Membrane reactor operating at high selectivity and substantially increased productivity for the oxidative dehydrogenation of ethane

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Outline

Process intensification aims on enhancing rates at least tenfold introducing suitable chemical engineering measures.

The example of a catalytic membrane reactor illustrates how employing structured reactors can enable substantial performance gains operating "a different kind of catalysis".

- **Motivation for oxidative dehydrogenation of ethane.**
- **Development of a laboratory membrane reactor.**
- **Performance in C_2H_6 activation over structured catalysts**
- **Conclusions and perspectives.**

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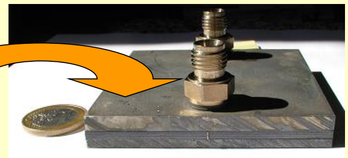
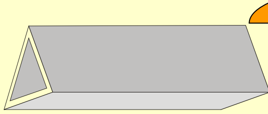
Some examples of structured reactors

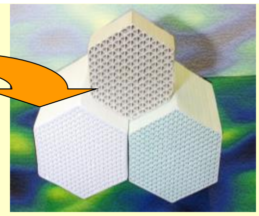
Structured reactors might lift many constraints in heterogeneous catalysis

- **Micro-structured devices:**



- **Monolith reactors**





However, catalyst stability remains the key in “intensified” systems.

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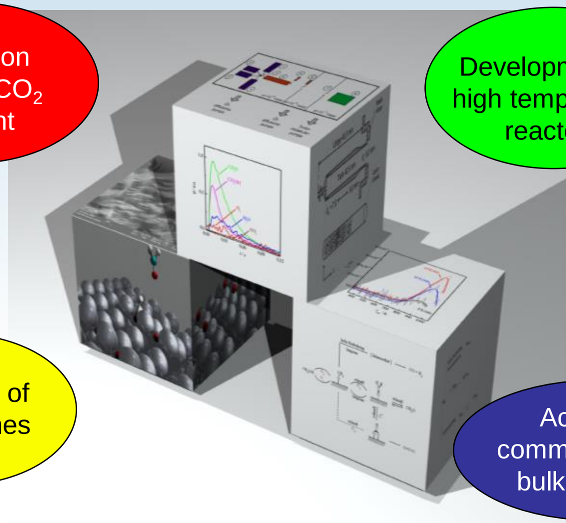
Interdisciplinary approach



Production with low CO_2 footprint

Development of high temperature reactors

Activation of light alkanes

Access to commodities and bulk chemical

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Upgrading of ethane to ethylene

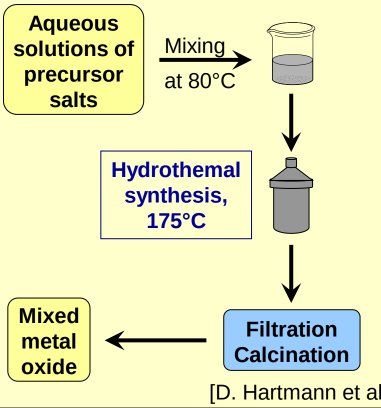
- **Context:**
  Shale gas brings access to C_{2+} hydrocarbons at sites remote from current cracker infrastructure.
- **Inconvenience:**
  Conventional steam cracking is energy intensive and optimized for very high capacities.
- **Approach:**
  Implementation of oxidative dehydrogenation of ethane as continuous smaller scale source of ethylene.
- **Challenge:**
  Suitable catalysts, reactor and process concepts need development.

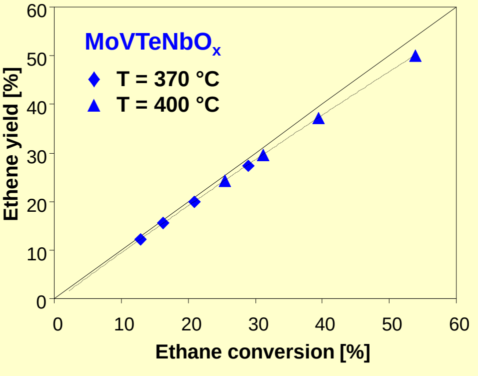
[Review: C.A. Gärtner et al., ChemCatChem **5** (2013), p. 3196.]

MoVTeNbO$_x$ catalysts (M1 phase)

Low temperature catalyst system

- The oxidative dehydrogenation of ethane with molecular oxygen over $MoVTeNbO_x$ proceeds at high selectivity
- What are the catalyst properties leading to the outstanding performance?

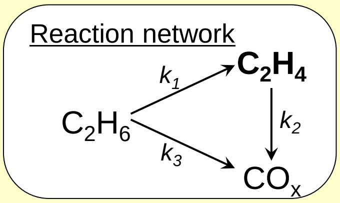


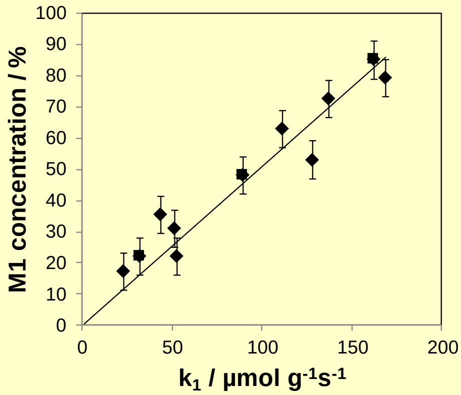


[D. Hartmann et al., 15th ICC (2012), Poster 2.02_8004 / Talk PS.02.]

Catalytic activity of the M1 phase

- Direct dependence of the rate constant on the M1 phase concentration through origin
- k_1 represents the rate constant of ethene formation
- T = 370 °C



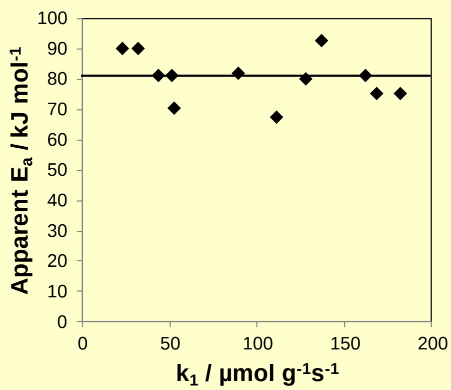


- **Catalytic activity originates solely from M1 phase**
- **Literature advances amorphous layers as active sites, but this must then be linearly related to the M1 phase**

$MoVTeNbO_x$ catalysts (M1 phase)

Apparent activation energy

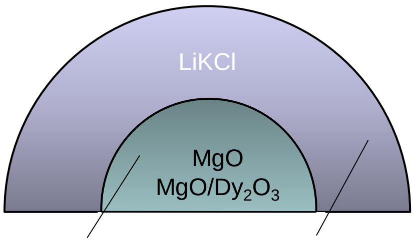
- Apparent activation energy for ethene formation is constant for various catalysts providing different rates
- E_a = 80 ± 10 kJ/mol
- k_1 represents the rate constant of ethene formation

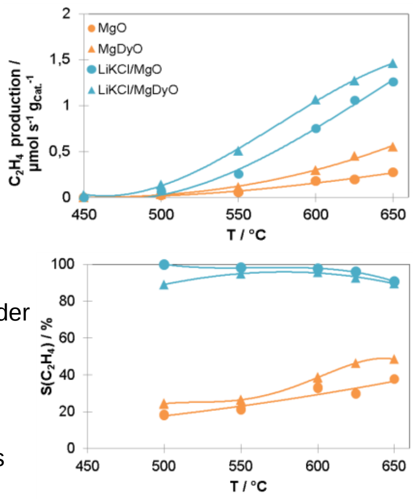


- **Similar M1 surface properties for all samples**
- **Upper temperature limit for reaction imposed by catalyst temperature stability (critical above 450°C)**

Supported alkali chloride catalysts

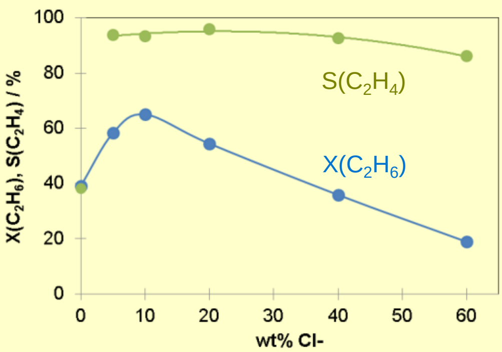
$2\ C_2H_6 + O_2 \rightarrow 2\ C_2H_4 + 2\ H_2O$





- The chloride overlayer is vital for the **activity** and the **selectivity**.
- 1 mol% Dy_2O_3 in the support increases the **activity**.

Influence of the overlayer thickness



- Conversion reaches **maximum** at 10 wt% Cl^- and **decreases with increasing chloride loading.**
- Ethene selectivity is enhanced by the presence of chlorides, but changes only modestly afterwards.

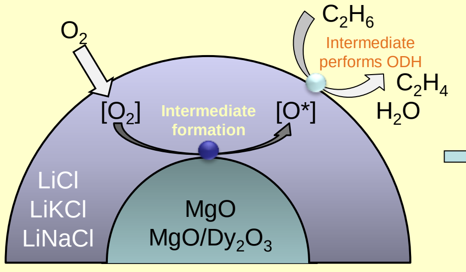
⇨ Overlayer plays an important role for reaction.

⇨ Decreasing activity with increasing layer thickness suggests transport influence.

LiKCl/MgDyO, T=600°C, WHSV = 0.8 h^{-1}, p_{ges} = 1 bar , $p_{Ethane} = p_{O_2}$ = 70 mbar

Solid core / molten shell catalysts

Reaction pathways for chloride catalysts



Spatial separation of oxidation and reduction sites.
Molten salt shell acts like an oxygen membrane

- Support has unselective sites and needs to be fully covered to achieve high selectivity.
- Chloride phase and/or interface stabilize and stores the oxidizing species.
- Ethane is not absorbed by the chloride layer, thus ODH step is assumed to take place on the surface.

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Catalytic membranes in selective oxidation

Catalytic membranes for oxidations

- **Context:**
  Atom efficient upgrading of light hydrocarbons could provide alternative feed-stocks for tomorrows chemistry.
- **Inconvenience:**
  Selective catalysts in fixed bed oxidative dehydrogenation (ODH) show reasonably low reaction rates.
- **Approach:**
  Dense catalytic membrane reactors suppress gas-phase oxygen enabling high catalyst selectivity and efficiency.
- **Challenge:**
  Need for membrane materials, reactor configurations, new catalysts and their thin film coating.

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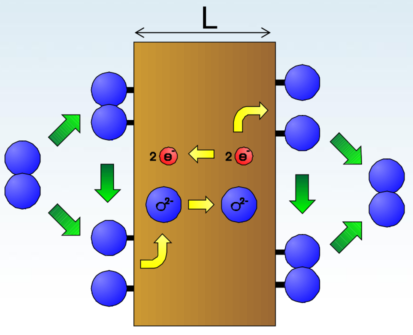
Catalytic membranes in selective oxidation

Transport through MIEC membranes

Porous membranes (at high T): “simple” viscous flow, Knudsen diffusion

Dense membranes: Complex scheme requiring multifunctional materials



1. Adsorption of molecular oxygen
2. Dissociation ?
3. Formation of oxygen ions
4. Diffusion of oxygen ions and electrons through the membrane
5. Formation of adsorbed oxygen
6. Recombination ?
7. Desorption of molecular oxygen

Each step might be a ”bottle neck”, Surface ≠ bulk transport kinetics. Thus, one needs to obtain information on each specific step.

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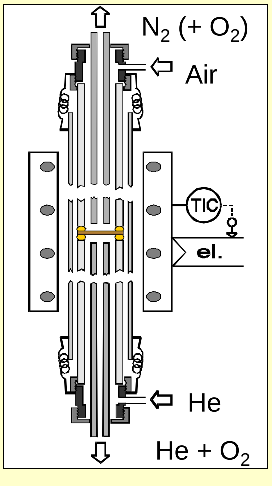
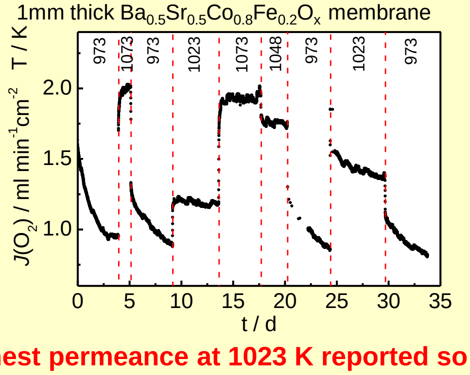
Catalytic membranes in selective oxidation

Permeation flux measurement



Feed Side : $F(O_2)$ = 10 ml min^{-1}, $F(N_2)$ = 40 ml min^{-1}
Permeate Side : $F(He)$ = 20 ml min^{-1}
1mm thick $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_x$ membrane



Highest permeance at 1023 K reported so far
Oxygen flux is not stable below 1023 K

[A.C. van Veen et al., Chem. Commun. **2003** (2003), p. 32.]

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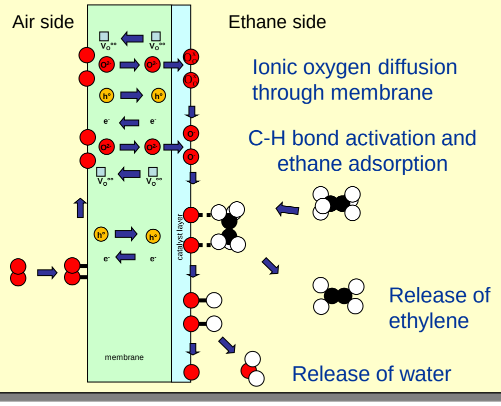
Catalytic membranes in selective oxidation

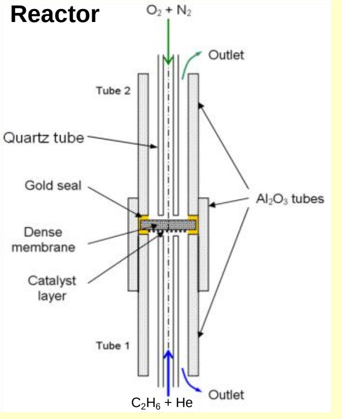
Oxidative dehydrogenation of C_2H_6

$$2\ C_2H_6 + O_2 \rightarrow 2\ C_2H_4 + 2\ H_2O$$

Ionic oxygen permeation and reaction



Reactor



Control of oxygen species and availability enhances selectivity.

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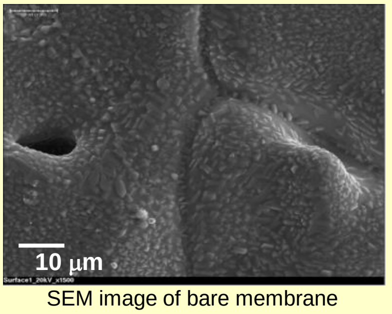
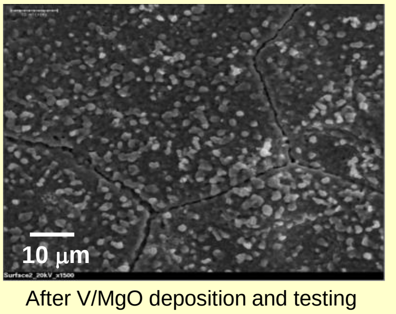
Catalytic membranes in selective oxidation

Catalytic modification by V/MgO

- Preparation by adapted Sol-Gel synthesis and spin coating
- Specific area (50 m²/g at 1075K)
- Direct coating of the membrane ensures best possible interface
- Well dispersed particles (coverage ≈ 40 %)



SEM image of bare membrane



After V/MgO deposition and testing

Catalyst inventory approximately 1mg per cm² of membrane.

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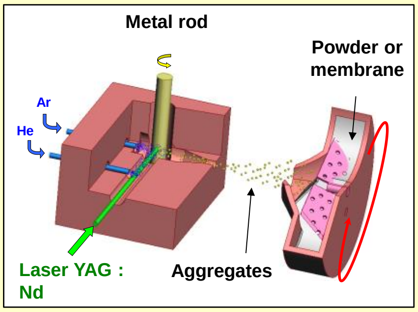
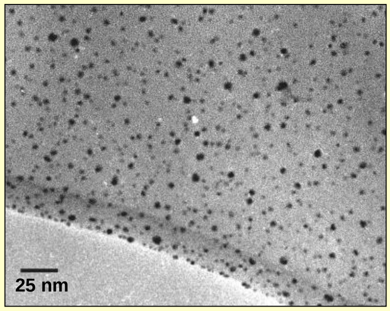
Catalytic modification by Pd

- Laser vaporization deposits metallic nano clusters
- Well dispersed particles
- Homogenous particles size
- Coverage ≈ 10 %

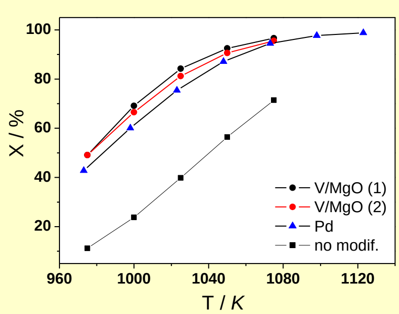


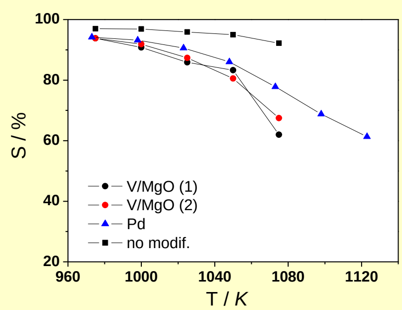
TEM image of Pd deposits (carbon replica image)



Catalyst inventory approximately 1 µg per cm² of membrane.

Use in oxidative dehydrogenation of C_2H_6





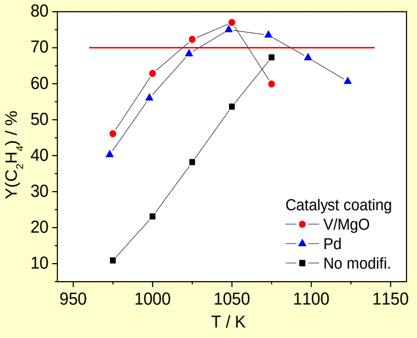
Reaction conditions:
Air compartment: F_{air}=50mL/min, p_{air}=1.2bars
C_2H_6 compartment: $F_{C2H6/He}$=37mL/min, p_{C2H6}=0.25bars

Clear impact of catalytic modification on ODHE performance.

Catalytic membranes in selective oxidation

Use in oxidative dehydrogenation of C_2H_6

Ethylene production by oxidative dehydrogenation of ethane (ODHE) is desirable, but high yields are economically vital.



No coke formation.
No limitation by equilibrium.
No flammability issues.

[M. Rebeilleau et al., Catal. Today. **104** (2005), p. 131.]

Membranes combine advantages of ODHE and steam-cracking.

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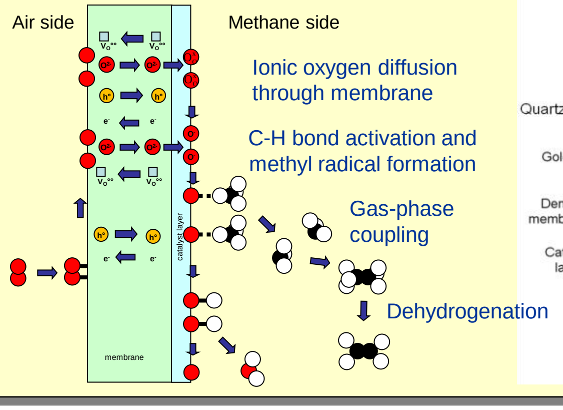
Catalytic membranes in selective oxidation

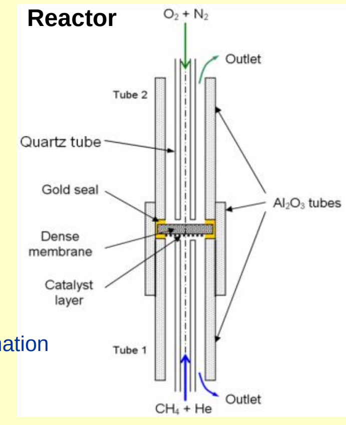
Oxidative coupling of CH_4

$$2\ CH_4 + O_2 \rightarrow C_2H_4 + 2\ H_2O$$

Ionic oxygen permeation and reaction



Reactor



Minimal presence of oxygen in gas-phase enhances selectivity.

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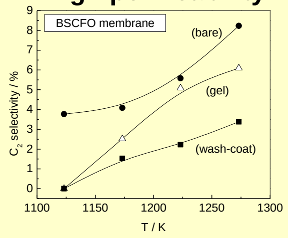
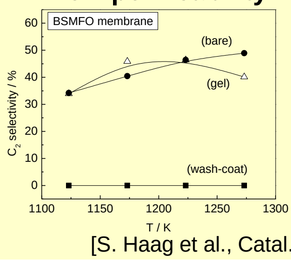
Use in the oxidative coupling of CH_4

High permeability:



Low permeability:



Probing the membrane action (using Pt/MgO model catalysts).

[S. Haag et al., Catal. Today. **127** (2007), p. 157.]

Catalyst	Temp	Permeate side Total flow	CH_4 feed	Performance data			
	°C	mL/min	%	S_2 / %	X_{CH4} / %	Y_2 / %	C_2H_6/C_2H_4
Pt/MgO	1000	83	52	50	5	3	1,2
LaSr/CaO	1000	83	35	61	28	17	2,0
Sr/La2O3	1000	85	75	33	17	6	0,6

Optimized BSCFO / catalyst: C_2-yield up to 17%.

[L. Oliver et al., Catal. Today. **142** (2009), p. 34.]

Dense membranes for selective oxidation

Identified benefit:

- No **operational costs** for oxygen separation
- Smaller **integrated systems** (multifunctional reactor)
- Green processes due to **higher selectivity** to target products
- **Increased security** by avoiding the use of gas-phase oxygen

Research subjects:

- Control the oxygen **permeation flux**
- Lower working **temperature**
- Improved **catalyst-membrane interface**
- Increase **scalability of the technology** (new membranes)

Conclusions

- Oxidation catalysis can be enhanced by dense membrane technology opening new operational windows.
- Mechanistic understanding is a prerequisite to design structured short contact time reactors.
- Structured reactors / catalysts enable outstanding performances when mutual development occurs.
- New structuring concepts could enable economically attractive performances in alkane activation (supporting technology).

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Perspectives

- Diversification of catalyst structuring compulsory to open new technology to more target reactions.
- Exploration of alkane activation with optimized catalysts (oxidative coupling).

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Acknowledgements

Helpful discussions:
Y. Schuurman, C. Mirodatos,
J. Lercher

PhD students:
M. Rebeilleau, L. Olivier, D. Hartmann, C. Gärtner

Financial support and material supply:
Acenet project AL2OL,
EU Projekts Cermox and Topcombi, Solvay S.A.

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Many thanks for your attention

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