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Optimization of Pd Membrane Reactor for Direct Oxidation of Aromatic Compounds

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Computational fluid dynamic has already become a widely used and indispensable design and optimization tool in many technical areas. In the present work, the CFD simulations have been coupled with complex chemical reactions to model a membrane tubular reactor which is used to produce phenol from benzene in the vapor phase. Hydrogen dissociates on the palladium layer and reacts with oxygen to give active oxygen species, which attack benzene to produce phenol. In principal, reaction occurs in the surface of palladium and conversion of benzene is increased by changing the length and diameter of the Pd coated PSS tubes. The reactor length and diameter are two geometrical factors which are concerned in the present study. Although increasing the reactor length increase the conversion of benzene to phenol but the concentration of the phenol start to decrease. Based on the data provided by the experiments, a mathematical model has been constructed to conduct a simulation which leads us to an optimum design of a new tubular membrane micro-reactor.

Keyword: Membrane Reactor, Modeling ,Pd Membrane ,Direct Oxidation

INTRODUCTION

Phenol is an important intermediate for the synthesis of petrochemicals, agrochemicals, and plastics. Examples of using phenols as an intermediate are in the production of Bisphenol A, phenolic resins, caprolactam, alkylphenols, and aniline. Nearly 90% of phenol capacity is based on oxidation of cumene to form cumene peroxide, which is then cleaved into phenol and acetone in a three-step process involving oxidation of cumene. The first step is the alkylation of benzene with propylene to cumene in the presence of silica supported phosphoric acid. This reaction can also be performed with Friedel-Crafts catalysts such as aluminium trichloride

($AlCl_3$) at 100 to 200ºC. Then the cumene is converted to cumene peroxide in a non-catalytic auto oxidation reaction. The final step is acidic cleavage of cumene hydroperoxide into phenol and acetone that is catalyzed by sulphuric acid at 60 to 100ºC. The advantage of the cumene process is that it takes two inexpensive starting materials, benzene and propylene, and converts them into two high value useful products, phenol and acetone, using air. Despite its great success, the cumene process has some disadvantages such as the production an explosive intermediate (cumene hydroperoxide), it has a high environmental impact, and it uses a corrosive catalyst. It is a multi-step process, which makes it difficult to achieve high phenol yields in relation to the benzene used and which leads to a high capital investment. It requires the use of aggressive media (dilute sulphuric acid at 60 to 70ºC) and has a high acetone production as a co-product which results in an over supply in the market. This is a serious problem since the acetone market demand is much smaller than that of phenol. Therefore the economics of this process significantly depends on the marketability of the acetone by-product [1]-[3].

A difficult field of catalytic chemistry is selec- tive oxidation of hydrocarbons. The main diff- iculty here lies in the creation of selective catalysts. Such catalysts should perform a dual function: activate dioxygen and generate a reactive catalyst-bound oxygen species, and activate organic molecules so as to direct the reaction to the desired products. A variety of oxygen sources such as O_2, H_2O_2, O_3, and N_2O are used for the reaction [3]-[7]. Most heterogeneous catalysts contain a transition metal, supply an oxygen species that has a negative charge such as O^-, O^{2-}, or O_2^-, and cause oxidation of benzene via an electrophilic reaction mechanism [8]. It is likely that hydrogen peroxide is formed and leads to the formation of hydroxyl radicals, water, and atomic oxygen [9].

There is considerable interest in use of a gas phase catalytic oxidation for phenol manuf- acture because it has potential economic advantages over the corresponding liquid phase process. A new route for producing phenol directly from benzene was based on using N_2O as an oxidizing agent in the gas phase, in the presence of modified ZSM-5 or ZSM-11 zeolite, containing such elements as Ga, B, In, Cr, Fe, Sc, Co, Ni, Be, Zn, Cu, Sb, As or V [10]. Kustov *et al.* [11] reported the conversion of benzene and the selectivity to phenol 39% and 98%, respectively. Ribera *et al.* [12] reported two isomorphously substituted Fe/ZSM-5 catalysts prepared by hydrothermal synthesis. Samples with a SiO_2/Al_2O_3 ratio of ≤100 contained 0.5-1 wt.% of iron with high selectivity (>99%) and high phenol yield (up to 27%).

Pirutko *et al.* [13] reported the hydroxylation reaction proceeds over the so called α-sites, which provided by the presence of a transition metal in the zeolite. It was concluded that the amount of transition metal depended on matrix composition, for example Al-ZSM-5 and Ga-ZSM-5 exhibited high activity comparing to the B-ZSM-5 and Ti-ZSM-5 with the same amount of transition metal. Several research groups have also investigated the nature of Fe active sites in Fe/ZSM-5 zeolites [3],[14]-[17].

Niwa *et al.* [9] reported a one step

catalytic process to convert benzene to phenol using a Pd membrane, giving a higher yield than the cumene process. In this system hydrogen and oxygen were supplied separately; hydrogen was fed into a stream of a substrate and oxygen gas mixture through a metallic thin layer. The membrane was prepared by coating a porous α-alumina tube with a thin layer of palladium by chemical vapour deposition (CVD).

In the present work, the CFD simulations have been coupled with complex chemical reactions to model a membrane tubular reactor which is used to produce phenol from benzene in the vapor phase.

MATERIAL

Palladium chloride ($PdCl_3$), SnCl2, NH_4OH, $Na_2EDTA._2H_2O$, Nitrous oxide (N_2O), Ammonia (NH_3), Hellium (He), HCl, and all other materials for this work purchased from different companies.

EXPERIMENTAL

Preparation of the Pd membrane reactor

0.2 µm porous 316 stainless steel tube (Mott Metallurgical Corp.) with 30 mm length, 3.175 mm inside diameter, and 0.5 µm porous 316 stainless steel tube (Fuji Filter) with 30 mm length, 7 mm inside diameters were cleaned by immersion in an alkaline solution for 30 to 60 minutes. Two of the support tubes were then oxidized in air at 600 and 800ºC for 2 hours, with heating and cooling rates of 3ºC min^{-1}. The oxidation layer formed acts as a diffusion barrier between the PSS substrate and the Pd catalyst. The activation procedure consisted of successive immersion in a $SnCl_2$ bath (sensitizing), followed by immersion in an acidic $PdCl_2$ and rinsing with 0.01M HCl solution to prevent hydrolysis of Pd^{2+} ions.

The PSS tubes were then coated with an electroless plating method using a solution with the composition given in Table 1. The hydrazine (reducing agent) was added just prior to plating, and the plating solution was renewed every 90 to 120 minutes.

Table 1:Pd Plating Solution

Pd Plating Solution	
$Pd(NH_3)_4Cl_2.H_2O$ (g/l)	4-6
$Na_2EDTA.2H_2O$ (g/l)	40-80
NH_4OH (28%) (ml/l)	190-400
H_2NNH_2 (1M) (ml/l)	5-10
Polyoxyalkylene alkyl ether (ml/l)	0.1-0.5
PH	10-11
Temperature (^oC)	60

The morphology of the membrane was observed using scanning electron microscopy equipped with an EDS light element detector for qualit- ative and quantitative analysis (INCA X-Sight, Oxford Instruments).

Reactor construction and reaction conditions

A prepared porous Pd membrane tube with 30 mm length, and 3.175 mm inside diameter (3 cm^2 inside surface area) had welded to each end a stainless steel tube. The whole tubular asse- mbly was then placed in a solid stainless steel cylindrical housing whose outer diameter was 21.5 mm and was used for all experiments. In some experiments a solid stainless steel rod with 2 mm diameter was also placed inside the membrane tube to reduce the reactants inventory in the reactor and increase the proportion of gas that flows near to the surface of the catalyst. The reactor was heated by an electric oven and all gas lines were heated by an electric heater to prevent condensation of the reaction products. The reactants were fed to the reactor using mass flow controllers (Aalborg, 0-200 ml min^{-1}). The reactor was placed in an oven with the temperature controlled to ±0.1°C (Ai Scientific). Helium, oxygen, and benzene were fed to the tube side of the Pd membrane, while hydrogen diluted with helium was flowed across the outer surface of the membrane. The exit line from the membrane tube was connected to a GC-MS (Hewlett Packard G1800A) using a capillary column DB-1701 (J&W Scientific).different flow rate were used in this reaction. During the reaction, the shellside gas pressure was 2 atm and a trans-membrane pressure of 1 atm was used.

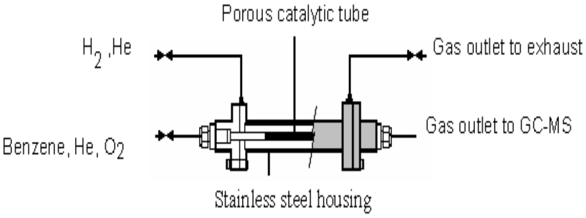

Fig.1: Schematic of Pd membrane reactor

Permeation measurements for hydrogen, helium, and argon were carried out at 200°C using the reactor shown schematically in Figure 1. The feed gas flowed from the shell side of the membrane and the permeate gas was collected on the tube side. The permeate side was kept at atmospheric pressure. The gas permeation rate was determined by a glass bubble flow meter (BFM) connected to the exit of the reactor. Reactions were carried out at 150–250°C and products were analysed by GC-MS.

Mathematical Modeling

Using an axial symmetric coordinate system (r, z) the mathematical model describing fluid flow can be written in terms of the conservation of mass and momentum equations.

Conservation of mass is written as:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\underline{V}) = 0 \qquad (1)$$

Conservation of momentum is shown as:

$$\rho(\frac{\partial \underline{V}}{\partial t}) + \rho \underline{V} \cdot \nabla \underline{V} = \rho \underline{g} + \nabla \underline{\underline{\sigma}} \qquad (2)$$

Where $\underline{V}$ is the velocity field, ρ is the fluid density and $\underline{g}$ is the body force per unit vol- ume of fluid. The Cauchy stress is given as:

$$\underline{\underline{\sigma}} = -p\delta + \underline{\underline{\tau}} \qquad (3)$$

Where *p* is hydrostatic pressure, δ is unit second-order tensor (Kronecker delta) and $\underline{\underline{\tau}}$ is the extra stress tensor. Substituting the Cauchy stress from equation (3) into equation (2) leads to the governing equations for the fluid region.

The general equation describing the mass balance is the convection-diffusion equation which is written as:

$$\frac{\partial c_i}{\partial t} + \nabla.(-D_i \nabla c_i + c_i \underline{V}) = R_i \qquad (4)$$

Where, c_i denotes the concentration of species *i*, D_i denotes its diffusion coefficient, $\underline{V}$ the velocity vector and R_i denotes the reaction term.

The rate of reaction, R_i, has the following general definition:

$$R_i=-k\ c_i \qquad (5)$$

Which *k* and c_i are the reaction constant and the concentrations of species *i*, respectively.

As The following reactions occur

simultaneously in the reactor:

$C_6H_6 + OH^o \rightarrow C_6H_5OH$ (6)

C6H5OH+ OHo → C6H4(OH)2 (7)

The rate of reaction for reactants and product reads:

$R_A = \quad k_1 c_A c_B$ (8)

$R_B = - k_1 c_A c_B - k_2 c_A c_C$ (9)

$R_C = \quad k_1 c_A c_B - k_2 c_A c_C$ (10)

Where A, B and C represent benzene, hydroxyl group and phenol, respectively.

RESULTS AND DISCUSSION

Benzene oxidation with H_2 and O_2

Effect of oxidation temperature on oxide barrier layer

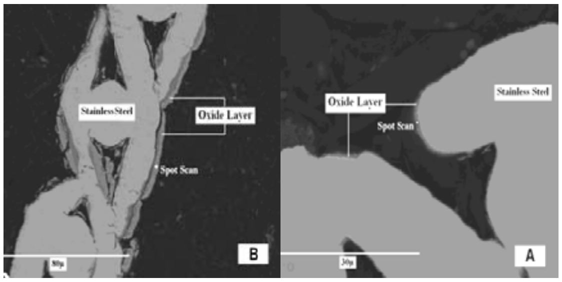

Fig.2: Cross section oxide of the layer of the Fuji PSS supports and EDS spot scans after oxidation on oxide layer at (A) 600ºC, and (B) 800ºC.

After cleaning, the tubes were oxidized in air in a high temperature furnace at constant temperature. Figure 2 shows the change of the properties of the 0.5 µm grade Fuji Filter PSS tubes following oxidation of the cleaned tubes. It was observed that the amount of oxygen on the support increased with higher oxidation temperatures, indicating a thicker oxide layer. Among the oxides that can be formed with the elements of stainless steel, Cr_2O_3 is the most stable due to its low Gibbs free energy, the low diffusion rates of elements in the oxide scale, and its high chemical stability under a H_2 atmosphere. Therefore, it is the most desirable oxide phase for use as a barrier layer to minimise intermetallic diffusion. From the SEM micrograph of the samples oxidized at 600ºC, a dark uniform thin layer was observed. The SEM micrograph of the PSS oxidized at 800ºC shows a thicker dark region, but its thickness is nonuniform. It was also observed that the surface of this oxide layer was crumbly.

Surface morphological changes during membrane synthesis

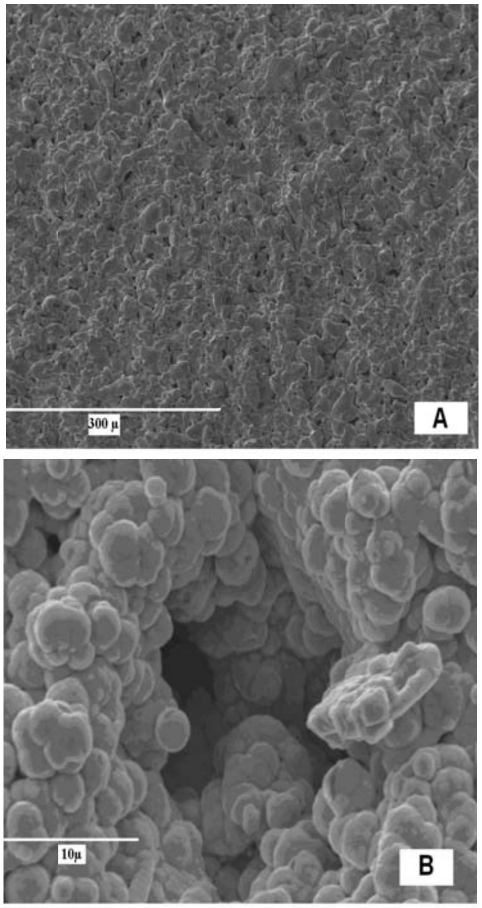

Fig.3: SEM photographs of stainless steel substrate

Figure 3 shows SEM photographs of the stainless steel substrate and the surface morphology of the Pd/PSS composite memb- rane. Electroless plating was used to deposit Pd on the PSS support, and activation of the support was necessary to initiate the plating process. After the substrate was coated with Pd, a dense Pd layer was obtained on the surface. To confirm that the Pd/PSS tube was permeable at temperatures lower than 200ºC, which is the reaction temperature for hydroxylation of aromatic compounds, the hydrogen permeance was investigated. The permeability of the tube to H_2 1.24 m^3 m^2 h^{-1} $atm^{-0.5}$; its permeability to Ar and He was 0.045 and 0.11 m^3 m^2 h^{-1} atm^{-1} respectively.

The different units for H_2 permeation through the membrane arise from the transport mechanism. The transport equation for H_2 flux (*J*) is:

$$J = -K\left(p^n_{H_2,feed} - p^n_{H_2,permeate}\right)\Big/L \qquad (11)$$

where *K* is the permeability (related to the hydrogen diffusion coefficient and its solubility), p_{feed} and $p_{permeate}$ are the hydrogen pressures on the upstream and downstream sides of the membrane respectively, and *L* is the membrane thickness.

Effect of inner tune in benzene conversion

For the annulus geometry, effect of increasing the inserted solid cylinder diameter on the conversion of phenol has been investigated.

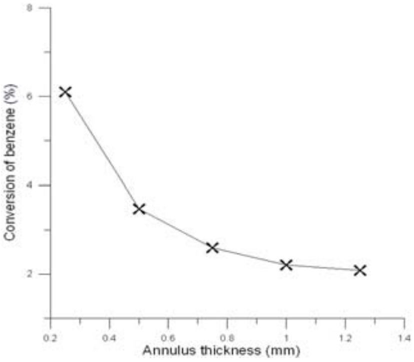

Fig.4: Conversion of benzene versus the annulus thickness

Figure 4 shows the conversion of benzene versus the annulus shell thickness (the area between the tube and inserted solid cylinder). Increasing the diameter of the inserted solid cylinder results in thinner shell area which increase the benzene conversion.

Modelling membrane tube

CFD, commercial software, has been employed to conduct the simulations. A membrane reactor was modelled to predict the influence of the geometrical parameters on the production of phenol. All the simulations were carried out in an isothermal situation. Table 2 shows the numerical values of the physical parameters used in the present simulation.

Table 2: Parameters Used in The Simulation

Reaction constant (k_1) concentration (mol/m^3s)	1.2e-6
Benzene inlet velocity (m/s)	0.01
Hydrogen inlet velocity (m/s)	0.001
Dynamic viscocsity (Ns/m^2)	0.008
Inlet benzene (mol/m^3)	0.01

The constructed model has been used to model the conversion of benzene to phenol in a 30mm long reactor with the cross section diameter of 3mm. Also the modelling carried out when a solid cylinder with 1 mm in diameter is inserted into the tube. The latter case results in an annulus shape geometry.

Comparing between experimental and modeling results in benzene conversion

To validate the constructed model, the results generated by the simulation are compared with the results from the experiments. Table 3 shows the comparison of the simulated and exp- erimental results for the conversion of benzene with and without the inner solid cylinder.

Table 3: Experimental and Simulation Results

	Experiment	Simulation
Phenol Productivity Without the inner tube (mmol/hr)	2	1.8
Phenol Productivity With the inner tube of 1 mm diameter (mmol/hr)	3	2.3

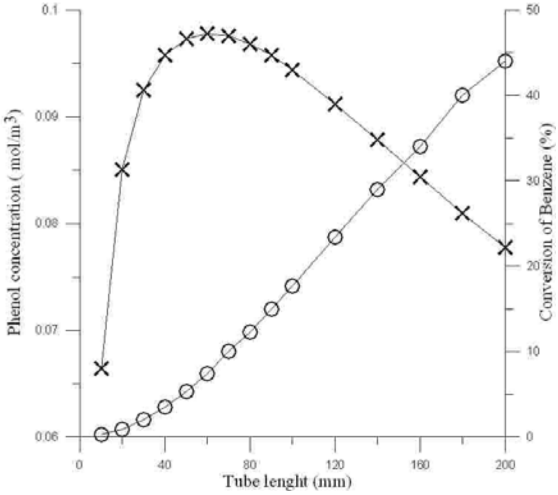

Fig.5: Concentration of phenol × and conversion of benzene ○ versus the tube length

Based on the good agreement between simulated and experimental results, the proposed model was employed to study the effect of the reactor tube length on the conversion of benzene to phenol. Figure 4 shows the concentration of the produced phenol and conversion of benzene versus the tube length, respectively. As it can be seen in the Figure 5, increase in the tube length results in the increase of phenol production up to the tube length of 60mm where the increase in tube length decreases the production of phenol. This length considers being the optimum length for which the production of phenol is maximum.

CONCLUSION

In the present work comparing between experimental and modeling for conversion of benzene to phenol on tube membrane reactor has been investigated. The constructed model has been used to model the conversion of benzene to phenol in a 30mm long reactor with the cross section diameter of 3mm. It was observed that increase in the tube length results in the increase of phenol production up to the tube length of 60mm where the increase in tube length decreases the production of phenol. This length considers being the optimum length for which the production of phenol is maximum.

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