

Double-membrane reactor for gas phase hydroxylation of aromatics: Direct conversion of benzene into phenol

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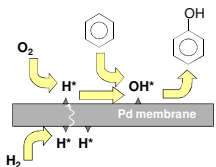
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Direct hydroxylation of benzene to phenol in a Pd-membrane reactor

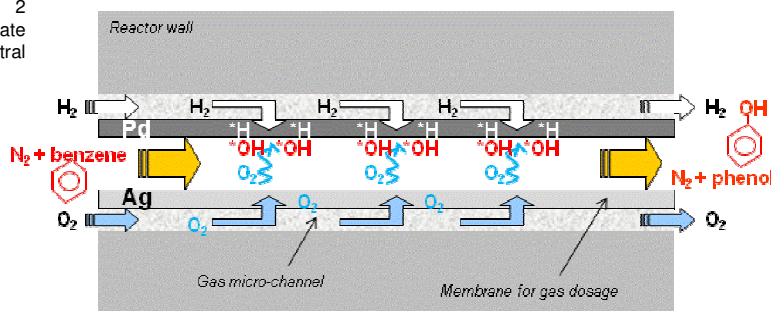
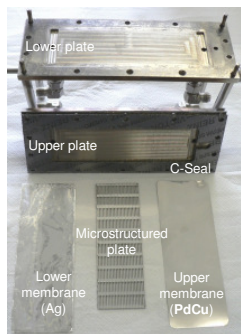


In the **Niwa concept** presented for first time in 2003 [1], AIST researchers describe an advanced method for directly producing **phenol from benzene** in a Pd-membrane reactor, with promising performances (phenol yields of up to 23%). The method has 3 major advantages: it is **direct** compared to the usual 3-step industrial process, it uses **cheap** oxidants (H_2 and O_2) and the process is **safe** as the membrane separating the two gas phases prevents explosion risks. However, drawbacks exist as gas concentration profiles in the tubular reactor limit the phenol production area. Moreover, other researchers have not managed to reproduce the same level of performance, mainly due to dominating side-reactions (water, CO_2).

The aim of this project is to study, from a fundamental research point of view, the benzene hydroxylation reaction in a similar membrane reactor limiting the side-effects using a new reactor design and modified catalysts.

Double-membrane reactor concept

Planar reactor designed with 2 membranes for the separate dosage of H_2 and O_2 in the central reaction channel.

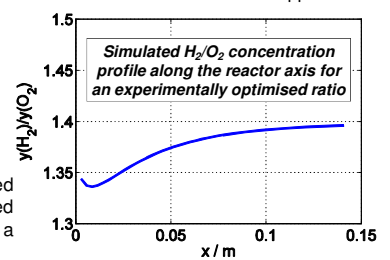


Active OH^* surface species directly convert benzene molecules absorbed on a Pd-based membrane into phenol. The formation of OH^* is achieved through the reaction between O_2 dosed in the system and H_2 permeating through the Pd alloy layer. O_2 is dosed via a thin Ag layer or via a porous membrane: *Double-membrane concept for a better atmosphere control in the reactor.*

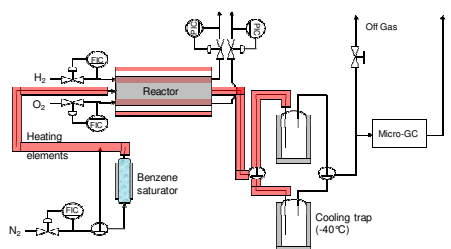
Promise of double-membrane concept:

The concentration profile H_2/O_2 can be kept quasi-constant along the reactor length (cf. Matlab simulation), leading to uniform hydroxylation conditions in the reactor and to an optimised area for phenol production.

Unknown: Will side-reactions be suppressed?



Laboratory setup



Process parameters:

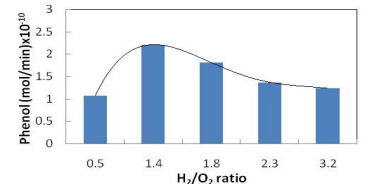
Reaction temperature, flows and retentate pressures (H_2 , O_2), membrane properties

Gas phase reaction carried out between $150^\circ C - 250^\circ C$ with N_2 as the benzene carrier gas. Reaction products (phenol, residual C_6H_6 and by-products) are condensed separately in a GC-MS system (Shimadzu QP 5050A). The gaseous species are analysed online in a 2-column micro-GC (Agilent 3000A).

Initial benzene hydroxylation results***

Side-reactions always dominate, large amounts of **water** and **CO_2** are produced. The highest phenol selectivity reached was **9.6%** at $H_2/O_2 = 1.4$.

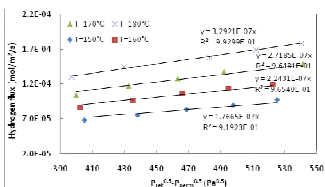
Exp. in the case of O_2 co-fed with benzene over a Pd-activated PdCu foil, surface = 48 cm^2	
Reaction temperature (C)	150
Total gas flow at reactor end (mL/min)	10,0
% of $N_2/H_2/O_2$ at reactor end	64,2/27,0/8,7
% of benzene in nitrogen feed	14,0
Benzene conversion (%)	< 1
Phenol selectivity _{benzene} (%)	1,7
CO_2 selectivity _{benzene} (%)	98,3
Phenol rate ($\times 10^{-7}$ mol/h)	0,09
Water rate (mol/h)	/



Phenol rate and selectivity are dependant on the gas phase composition in the reactor: an optimal ratio exists.

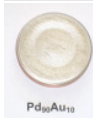
An increase of T_R reduces the phenol selectivity and favours benzene total oxidation.

Surface modification with catalytic metals

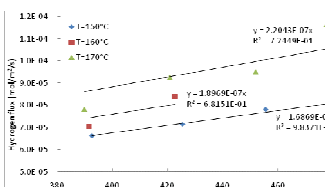


$50 \mu\text{m}$ self-supported $Pd_{60}Cu_{40}$ membranes have been employed in the reactor for the supply of active surface species for the hydroxylation reaction.

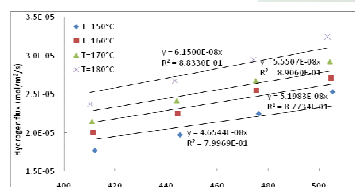
H_2 permeance of a non surface-modified $Pd_{60}Cu_{40}$ membrane:
 $Q_{H_2} = 9,07 \cdot 10^{-5} e^{-16100/(RT)} \text{ mol/m}^2/\text{s}/Pa^{0,5}$



Magnetron-Sputtering of active metals on the Pd-based membrane in order to increase its catalytic properties. **New permeation properties** are obtained (note that the sputtered membranes were *not* diffusion heat-treated prior to the measurements). Their characterisation is in progress.



H_2 permeance of the $50 \mu\text{m}$ $Pd_{60}Cu_{40}$ membrane sputtered with $1 \mu\text{m}$ $Pd_{90}Au_{10}$:
 $Q_{H_2} = 6,25 \cdot 10^{-5} e^{-20830/(RT)} \text{ mol/m}^2/\text{s}/Pa^{0,5}$



H_2 permeance of the $50 \mu\text{m}$ $Pd_{60}Cu_{40}$ membrane sputtered with $5 \mu\text{m}$ $Pd_{50}Ga_{50}$:
 $Q_{H_2} = 2,78 \cdot 10^{-6} e^{-14375/(RT)} \text{ mol/m}^2/\text{s}/Pa^{0,5}$

Reaction performance with surface-modified membranes

$Pd_{90}Au_{10}$ -modified PdCu membrane:

Exp. in the case of O_2 co-fed with benzene over a PdAu surface-modified PdCu foil, S = 48 cm^2	
Reaction temperature (C)	150
Total gas flow at reactor end (mL/min)	80,5
% of $N_2/H_2/O_2$ at reactor end	72,2/23,5/4,2
% of benzene in nitrogen feed	4,0
Benzene conversion (%)	< 1
Phenol selectivity _{benzene} (%)	41,5
CO_2 selectivity _{benzene} (%)	58,5
Phenol rate ($\times 10^{-7}$ mol/h)	2,4
Water rate ($\times 10^{-3}$ mol/h)	4,7

$Pd_{50}Ga_{50}$ -modified PdCu membrane:

Exp. in the case of O_2 co-fed with benzene over a PdGa surface-modified PdCu foil, S = 48 cm^2	
Reaction temperature (C)	150
Total gas flow at reactor end (mL/min)	52,0
% of $N_2/H_2/O_2$ at reactor end	98,5/0,7/0,7
% of benzene in nitrogen feed	4,0
Benzene conversion (%)	< 1
Phenol selectivity _{benzene} (%)	26,0
CO_2 selectivity _{benzene} (%)	74,0
Phenol rate ($\times 10^{-7}$ mol/h)	0,16
Water rate ($\times 10^{-3}$ mol/h)	10,0

Experiments carried out with surface-modified membranes, under the same process conditions (co-feed), lead to an improvement of the phenol selectivity and production rate:

- with **PdAu**, the selectivity was increased to **41,5%** and the phenol rate increased by a factor **25**. PdAu is known for catalysing the production of H_2O_2 [2], delivering OH^* radicals for benzene hydroxylation. However, side-reactions still dominate as H_2O and CO_2 remain the main products in the system;

- experiments performed using the **PdGa**-coated membrane also resulted in improvements, to a lesser degree in the phenol rate, however the selectivity reached **26,0%**. Pd $_{50}$ Ga $_{50}$ was selected as Pd atoms are strictly separated from each other by Ga atoms (active-site isolation [3]) favouring an α -adsorption of benzene on the catalytic surface.

Another catalytic system with redox properties (V_2O_5/Pd) is currently being investigated.

[1] S.Niwa et al., Catal. Comm. 4, 2003, 243
[2] J.K. Edwards et al., J. Catal. 236, 2005, 69
[3] PhD thesis Jürgen Osswald, TU Berlin, 2006
*** Submitted for publication in Sep. Purif. Technol.