Development of a novel microstructured membrane reactor for hydroxylation of aromatics with gas phase oxygen

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Objectives

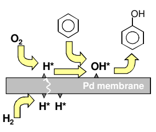
Phenol is a commodity product in the chemical industry. It is the basis for phenolic resins that are widely used in plywood manufacturing, in the construction sector and in the automotive industry. Worldwide phenol production is predominantly via the cumene process, a three step process involving the synthesis of cumene as intermediate product and yielding acetone as byproduct.

Our project aims at the investigation, in laboratory scale, of a single-step route to phenol through direct hydroxylation of benzene using a novel double membrane reactor. Experiments carried out in Japan[a] in a tubular membrane reactor proved the feasibility of this reaction with phenol yields of up to 23% reported. However, in follow-up studies by other researchers much lower phenol yields were detected, and it was speculated that hydroxylation occurs only in a narrow zone in the reactor where an optimum concentration ratio of O_2 versus H_2 exists. In the entrance region, at high oxygen partial pressure, oxidation to CO_2 dominates whereas towards the end, at high hydrogen partial pressure, hydrogenation occurs.

Through the use of two separate membranes for distributed supply of hydrogen and oxygen, respectively, the optimum H_2/O_2 concentration ratio for hydroxylation can be established over the whole reactor length, thus enabling higher phenol yields. Moreover, by catalytic modification of the surface of the Pd alloy membrane, the selectivity to phenol could be increased.

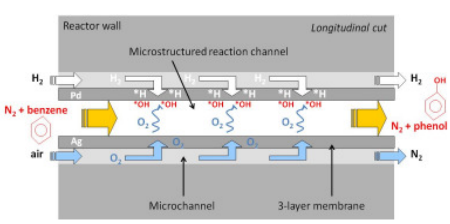
[a] *N.Itoh, S.Niwa, F.Mizukami, T.Inoue, A.Igarashi, T.Namba, Catal. Comm. 4 (2003) 243-246.*

Principle of the direct hydroxylation of aromatics

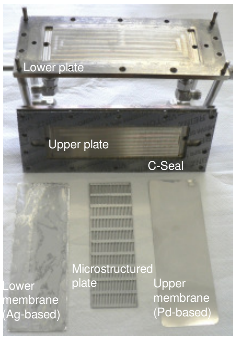


Active OH* surface species directly convert benzene absorbed on a Pd alloy surface into phenol. The formation of OH* is achieved in a Pd alloy membrane reactor through the reaction between O_2 and H_2 permeating through the Pd alloy layer. By-products H_2O and CO_2 are also generated through the reaction between H_2 and O_2, and benzene and O_2, respectively.

Reactor concept

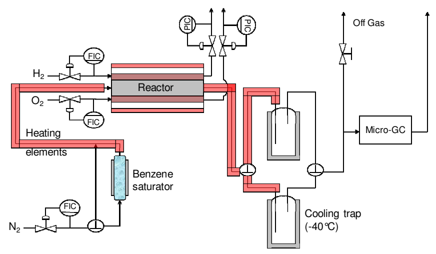


- Planar reactor design using 2 adjacent membranes for the dosage of H_2 and O_2.
- Benzene is introduced with N_2 as a carrier gas into microchannels between the membranes.
- The conversion of benzene to phenol takes place on the surface of the Pd membrane.



- The reactor is composed of 2 plates engraved with microchannels for the supply of O_2 and H_2.
- They support the membranes employed for gas supply. Membranes are Pd- and Ag-based for selective permeation of H_2 and O_2, respectively. The permeation flux is controlled by the partial pressure difference between both sides of the membranes.
- A microstructured plate is used in the central part of the reactor to guide the N_2 / benzene flow.
- The two plates are pressed together with planar carbon-seals acting on the membrane edges.
- The surface of the catalytic Pd alloy membrane is 48 cm².

Laboratory setup



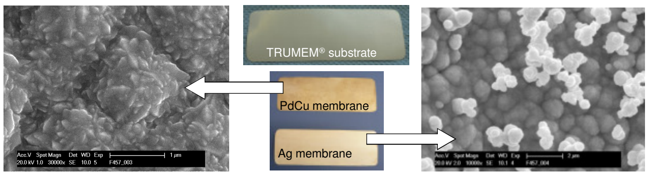
Reaction temperature, gas partial pressures, gas flow rates and membrane properties are among the process parameters.

The direct hydroxylation takes place in the gas phase between 150°C and 250°C. The reaction products (phenol, residual benzene and by-products) are condensed and analyzed separately in a GC-MS system (Shimadzu QP5050A). The gaseous species are analyzed online in a 2 column micro-GC (Agilent 3000A).

Membrane preparation

Two different types of membranes are tested in the reactor: dense metal foils and composite membranes produced by coating of commercial supports (TRUMEM®) with metallic layers. Selective top layers are applied by electroless plating:

- Ag for the O_2-selective membrane;
- PdCu, PdAg or PdAu (alloys) for the H_2-selective membrane. Pure Pd is not an option due to hydrogen embrittlement at low temperature.

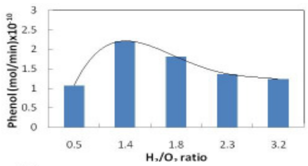


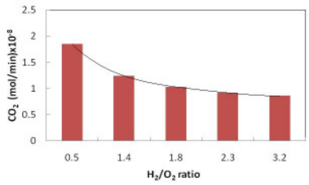
View of a top Pd layer before heat treatment **Microstructure of an Ag layer**

Current results

<u>Result obtained after several parameter changes</u>: the side reactions are dominant, large formation of water and CO_2 in the system. The highest phenol selectivity obtained so far is ca. 10%.

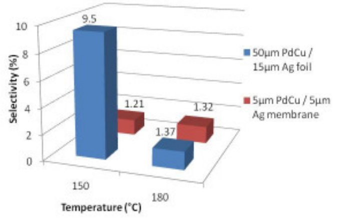
Reaction parameters	
Reaction temperature (K)	423.15
Total gas flow (mL/min)	13.0
% of $N_2/H_2/O_2$ at reactor end	90.6/5.3/4.0
% of benzene in nitrogen feed	14.0
Weight of Pd catalyst on the membrane (mg)	20.0
Benzene conversion (%)	0.02
Phenol selectivity$_{benzene}$ (%)	9.6
CO_2 selectivity$_{benzene}$ (%)	90.4





<u>Influence of process parameters</u>:

Among the various parameters, the influence of the H_2/O_2 concentration ratio on the reaction performance has been determined. The phenol rate reaches a maximum for a H_2/O_2 ratio of 1.4, which corresponds to a phenol selectivity peak of 9.6%. The CO_2 formation rate decreases due to a lower O_2 partial pressure in the reactor. These results have been included in a MATLAB reactor model. Other key parameters are currently being studied.



Experiments carried out at 2 different temperatures; employing plated composite membranes and dense foils. Higher phenol selectivity obtained with the foils at 150°C.

Perspectives

The direct synthesis of phenol from benzene in the gas phase was obtained in the double membrane reactor, however with a low phenol selectivity and yield. An optimization of the phenol yield by modifying the process parameters (gas partial pressures, residence time) and by catalytic modification of the Pd alloy membrane surface (magnetron sputtering of active metallic and oxide phases) will be undertaken, with the aim of reducing the effect of side reactions.