,4'-hexafluoroisopropylidene-dibenzoic acid various aromatic diamines - \uparrow in specific volume



Polymers with high potential for application

Membrane Material	Application
CA: cellulose acetate	RO, UF, MF, D, GS
CTA: cellulose triacetate	RO
CN: cellulose nitrate	UF
PE: polyethylene	PV, GS
PVC: poly(vinyl chloride)	MF
PVDF: poly(vinylidene fluoride)	UF, MF, ED
PTFE: polytetrafluorethylene	MF, ED
PAN: polyacrylonitrile	D, UF
PMMA: polymethyl methacrilate	D
PVA: poly(vinyl alcohol)	D, PV
PP: polypropylene	MF, MD
PMP: poly(methyl pentenal)	GS
PET: poly(ethylene terephthalate)	MF

Membrane Material	Application
PBTP: poly(butylene terephthalate)	GS
PC: polycarbonate	D, MF
PDMS: polydimethylsiloxane	GS, PV
PTMSP: polytrimethylsilyl propyne	GS
Psu: polysulfone	UF
PESu: poly(ether sulfone)	UF
PPO: poly(phenylene oxide)	UF, GS
PA: polyamide	UF
PEBA: poly(ether block amide)	PV
PEI: poly(ether imide)	GS
PAI: poly(amide imide)	GS, UF
PPN: polyphosphazene	GS, PV
PEEK: poly(ether ether ketone)	GS

Reverse Osmosis **RO**, Ultrafiltration **UF**, Microfiltration **MF**, Dialysis **D**, Pervaporation **PV**, Gas separation **GS**



Selected catalytic membranes and catalytic reactions performed

Catalyst–membrane material	Reaction
PVP–Pd/CA, PVP–Pd/PAN, EC–Pd/CA, AR–Pd/CA	Hydrogenation of cyclopentadiene
Mono- and bimetallic polymeric fibers	Hydrogenation of butadiene in 1-butene
Pd–PVP/CA	Partial hydrogenation of alkines
Pd/Polymethyltetracyclododecene	Hydrogenation of ethylene and propylene
PdPVDF ₂₀ PVP ₁₀ , PdPVDF ₂₀	Hydrogenation of methylene–cyclohexane
Pd, Ag/PAl _s , Pd/Ag	Reduction of nitrous oxide
H ₃ PW ₁₂ O ₄₀ /PPO/Al ₂ O ₃	MTBE decomposition
Nafion SAC-13/Teflon/PDMS	Dimerisation of isobutene
HPA-PVA	Dehydration of ethanol
PAN-PSSA, PVA-PSSA	Pervaporation aided esterifications

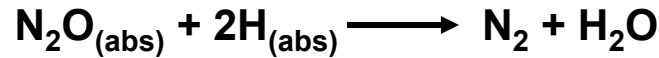


Hydrogenation

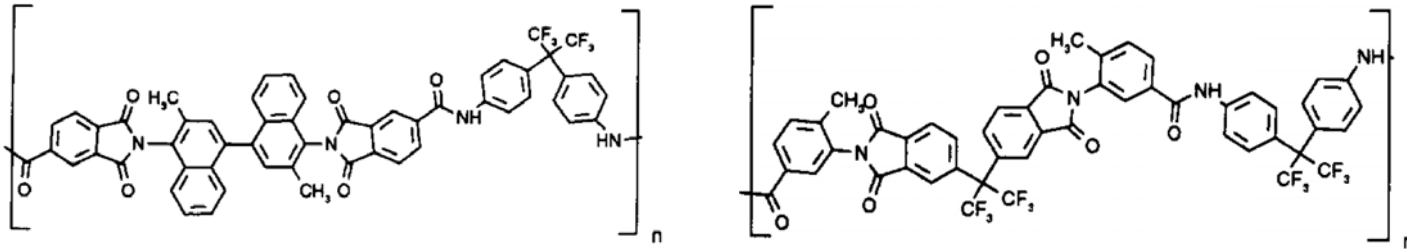
- **PVP–Pd/CA and PVP–Pd/PAN hollow fibers** - Selective hydrogenation of cyclopentadiene (91% conversion) under mild conditions of 40 °C and 0.1 MPa
- **CMR setup** diene at the inner side of the fiber and H₂ permeating from the outer side, conversion & monoene selectivity is higher than 90% - impossible in a fixed bed reactor
- The catalytic results depended strongly on the polymer type used to prepare the hollow fiber and also on the one used to anchor the metal (PVP > EC & AR)
- **PVP–Pd, EC–Pd or AR–Pd and PVP–Pd–0.5Co(OAc)₂** - purification of 1-butene using butadiene as model impurity
- **Complexity of the process** - over hydrogenation of 1-butene to butane, 2-butene may be formed by the isomerization of 1-butene or 1,4-addition of butadiene in the hydrogenation
- **Bimetallic hollow fiber** - isomerization of 1-butene was inhibited & the synergic effect of bimetallic catalyst was significant
 - using NaBH₄ instead of hydrazine lead to small Pd clusters deposited on superfine cobalt boride particles



Reduction of nitrous oxide



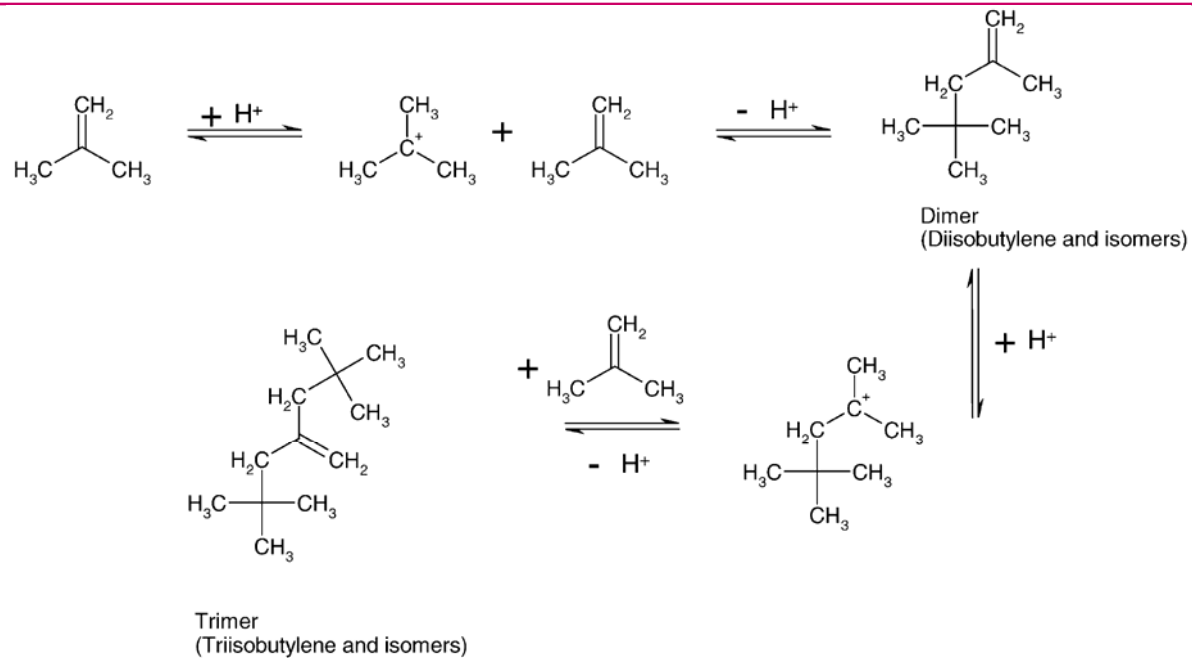
- Two catalytically active polymeric membranes containing 15% Pd/Ag (77/23)
- Poly(amide imides) consisting of structures with moieties of 3,3'-dimethylnaphthidine and hexafluoroisopropylidene (6F) or hexafluoroisopropylidene-2,2-bis(phthalic acid anhydride) (6FDA)



- Polymers exhibit very high gas permeability and high selectivity
- The composition of the feed gas mixtures varied in $\text{N}_2\text{O}/\text{H}_2$ from 1/5 to 1/1 v/v; diluting gas were He, Ar, or CH_4
- With H_2 of at least molar ratio to N_2O in the feed gas, no N_2O was detected in the permeate, the reaction products H_2O and N_2 were detected in the permeate
- When turning of H_2 , N_2O was identified in the permeate.
- Membranes were found to be successful for decomposition of N_2O by hydrogen



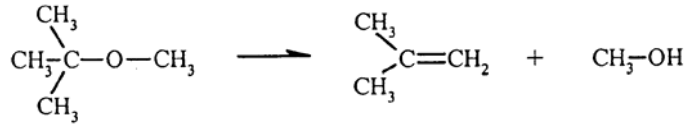
Dimerisation of isobutene



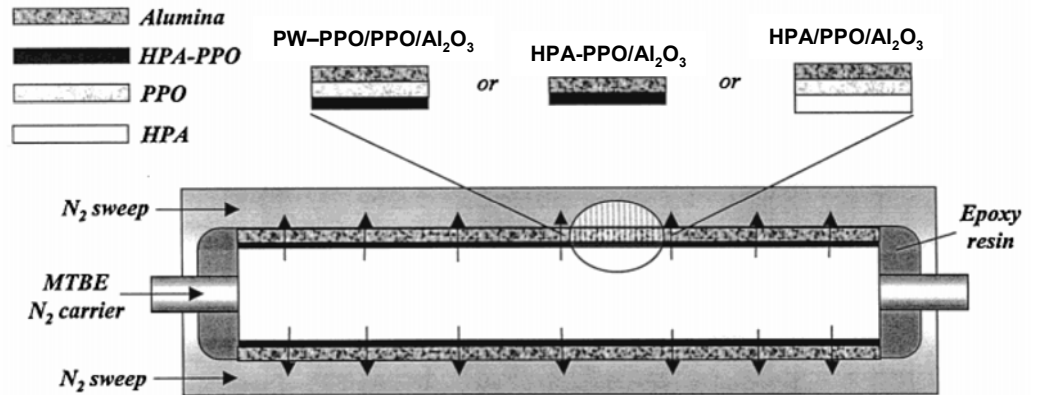
- Problems - low selectivity, conversion & catalyst poisoning by-products such as diolefins or acetylene
- Polymers (PAN, PDMS) with Nafion SAC-13, Amberlyst™ 15 & silica supported phosphotungstic in various composition –for dimerisation of isobutene to isooctene
- PDMS film acted as flow regulator and enabled selective product removal
- No poisoning by generation of oligomers and polymers & not found within operation for a week
- Catalytic membranes provide removal of isooctane, thus inhibiting secondary reactions
- For all membranes tested with \uparrow temperature the conversion \uparrow but selectivity \downarrow
- Silicon film makes double effect: selectivity is higher - isooctene passes through it faster than isobutene & conversion is higher -the residence time of isobutene is longer



MTBE decomposition



MTBE synthesis and the decomposition - reversible and acid-catalyzed reaction



- Performances – **PWA-CA** CMRs(7%) > fixed bed reactor
- Selective removal of methanol - equilibrium shift
- Polyphenylene oxide (**PPO**)/ $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalytic membranes coated on PPO separative layers is superior than **HPA-PPO** coating or an **HPA layer on top of a PPO** coating (60–62% isobutene selectivity)
- Perm-selectivity - **PW-PPO** catalytic membrane and the sub-layered PPO membrane.
- PPO - superior membrane polymer in comparison with PSf, CA, poly(carbonate) & poly(arylate)
- To verify the selective removal of methanol - a closed loop recycling reaction was carried out in the **PW-PPO/PPO/Al₂O₃** catalytic membrane reactor
- MTBE conversion & isobutene selectivities in the tube side - increased with increasing recirculation time
- Equilibrium shift in the membrane reactor
- **PW-PPO/PPO/Al₂O₃** & bulk PW - reaction species in the CMR have higher mass transfer resistance than fixed bed reactor



Dehydration

- **HPAs** - acidic and redox catalytic properties
- Characteristic adsorption behavior - nonpolar chemicals are adsorbed only on their surface
- polar chemicals penetrate into the bulk to form pseudoliquid phase
- **PSf - $H_3PMo_{12}O_{40}$** - DMF as the casting solvent
- 2-propanol was permeated as a gas through the catalytic membrane
- Two competing reactions - an acid catalyzed dehydration to propylene &
- an oxidative dehydrogenation via a redox mechanism to acetone
- DMF sorbed strongly on the acidic sites of the HPA, thus greatly decreasing the propylene formation
- The incorporated catalyst was much more active in the formation of acetone due to the enlarged active surface
- The large surface was created by the uniform and fine distribution of the HPA in the PSf
- Twice as high permeability of the membrane for acetone than for propylene was suggested to further increase the selectivity for acetone
- **15-fold increase** of the acetone/propylene ratio as compared with a reaction in a fixed bed with unsupported HPA

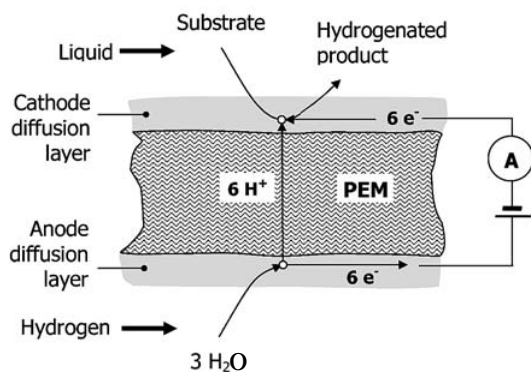


Dehydration of ethanol

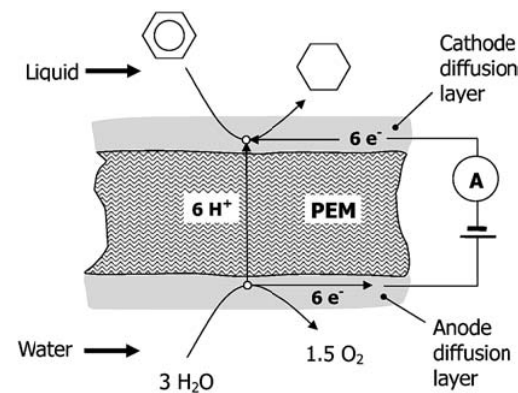
- **PVA-HPA** dehydration of ethanol coupled to a PSf membrane to remove the produced vapors.
- Selectivity for ethylene - **7 times higher** than that for a fixed bed reactor.
- Ascribed to the greater ethylene permeability ($2 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, ethanol and diethylether 6×10^{-9} & $3.2 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ respectively)
- Less permeable compounds ethanol and diethylether were retained and could thus readsorb into the bulk of the HPA to be converted to ethylene.



Catalysed hydrogenations performed on solid polymer electrolyte membranes



Liquid phase hydrogenation driven by electrochemical hydrogen pumping through PEM

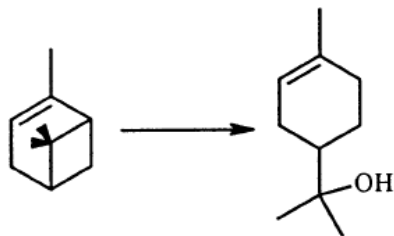


Liquid phase hydrogenation of benzene combined with water electrolysis to supply the required hydrogen

- PEM - Dense membrane needs high productivity, sufficiently large catalyst surface area & an efficient contact between the membrane, the fluid phases and the active catalyst
- Electrodes on both sides - enable the desired electrocatalytic reactions & good electronic conductivity
- Electrode/membrane interface - ion conducting material (e.g. Nafion), an electron conducting material (e.g. carbon) and an active catalyst (e.g. Pt or Pt/Ru)
- Fuel cells - Catalytic membrane layers in connection with multiphase reactions
- Rh-Pt/Nafion 117/Pt - hydrogenation of benzene to cyclohexane and its coupling to water electrolysis
- Ag/Nafion 117/Pt - benzaldehyde to benzyl alcohol coupled with water electrolysis (~100% selectivity)



Acid catalysed Hydration of α -Pinene to α -terpineol



- **PVA-PMA** crosslinking with succinic acid and acetic anhydride in order to modulate the hydrophilic/hydrophobic properties of the catalytic membranes
- Acetic anhydride modified the transport and sorption properties of polymeric catalytic membranes consisting of HPMo entrapped in PVA crosslinked with succinic acid
- The catalytic activity of the PVA membranes is strongly affected by membrane acetylation
- Selectivity to the desired product α -terpineol achieves its maximum value for the most acetylated membrane
- Increased catalytic activity - improvement of membrane water transport
- **PDMS - ultrastable zeoliteY, zeolite β** as catalysts membranes
- Filled and unfilled membranes, incorporation of zeolites lead to a reduced swelling
- cross-linking of the zeolite
- α -terpineol-selectivity ascribed to particle size (from 10 to 20 μm) and water sorption of the catalysts



Applications of pervaporation for chemical reactions

Esterification processes- both inorganic and polymeric membranes have been used to increase the yield using pervaporation

For PV-membrane-based reactive separations, the membrane either removes the desired product or the undesired product (water for esterification reactions)

Pervaporation enhanced reactors are expected to provide a promising alternative

1. PV is a rate-controlled separation process, and the separation efficiency is not limited by relative volatility
2. In PV only a fraction of feed that is permeated by membrane undergoes the liquid- to vapor-phase change & energy consumption is generally low
3. PV can be operated at the optimal temperature for reaction

Hybrid process- PV-distillation & PV-reaction hybrid processes found industrial applications

Catalyst/membrane material	Reaction
PSSA/PAN, PVA	Propanol and propionic acid esterification
PVA/PAA-Zr(SO ₄) ₂₄ H ₂ O	N-Butyl alcohol-acetic acid esterification
H ₃ PW ₁₂ O ₄₀ /PVA	N-Butyl alcohol-acetic acid esterification
PEBA-Pd	Hydrogenation of 4-chlorophenol

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Major challenges in the development of membrane reactors

Materials science

- Synthesizing defect-free and homogeneous membranes having pores of molecular dimensions ($< 10 \text{ \AA}$)
- Reducing the membrane thickness ($< 10 \text{ \mu m}$)
- Reproducing the above results on large scale membranes
- Working out reliable, quick, non-destructive analysis techniques to measure pore diameters $< 10 \text{ \AA}$
- Improving membrane resistance to temperature and thermal fatigue
- Addressing problems of brittleness for both ceramic and Pd alloy membranes
- Improving chemical stability of polymer/inorganic membranes
- Developing relatively cheap high-temperature sealing systems
- Reducing membrane initial and replacement costs

Catalysts science

- Developing new membrane catalysts less sensitive to poisoning or coking
- Getting a better reproducibility & predictability of the catalyst performance (especially for Pd alloys)
- Getting a better control of the catalytic activation

Chemical engineering

- Understanding and modelling highly selective transport mechanisms
- Increasing the membrane area per unit volume
- Developing complex modelling for large-scale membrane reactor modules
- Developing technologies for heat supply and temperature control in large-scale modules
- Finding alternative solutions to eliminate the use of large amounts of sweep gas
- Developing criteria for the choice of the optimal size of membrane reactors, of the flow patterns and of the number of stages/recycles/intermediate feeds



Concluding Remarks

- **The multidisciplinary nature of the CMRs is manifest and makes it a challenging but difficult domain**
- **Three major fields of research are necessary to be mastered for the successful development and operation of CMRs: catalysis, membrane technology, and reactor engineering**
- **Developing new concepts or improving the existing ones is therefore more than just selecting the best of each field: it is the challenge to pick in each field those that will lead to the best possible combination**



THANK YOU
