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Direct Oxidation of Benzene to Phenol

By

Mohammad Hossein Sayyar

A Doctoral Thesis

Submitted in partial fulfilment of the requirements for award of Doctoral of Philosophy of Loughborough University

Department of Chemical Engineering

2008

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ABSTRACT

This thesis deals with two major process routes for the direct oxidation of benzene to phenol. The main objective of the first route was to understand the properties of the porous stainless steel (PSS) needed for support of a catalyst deposited onto its surface, to identify the morphologies of the Pd membrane deposited onto the PSS, to design a catalytic membrane reactor, to characterise membrane in terms of its permeability to hydrogen, and then to investigate hydroxylation of benzene using oxygen as an oxidant. It was observed, using Mo or zeolites as a second catalyst and the reactor design affect the productivity and selectivity towards phenol.

This research has also shown the effects of the catalytic properties of iron zeolites with a focus on reactions involving the decomposition of nitrous oxide and direct oxidation of benzene to phenol using nitrous oxide as the oxidant. The main objective of this second route was to identify the active sites in the catalysts, and to a design catalyst based on the acquired knowledge. The methodology was to incorporate iron either at framework positions via hydrothermal synthesis of the zeolites followed by controlled migration to extra-framework positions, or directly at extra-framework positions via sublimation of FeCl₃ or liquid ion-exchange. In this project, different catalysts were characterized and their catalytic activities compared. It was observed contaminants such as N-containing compounds, O₂, CO, and water affected the catalytic properties and catalyst half-life.

In this thesis, two different methods were used to improve productivity when using a Pd/PSS membrane. First, changing design of the reactor, and second, using Mo as a second catalyst. It was observed that higher productivity was obtained when the reactor tube was packed with Fe/ZSM-5 and N₂O using as the oxidant. From an economic point of view, using N₂O in the presence of zeolite in a fixed-bed reactor is expected to offer more advantages than Pd membrane for oxidation of aromatic compounds.
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CHAPTER 1
INTRODUCTION
INTRODUCTION

1.1 General background

Phenol is an important intermediate for the synthesis of petrochemicals, agrochemicals, and plastics. The average annual growth from 1995 to 2000 and 2001 to 2006 were 4.2% and 3%, respectively. [1]. Nearly 90% of global phenol capacity (9 MMT in 2006) is based on oxidation of cumene to form cumene peroxide, which is then cleaved to phenol and acetone. The cumene process shows several disadvantages, i.e. it uses three step reactions, requires high capital investment, acetone with the same molar ratio to phenol produces as a by-product, and it generates a highly reactive intermediate.

The efficient production of active oxygen species on a catalyst remains difficult. Active oxygen can be produced by different sources such as H$_2$O$_2$, N$_2$O, and O$_2$. The direct oxidation of benzene to phenol applying H$_2$O$_2$ has been studied [2-5]. The experiments show the benzene conversion and selectivity to phenol is lower than using N$_2$O and the cost of using H$_2$O$_2$ is also higher than for N$_2$O. Some researcher groups reported that using O$_2$ has advantage for partial oxidation of aromatic compounds using a Catalytic Membrane Reactor (CMR) [6-8]. However, cheaper H$_2$O$_2$ can be produced with a Pd membrane. Due to the high cost of Pd and relatively low hydrogen flux, commercially available Pd foils and tubes are not suitable for large scale industrial applications. Composite membranes consisting of a thin Pd film supported on a porous substrate, such as vycor glass, ceramic, stainless steel, quartz, etc., are a good alternative that provides both mechanical strength and a thin separation layer for a high hydrogen flux and reduced Pd cost. Ceramic or vycor glass supported Pd membranes are relatively difficult to assemble. PSS supported Pd membranes, on the other hand, are advantageous due to their thermal expansion coefficient close to that of Pd-based films, ease of fabrication, high mechanical strength, high resistance to corrosion and low cost. When porous metal supports are used at high temperatures, the intermetallic diffusion of metal elements in
the substrate to the palladium separation layer causes the hydrogen flux to deteriorate. One way to improve the membrane stability is to create an intermediate intermetallic diffusion barrier layer, which is stable in a reducing atmosphere and at high temperatures. Further, among several deposition techniques, electroless plating is the most commonly used technique for Pd deposition because it provides very good uniformity on complex shapes, hardness of deposited film, low cost, and it requires very simple equipment.

Another new route for producing phenol directly from benzene is based on using N₂O as an oxidizing agent in the gas phase and iron containing zeolites as a catalyst. Zeolites are hydrated crystalline materials that are built from a three dimensional framework of (SiAl)O₄, tetrahedral with all four oxygen atoms shared by adjacent tetrahedral. However, unpromoted zeolites show limited applications so addition of promoters such as transition metal ions are necessary. Many papers are published on the characterization and reactivity of such transition metal containing zeolites. Among those, iron in the MFI zeolites is of considerable interest to catalysis. The introduction of iron into extra-framework positions of zeolites can be achieved by impregnation, ion exchange which includes solid state ion exchange or sublimination of a suitable iron precursor, and hydrothermal synthesis [9]. These materials generally need to be activated to remove part of the Fe to extra-framework positions. In general, Fe ions can occupy three positions in the matrix of ZSM-5: (1) as isolated ions in framework positions, (2) as cationic or neutral iron-oxo complexes in the intracrystalline micropores space, and (3) as clusters or finely dispersed iron oxide particles on the external surface of the zeolite crystals. Many attempts have been made to elucidate the active structures and functioning of the redox sites, but no definite conclusions have been drawn yet.

Producing phenol from N₂O is suggested only if the expensive N₂O is available as an industrial waste product in adipic acid plants. The global N₂O emission from adipic acid plants is not sufficient for producing 9 MMT phenol per year. Phenol needs technological processes for N₂O synthesis at the unit capacity up to 100 KT/y. Solutia and BIC recently developed a new large-scale catalytic process for the synthesis of nitrous oxide via selective oxidation of ammonia over a Mn-Bi-O/α-Al₂O₃ catalyst [10].
1.2 Objectives

This thesis deals with the study of two major technologies regarding oxidation of benzene to produce phenol. First, the vapour phase hydroxylation of benzene with a mixture of oxygen and hydrogen using a Pd membrane reactor with and without a second catalyst. Hydrogen dissociates on the palladium layer and reacts with oxygen to give active oxygen species, which attack benzene to produce phenol. This research shows the second catalyst does not increase the productivity. In principal, reaction occurs on the surface of palladium and conversion of benzene is increased by changing the length and diameter of the Pd coated PSS tubes. Hydroxylation of benzene using a Pd membrane reactor is far from an industrial method because phenol productivity is too low. The second method includes the decomposition of nitrous oxide and the selective oxidation of benzene to phenol. The main objectives of the research in this section are to identify active sites, design the catalyst which is able to delay coke formation, and define the methodology to incorporate iron either at framework positions of the zeolites directly or at extra-framework positions via sublimation of iron chloride, wet ion exchange or hydrothermal synthesis methods, and to characterize the resulting materials and compare their catalytic activities.
References

CHAPTER 2

LITERATURE REVIEW
2.1 *Background of phenol industrial process*

Phenol was firstly known as carbolic acid. It received this name because it was isolated from coal tar when it was discovered for the first time in 1834 [1]. It is an important intermediate for synthesis of petrochemicals, agrochemicals, and plastics. Figures 2.1 and 2.2 show the growth of phenol capacity, production, and consumption [2].

![Figure 2.1 Comparing capacity, production, and consumption of phenol.](image1.png)

![Figure 2.2 Phenol consumption in 2002.](image2.png)
Bisphenol A is used to produce epoxy resins for paints coatings and mouldings, and in polycarbonate plastics, familiar in CDs and electrical appliances.

\[
\begin{align*}
\text{CH}_3 & \quad \text{H} \\
\text{HO} & \quad \text{C} \quad \text{OH} \\
\text{CH}_3 & \quad \text{HO}
\end{align*}
\]

Caprolactam is consumed in the manufacture of nylon and polyamide plastics used in the manufacture of carpets, clothing, moulded components, and packaging.

\[
\begin{align*}
\text{C} & \quad \text{N} \\
\text{H}
\end{align*}
\]

Phenyl amine (Aniline) is used in rubber manufacture as an antioxidant. It is also consumed as an intermediate in herbicides, pigments, and pharmaceuticals. It is used to make isocyanates for the production of polyurethanes.

\[
\begin{align*}
\text{NH}_2 & \\
\text{H}
\end{align*}
\]

Alkylphenols are used in the manufacture of surfactants, detergents and emulsifiers, and also in insecticide and plastics production.

\[
\begin{align*}
\text{OH} & \\
\text{CH}_3
\end{align*}
\]

Chlorophenols are used to make antiseptics and bactericides such as Tri Chloro Phenylmethyliodosalicyl (TCP) and Dettol. They are also used to manufacture a range of pesticides.

\[
\begin{align*}
\text{OH} & \\
\text{Cl}
\end{align*}
\]
Salicylic acid is used in the production of aspirin and other pharmaceuticals.

\[ \text{OH} \]

\[ \text{C} \]

\[ \text{OH} \]

The progress of the phenol processing industry is reviewed in what follows.

### 2.1.1 Sulphonation process

Sulphonation of benzene was used by BASF in 1899 and continued until the 1960s. Figure 2.3 shows schematically the sulphonation process to produce phenol. The main disadvantage was the poor atom economy (36.7%) of the reaction (which is the percent ratio of molecular mass of the desired product to the molecular mass of reactant). This means that considerably less than half the mass of reactants ends up in the required product, even if we assume 100% yield. In practice the yield is more likely to be in the region of 88%, giving an atom economy of 32.3%, barely a third of the reactant mass. Sodium sulphite is consumed in the wood pulp and paper industries but the large amount of waste produced was one of the reasons why the benzene sulphonation route is no longer used [3].

![Figure 2.3 Phenol production via sulphonation process.](image)

Figure 2.3 Phenol production via sulphonation process.
2.1.2 Chlorination process

Figure 2.4 shows the chlorination process developed in 1924 in the USA and was implemented by DOW Chemical. In this process benzene is converted to Chloro benzene, which is then reacted in the presence of sodium hydroxide to form phenol. This method is no longer used because of the adverse economics of chlorine and alkali production [1].

\[
\text{Figure 2.4 Phenol production via chlorination process.}
\]

2.1.3 Cyclohexanone process

Cyclohexane is oxidized to a mixture of cyclohexanol and cyclohexanone and then dehydrogenated to phenol in the cyclohexanone process (Figure 2.5). This process appeared in the sixties and was used by Monsanto in Australia for a few years before being replaced [1].

\[
\text{Figure 2.5 Phenol production via cyclohexanone process.}
\]

2.1.4 Benzoic acid process

Dow Chemical of Canada commercialized another process using methylbenzene in 1961. This process accounts for 5% of world production of phenol [3, 4]. The advantage of the oxidation of methylbenzene is that it produces no propanone co-product and also very few impurities. It has a high theoretical atom economy, a high yield, and produces far less waste than the cumene oxidation process. This process is up to 3 to 4 times more energy
intensive than the cumene oxidation process, and so it is not widely used. This process has an atom economy of 60.1% if phenol is the only useful product, which is a further improvement on the previous processes.

![Chemical Reaction](image)

**Figure 2.6** Phenol production via benzoic acid process.

### 2.1.5 Cumene process

This route was first discovered in 1942 in Russia. The first industrial plant was put to operation in 1949 in Dzerzhinsk city. Use of this process was started in the USA in the early 1950s. In fact, nearly 90% of the world’s 9 million tones (in 2006) of phenol capacity uses the cumene hydroperoxide route [4]. Phenol and acetone as a by-product are produced at the same time in equimolar amounts. Such processes provide excellent economics if the ratio and volume of the two products match market demand. The advantage of the cumene process is that it takes two inexpensive starting materials, benzene and propylene, and converts them into two expensive useful products, phenol and acetone.

#### 2.1.5.1 Production of 1-methylethylbenzene (cumene)

Cumene is made from benzene and propene (Figure 2.7). The reaction is catalysed by acid, and can be carried out in either the vapour or liquid phase. Solid pelletised phosphoric acid is used as a catalyst in the vapour phase reaction. Disposal of the corrosive catalyst from this process can be a problem. The catalyst can not easily be regenerated when it reaches the end of its useful life. Aluminium chloride is consumed as the catalyst in the liquid phase. The reaction takes place at 100°C and atmospheric pressure.
2.1.5.2 Oxidation of cumene

The reaction is carried out at temperatures in the range 90 - 130°C and pressures of 1-10 atmospheres. Control of acidity levels, temperature and pressure are vital because at higher temperatures, the hydroperoxide is unstable and can decompose violently. To help reduce the risk of this happening, only 25% of the cumene is allowed to react at any one time in order to keep the concentration of the hydroperoxide within safe limits. Unreacted cumene has to be separated and recycled.

\[
\text{Phenol} + \text{Acetone} \quad \text{Oxidation of cumene}
\]

2.1.5.3 Decomposition of cumene hydroperoxide to phenol

The hydroperoxide is mixed with dilute sulphuric acid at 60 - 70°C to produce both phenol and acetone as products. If we assume that both phenol and propanone are desired
products, and that the yield is 100%, this will clearly give an atom economy of 100%, all the atoms in the reactants appearing in the products. In practice the yield is more likely to be in the region of 90%, but even taking this into account, and assuming all the propanone is waste, still gives an atom economy of 55.7%, comparing favourably with the old sulphonation process at 36.7%. Figure 2.9 shows phenol production from cumene hydroperoxide.

![Chemical reaction](attachment:chemical.png)

**Figure 2.9** Production of phenol via cumene process.

Despite its great success, the cumene process has some disadvantages such as producing an explosive intermediate (cumene hydroperoxide), and corrosive catalyst. It is a multi-step process, which makes it difficult to achieve high phenol yields compared to the benzene used and needs a high capital investment due to its multi-step nature. It requires the use of aggressive media ($\text{H}_2\text{SO}_4$) and has a high acetone production as a co-product resulting in an over supply in the market. This is a serious problem since the acetone market demand is much smaller than that of phenol. Figure 2.10 shows the economics of this process significantly depends on the marketability of the acetone [5].
Oxidation catalytic reactions are of prime importance at an industrial level and correspond to a huge market. One of the most difficult fields of catalytic chemistry is selective oxidation of hydrocarbons. The main difficulty here consists of the creation of selective catalysts. Such catalysts should be able to create active oxygen from different sources such as $\text{H}_2\text{O}_2$, $\text{N}_2\text{O}$, and $\text{O}_2$, then generate some catalyst-bond oxygen species and finally, an active organic molecule so as to direct the reaction to the desired products [6]. Heterogeneous catalysts can offer a variety of different sites for activation of the mentioned oxidants. A summary of some research on the hydroxylation of benzene using heterogeneous catalysts are explained below.

### 2.2 Hydroxylation of benzene with $\text{H}_2\text{O}_2$

Direct oxidation of benzene to phenol applying $\text{H}_2\text{O}_2$ in the presence of different catalysts such as vanadium (V), TS-1, and Cu containing ternary hydrotalcites has been studied. Nomiya et al. [7] reported synthesis of vanadium (V)-substituted polyoxomolybdates $\text{Na}_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}]$, and compared their performance with the traditional vanadium (V)-substituted polyoxomolybdates such as $\text{H}_4[\text{PMo}_{11}\text{VO}_{40}]$, $\text{H}_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}]$, and
$\text{H}_6[\text{PMo}_9\text{V}_3\text{O}_{40}]$. It was observed that $\text{Na}_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}]$ showed much lower catalytic activity but was a very stable catalyst precursor comparing with traditional catalysts. They also reported using tetrabutylammonium salts of three types of mono-vanadium (V) substituted heteropolyanions as catalyst precursors [8]. Using $[\text{PVMO}_{11}\text{O}_{40}]^+$ as a single species exhibited a requirement for one vanadium centre acting in cooperation with the molybdenum (VI) atom constructed on the A-site of the $\alpha$-Keggin polyoxoanion structure.

They also reported using tetrabutylammonium salts of three types of mono-vanadium (V) substituted heteropolyanions as catalyst precursors [8]. Using $[\text{PVMO}_{11}\text{O}_{40}]^+$ as a single species exhibited a requirement for one vanadium centre acting in cooperation with the molybdenum (VI) atom constructed on the A-site of the $\alpha$-Keggin polyoxoanion structure.

The result was a better catalyst stability of the mono-vanadium (V) substituted heteropolymolybdate in comparison with the di and tri- substituted heteropolymolibdates.

Kumar et al. [9] observed significant enhancement in reaction rates of the hydroxylation of aromatics under solvent-free, triphase conditions (solid-liquid-liquid), catalyzed by TS-1 using $\text{H}_2\text{O}_2$. The selectivity and conversion were 90.4% and 41.1%, respectively. It was also shown that the relative hydrophobic nature and restricted pore dimensions of titanium silicates, competitive diffusion of substrate with co-solvent, and Bronsted acidity of titanium silicates are important factors responsible for increasing activity.

This investigation aimed at studying the possibility of converting benzenes to phenol have shown low phenol yield using molecular oxygen as an oxidant. Kuznetsov et al. [12] reported $\text{Cu}$ catalyst incorporated on an $\text{Al}_2\text{O}_3$ catalyst prepared by a coprecipitation method yielded less than 3% of phenol, at 0.67 mmol/g $\text{Cu}$. They are also observed that a higher $\text{S/P}$ ratio resulted in higher selectivity to phenol.
Bengoa et al. [10] investigated the influence of the preparation method on catalyst activity. The presence of sodium traces in the solid or CH₃OH in the reaction mixture can change the activity drastically. In addition, the synthesis conditions must be controlled carefully to get pure TS-1, since the presence of extra-framework titanium inhibits benzene hydroxylation.

Liptakova et al. [11] studied the direct synthesis of phenol from benzene over hydroxyapatite catalysts in the gas phase. Phenol selectivity and yield were reported as 97% and 3.5%, respectively. However, the system with which they worked was complex regarding the catalyst and the operating conditions, and aniline was observed as by-product.

### 2.3 Hydroxylation of benzene with H₂ and O₂

Most of the investigations aimed at studying the possibility of converting benzene to phenol have shown low phenol yield using molecular oxygen as an oxidant. Kanzaki et al. [12] reported Cu catalyst impregnated on an Al₂O₃ catalyst prepared by a co-precipitation method yielded less than 3% of phenol, or 0.67 mmol for 2 wt% Cu. They are also observed that a higher Si/Al ratio resulted in higher selectivity to phenol.
Miyake et al. [13] showed that Pd, Rh, Ir, and Pt supported on silica formed phenol with a large amount of water. Their experiments showed 88.2% (0.351 mmol/h) and 99.7% (0.292 mmol/h) phenol selectivity using Pd and Rd, respectively. They also found that a higher V_2O_5 wt% decreased phenol productivity. Miyake et al. [14] also reported that the rate of phenol formation on the platinum catalyst supported on silica was accelerated when acetylacetonates of vanadium, iron, lanthanum, and yttrium, especially vanadium acetylacetonate were added. Productivity of phenol was 0.412 mmol/h for a concentration of 19.2 ppm V(acac)_3, 0.5 wt% Pt/SiO_2.

Kuznetsova [15] prepared a number of silica supported M-HPC catalysts by a single impregnation with a solution containing both H_2PtCl_6 and HPC. The hydroxylation reaction was performed in a fixed bed flow reactor at ambient pressure. The highest catalyst productivity of (270-380 mol phenol/g-atom metal h) was recorded for the M-PMo_{12} and M-PMo_{11}V systems where M = Pt or Pd. At a benzene conversion of 0.3% selectivity to phenol formation was 95-98% and the only side product was biphenyl.

Lee et al. [16] reported that vanadium-containing molecular sieves are able to incorporate into the framework sites and act as the active sites. It was found that mesoporous materials such V-MCM-41 and V-MCM-48 showed higher catalytic activities than microporous materials such as VS-1 and V-BEA. Two reasons were suggested: one is mesoporous molecular sieves make benzene molecule favourable to move easily toward active sites; the other is mesoporous molecular sieves have very high surface area where they provide active sites.

Heteropolyacids were used as the reoxidant for palladium in the direct oxidation of benzene to phenol using molecular oxygen which represents a complicated method for producing phenol. It was observed that 15% and 70% benzene conversion and selectivity to phenol was achieved after 4 hours at 130°C, respectively [17].
2.3.1 What is a membrane reactor?

A membrane reactor is essentially a plug-flow reactor that is made up of cylindrical porous within it, similar to the tube within the shell of a shell and tube heat exchanger. This porous tube is the membrane that gives the membrane reactor its name. The membrane is a barrier that only allows certain components to pass through it. The selectivity of the membrane is controlled by its pore diameter, which can be of the order of Angstroms for microporous layers or of the order of microns for macroporous layers.

Membrane reactors are most commonly used in conjunction with catalytic reactions. Three types of catalytic membrane reactors (CMRs) have been proposed according to the way of combining catalyst and membrane by Miachon [18].

The membrane can be used to remove a reaction product from the reaction zone. This type of CMR, called an extractor, has been the subject of many studies. An extractor can be used to increase reaction yields. This is obtained either by improving the conversion in an equilibrium-restricted reaction or, in consecutive reactions, by improving the selectivity towards a primary product via its selective extraction through the membrane [19]. Dense palladium membranes, used as catalytic membranes for equilibrium displacement of hydrogen-producing reactions, do not suffer from reactant loss.

When compared to what exists in a conventional reactor, the distribution of one reactant through the membrane will modify the local reactant composition in the catalyst bed. This may directly affect the catalyst state. Distributors have mainly been used for selective oxidations and oxidative dehydrogenations.

A membrane may be used to facilitate the contact between reactants and catalyst. This CMR type, called contactor, takes advantage of a very unique configuration of the membrane pore, which contrary to pores of conventional solids, presents two distinct ways of access, corresponding to the two sides of the membrane. In contactors, the membrane generally also acts as the catalyst support.
2.3.2 Development of palladium-based membrane

Palladium-based membranes have been used for decades to provide ultra-pure hydrogen, e.g. in the semiconductor industry and for the operation of fuel cells [20, 21]. In recent years there has been a growing interest in the industrial application of palladium-based membranes for hydrogen producing reactions. Extensive investigations were conducted for the employment of the palladium-based membranes for hydrogen removal to shift thermodynamic (equilibrium) limitations towards higher conversions, e.g. during dehydrogenation of hydrocarbons [22], steam reforming of methane [23], and the water-gas-shift reaction [24]. It was shown that hydrogen feeding through palladium membranes can improve the selectivity of hydrogenation reactions [25]. Key requirements for the successful development of palladium-based membranes are low costs as well as high hydrogen permeability and perm-selectivity combined with good mechanical/thermal and long term stability.

2.3.2.1 Method of Pd deposition onto porous substrate

Four methods are commonly used for composite Pd synthesis on porous substrates.

Chemical Vapour Deposition (CVD) is the reduction or decomposition of a volatile compound of a coating material upon a heated surface. CVD allows depositing coatings of most refractory metals while other techniques are unsuccessful. CVD leads to pure and thin layers on small substrates. However the procedures are tedious and nearly impossible for industrial purposes. Metal-Organic Chemical Vapour Deposition (MOCVD) differs from CVD in that only high purity organo-metallic compounds are used.

Manetron sputtering deposition is achieved by applying a high voltage across a low-pressure gas (usually argon and about 5 mtorr) to create “plasma”, which consists of electrons and gas ion in a high-energy state. During sputtering, energized plasma ions strike a “target” composed of the desired coating material, and cause atoms from that target to be ejected with enough energy to travel to, and bond with, the porous substrate.
A powerful magnet is used to confine the "glow discharge" plasma to the region closest to the target plate. A similar technique, Electron Beam (e-beam) evaporation can be used for Pd and Pd alloy deposition. In e-beam evaporation the porous substrate is placed in a high vacuum chamber at a desired temperature with a crucible containing the material to be deposited. An electron beam is aimed at the material in the crucible causing it to evaporate and condense on all exposed surfaces in the vacuum chamber and substrate. Several crucibles, with different compounds (or metals), are available in the same chamber and switching crucibles leads to the evaporation and condensation of different compounds. Ion-Beam (i-beam) evaporation is essentially the same as e-beam but using argon ions instead of electrons. Magnetron sputtering, e-beam evaporation and ion beam evaporation, which are called physical vapour deposition (PVD), are generally applied when depositing alloys. The main drawback of sputtering techniques is that sputtering chambers have a confined space and coating of large supports for large scale high purity H₂ production is almost impossible. CVD and sputtering techniques offer the very attractive advantage that they allow for the support to be heated during deposition, which in turn allows for the possibility of controlling the film microstructure [26]. The microstructure of the Pd thin film is a determinant parameter in long-term composite membrane stability, since the microstructure changes as the composite Pd membrane is exposed to reaction conditions [27].

Electrodeposition of metals involves the movement of positive metallic ions towards the cathode to be reduced and finally be incorporated in the metallic growing film. The film thickness depends on the electrolyte used, temperature, and pH and mainly on current density and time. Variants of electrodeposition are vacuum electrodeposition, where vacuum is applied at the cathode, and pulsed electrodeposition where the electrical potential is varied over time (pulse) to improve the uniformity of the deposition. Vacuum electrodeposition led to thinner and more selective films than electrodeposition [28].

Electroless deposition is the reduction of metastable metallic salt complexes by a reducing agent on a target surface. It has been widely used for Pd membrane synthesis. This is due to the low cost, easy procedures and simplicity of the needed equipment. The
advantage of electroless deposition over electrodeposition is that the substrate does not have to be conductive and one can cover the surface of complicated shapes uniformly, where electrodeposition tends to cover “hills” with a thicker layer while leaving “valleys” poorly covered. The main drawback of electroless (and electrodeposition) deposition is that the deposition of alloys represents a challenge since co-deposition of two metals is difficult, in general, when a Pd-alloy is desired, and the two metals are deposited sequentially and heat-treated at high temperatures to obtain the alloy. Such a process was described as a coating and diffusion technique [29].

2.3.2.2 Electroless deposition of Pd

Prior to electroless deposition, the porous substrate needs to be activated. The activation process can be achieved using sequential dipping in SnCl₂-HCl (1 g/l, pH=2) and PdCl₂-HCl (1 g/l, pH=2) solutions. Sn⁺² reduces Pd⁺² by the following equation leading to the deposition of active Pd nuclei on the surface of the substrate [30].

\[ \text{Sn}^{+2} + \text{Pd}^{+2} \rightarrow \text{Sn}^{+4} + \text{Pd}^0 \quad \text{Eq. 2.1} \]

This activation method has been widely used when electroless plating was applied. Moreover a wide range of substrates, including plastics and metals, can be activated. High resolution XPS scans of the Sn 3d₅/₂ and Pd 3d₅/₂ peaks were conducted after sensitizing (in the SnCl₂ solution), activation (in the PdCl₂ solution), thorough washing with deionized water, and finally Cu deposition of fly-ash particles [31]. It was found that SnCl₂ was present on the surface just after sensitizing, indicating the good adhesion of Sn⁺² ions on the surface of fly-ash particles. After activation, SnCl₄, PdCl₂, and Pd⁰ were found on the surface confirming the reaction step leading to Pd nuclei. The deionized water cleaning step led to Sn(OH)₄, PdO, PdCl₂, and Pd⁰, indicating that Sn⁺⁴ and Cl⁻ ions remained on the surface even after the washing step. After the Cu deposition step, Sn⁺⁴ and Cl⁻ were neither detected on the surface of the Cu deposit nor underneath the coating using EDX analysis on a cross section of a particle. However, an elemental composition less than 1 wt% cannot be detected by EDX, therefore, traces of Sn⁺⁴ and Cl⁻ could still
remain underneath the Cu coating. The absence of Cl\(^-\) and Sn\(^{4+}\) impurities after Cu plating was attributed to the dissolution of Sn(OH)\(_4\) and PdCl\(_2\) by the alkaline Cu plating solution.

A new trend in the past 10 years consisted of applying an activated layer on the support, which decreases the number of synthesis steps and the amount of raw materials. Ceramic supports were activated with a Pd(II)-modified boehmite sol gel. After calcination and reduction under H\(_2\) at 500\(^\circ\)C, Pd nuclei were obtained on the substrates [32]. ZrO\(_2\) sols were also doped with Pd nuclei, cast on PSS substrates to form a smooth activated surface for the deposition of Pd [33].

A Palladium plating bath includes a palladium ion source (PdCl\(_2\), Pd(NH\(_3\))\(_4\)Cl\(_2\), Pd(NH\(_3\))(NO\(_3\))\(_2\), Pd(NH\(_3\))\(_4\)Br\(_2\)), a complexant (ethylenediamine tetra acetic acid (EDTA), ethylenediamine (EDA), ammonia (NH\(_3\)), a reducing agent (hydrazine (N\(_2\)H\(_4\))), sodium hypophosphite (NaH\(_2\)PO\(_2\).H\(_2\)O), triethylamine boran, stabilizers, and accelerators. The first hypophosphite based Pd plating bath had EDTA and EDA as the complexing agents to stabilize the solution. More stable baths were developed using NH\(_3\) as the complexing agent and hypophosphite as the reducing agent [34]. Other hypophosphate based baths were used for correction protecting in nuclear plants and chemical industries [35]. The main drawback of hypophosphite based Pd baths is that phosphorous is included in the Pd coating, thereby affecting the H\(_2\) permeability of the membrane. Moreover, when removing substrates from plating bath, cracking appeared in the Pd layer due to H\(_2\) gas production during plating [34]. In fact, H\(_2\) was produced and adsorbed by the Pd layer when using hypophosphite. At the plating temperatures of 60-70\(^\circ\)C, the \(\beta\) phase nucleated leading to distortions and cracking of the Pd layer.

The use of hydrazine as a reducing agent did not lead to the formation of H\(_2\) but N\(_2\), which avoided the cracking of the freshly deposited Pd film [36]. Rhoda's plating bath stability was further improved by the addition of thiourea as the stabilizer [37]. Formaldehyde was used to deposit Pd with strong acidic baths [38]. It was reported that Pd(NH\(_3\))(NO\(_3\))\(_2\) led to a better Pd conversion than Pd(NH\(_3\))\(_4\)Cl\(_2\) and that pH should be...
between 9 and 11 for better solution stability [39]. Also, EDTA to Pd molar ratios between 20:1 and 40:1 and T>65°C resulted in Pd salt conversion levels greater than 80% [39].

### 2.3.2.3 Membrane gas permeation

Gas permeation is the term used to describe a membrane separation process using a non-porous semi-permeable membrane. In this membrane process, a gaseous feed stream is fractionated into permeate and non-permeate streams. The non-permeation stream is typically called the non-permeate in gas separations terminology, and referred to as the retentate in liquid separations. Transport occurs by a solution diffusion mechanism, and membrane selectivity is based on the relative permeation rates of the components through the membrane. Each gaseous component transported through the membrane has a characteristic permeation rate that is a function of the ability to dissolve and diffuse through the membrane material. The two relationships upon which the equations are based are Fick’s law (diffusion) and Henry’s law (solubility).

Fick’s laws of diffusion were derived by Adolf Fick in 1855. Fick’s first law is used in steady-state diffusion, i.e., when the concentration within the diffusion volume does not change with respect to time ($J_{in} = J_{out}$)

\[
J = -D \frac{dC}{dx} \quad \text{Eq. 2.2}
\]

In Equation 2.2, $J$ is the diffusion flux (mol/m².s), $D$ is the diffusion coefficient (m²/s), $x$ is a distance on a length coordinate (m), and $C$ is the concentration (mol/m³).

Henry’s Law is used to determine the solubility of gases.

\[
C = S \cdot P \quad \text{Eq. 2.3}
\]
where $S$ is the solubility constant in the membrane (mol/m$^3$Pa), and $P$ is the partial pressure of a component in gas phase (Pa).

2.3.2.4 Membrane for $H_2$ permeation (Sievert's law and $n$ value)

Pd membranes are required to have high and stable $H_2$ permeance with high perm-selectivity. Today it is well known that hydrogen permeates with an infinite selectivity via a solution-diffusion mechanism through Pd and its alloys. The hydrogen permeation through Pd membranes is based on a multi-step process: adsorption, dissociation, ionisation, diffusion, recombination, and desorption. First, molecular hydrogen is adsorbed on the palladium surface, where the dissociation into atomic hydrogen takes place. Then the hydrogen atoms enter the palladium lattice and diffuse through it, while the electrons interact with the metal lattice. On the adjacent side the hydrogen atoms leave the lattice and recombine on the surface, before they are finally desorbed as hydrogen molecules.

![Diagram of hydrogen permeation through a Pd membrane.](image)

**Figure 2.13** Hydrogen permeation for a Pd membrane.

Hydrogen transport through the membrane can be described by the 'flux', which is defined as the rate of hydrogen passing through the membrane per unit area. When the rate limiting step for hydrogen permeation is diffusion of hydrogen through the bulk Pd
layer, the H$_2$ flux through the membrane can be obtained by integration of first Fick's law.

\[
J = -D \frac{dC}{dl} = \frac{D}{l} (C_{H_2} - C_{H_2})
\]

Eq. 2.4

where \( l \) is the thickness of the membrane.

The hydrogen concentrations can be expressed as,

\[
C = \kappa n
\]

Eq. 2.5

Where, \( \kappa \) is the hydrogen concentration at constant pressure (mol/m$^3$) and \( n \) is the atomic \( H/Pd \) ratio, the solubility of hydrogen in palladium. Figure 2.14 shows the relationship between the partial pressure of hydrogen and solubility, the ratio of \( H/Pd \) atoms, at various temperatures.

![Figure 2.14](image)

**Figure 2.14** Equilibrium isotherms of Pd – H system \((n = \text{atomic hydrogen} / \text{atomic Pd})\) (Frieske and Wicke, 1973).

It is also well known that the use of pure palladium membranes is hindered by the fact that palladium shows a transition form the \( \alpha \)-phase (hydrogen-poor) to the \( \beta \)-phase
(hydrogen-rich) at temperatures below 300°C and pressures below 2 MPa, which depends on the hydrogen concentration in the metal. Since the lattice constant of the β-phase is 3% larger than that of the α-phase this transition leads to lattice strain and, consequently, after a few cycles to a distortion of the metal lattice. Alloying the palladium, especially with silver or copper, reduces the critical temperature for this embrittlement and leads to an increase of the hydrogen permeability. A maximum value of the hydrogen flow is reached for an alloy with approximately 23 wt% silver [40]. As can be seen in Figure 2.14, at very low concentrations of hydrogen, n is linearly dependent on the square root of partial pressure of hydrogen.

\[ p_h^{0.5} = K_s \cdot n \]  
\text{Eq. 2.6}

In Equation 2.7, \( K_s \) is the Sievert’s constant which is equivalent to Henry’s constant. Combining Equations 2.4, 2.5 and 2.6 gives,

\[ J = \frac{D (\kappa / K_s)}{l} \left( p_{h_1}^{0.5} - p_{h_2}^{0.5} \right) \]  
\text{Eq. 2.7}

The term \( \kappa / K_s \) is the hydrogen solubility, S, in the palladium layer (mol/m\(^3\).Pa\(^{0.5}\)).

The product of diffusivity (D) and solubility (S) is termed the permeability, Q, of the membrane and is a function of temperature, composition and microstructure of the membrane layer. D and S are related to temperature by

\[ D = D_0 \exp\left( -\frac{E_D}{RT} \right) \]  
\text{Eq. 2.8}

\[ S = S_0 \exp\left( \frac{\Delta H}{RT} \right) \]  
\text{Eq. 2.9}
where $E_D$ is the activation energy for hydrogen diffusion (J/mol), $\Delta H$ is the solubility enthalpy of hydrogen (J/mol), $R$ is the universal gas constant and $T$ is the absolute temperature (K). Combining Equations 2.7, 2.8, and 2.9 gives the Sievert's law.

$$J = \frac{Q_0}{l} \left( P_{H_2}^{0.5} - P_{H_2}^{0.5} \right) = \frac{Q_0}{l} \exp\left( -\frac{E_0}{RT} \right) \left( P_{H_2}^{0.5} - P_{H_2}^{0.5} \right)$$

Eq. 2.10

where,

$$Q_0 = D_0 \cdot S_0$$

Eq. 2.11

$$E_Q = E_D + \Delta H$$

Eq. 2.12

At this point it is important to remember that the Sievert's law is only valid in certain cases: (i) for the case of dilute Pd-H solution ($n << 1$). As seen from Figure 2.14, for each isotherm, Sievert's law can be applied up to a certain pressure value. (ii) For the case when the rate limiting step for permeation is H$_2$ diffusion through the membrane. Usually when the membrane is ultra thin or when the process stream has some contaminants, the surface process become much slower than the diffusion of H$_2$.

Alternatively, when Sievert's law is not valid, an expression for the flux can be derived as being proportional to the difference of the hydrogen partial pressure raised to an exponent with a value of 'n' as shown in the Equation 2.13.

$$J = \frac{Q_0}{l} \exp\left( -\frac{E_0}{RT} \chi \left( P_{H_2}^{*} - P_{H_2}^{*} \right) \right)$$

Eq. 2.13

### 2.3.3 Hydroxylation of benzene using Pd membrane reactor

Niwa et al. [40, 41] reported a one step catalytic process to convert benzene to phenol using a Pd membrane.
According to their work, this technique has a benzene conversion of 15% and phenol selectivity of 95%. In this system hydrogen was introduced from the shell side and a mixture of oxygen and benzene was fed from the tube side. Hydrogen was passed through a metallic layer and reacted with the oxygen gas mixture. The membrane was prepared by coating a porous α-alumina tube with a thin layer of palladium by means of the metallic chemical vapour deposition technique. The hydrogen and nitrogen permeation rates of their membranes were $1.0-3.0 \times 10^{-3}$ and $0.1-1.0 \times 10^{-10}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-0.5}$ at 300°C, respectively.
Table 2.1  Direct hydroxylation of benzene to phenol with oxygen and hydrogen catalyzed by a palladium membrane. "inner" and "outer" mean that a gaseous mixture containing a hydrocarbon was flowed inside or outside of the palladium membrane tube, respectively. Selectivity was based on the amount of benzene consumed [40].

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction temp. (°C)</th>
<th>Benzene/O₂/He (28 ml/min)</th>
<th>H₂/He (14 ml/min)</th>
<th>Reactant Conv. (%)</th>
<th>Product Select. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd membrane (inner)</td>
<td>150</td>
<td>0.40/1.29/24.6</td>
<td>2.43/20.0</td>
<td>13.25</td>
<td>85.3</td>
</tr>
<tr>
<td>Pd membrane (inner)</td>
<td>160</td>
<td>0.45/4.70/29.8</td>
<td>6.72/28.2</td>
<td>1.60</td>
<td>96.3</td>
</tr>
<tr>
<td>Pd membrane (inner)</td>
<td>250</td>
<td>1.80/8.51/24.6</td>
<td>10.06/24.9</td>
<td>2.05</td>
<td>92.7</td>
</tr>
<tr>
<td>Pd membrane (outer)</td>
<td>150</td>
<td>2.00/1.29/24.6</td>
<td>2.43/20.0</td>
<td>2.11</td>
<td>94.8</td>
</tr>
<tr>
<td>Pd membrane (outer)</td>
<td>200</td>
<td>2.00/1.29/24.6</td>
<td>2.43/20.0</td>
<td>3.00</td>
<td>93.3</td>
</tr>
</tbody>
</table>

Figure 2.16  Oxidation of benzene with oxygen and hydrogen catalyzed by a palladium membrane at 200°C. Flow rates: shell, 25 ml/min (H₂/He = 5.6/20, Volume ratio); tube, 25 ml/min (benzene/O₂/He = 0.4/3.8/25, volume ratio). Solid pink circles, blue squares, and orange open circles denote benzene conversion, phenol yields, and phenol selectivity, respectively [40].

Hydrogenation and oxidation of numerous compounds via side reactions have been investigated. These side reactions were related to the gas balance between oxygen and hydrogen. Sato et al. [41] reported oxygen-rich conditions caused complete oxidation, whereas oxygen-poor conditions induced high hydrogenation activity.
Rimias et al. [42] reported an oxidation procedure that couples metallic palladium-catalysed in situ hydrogen peroxide generation from molecular hydrogen and oxygen with a second vanadium or iron catalyst that utilizes the hydrogen peroxide for the hydroxylation of benzene and cyclohexane. Their studies indicated that the slowest step in the overall reaction is the formation of usable hydrogen peroxide, and the mechanism of hydroxylation by the second catalyst is not affected by the presence of metallic palladium. The reported procedure, which resembles monooxygenases, allows the direct use of dioxygen in catalyst oxidations. Also, they reported that comparison between an in situ method of hydrogen peroxide generation and hydrogen peroxide added via a syringe pump show that the in situ method is more selective. The results of running these experiments are shown in Table 2.2.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Hydroxylation Catalyst</th>
<th>Benzene (mmol)</th>
<th>Phenol (mmol)</th>
<th>Benzoquinone (mmol)</th>
<th>Conversion to phenol (%)</th>
<th>Selectivity to phenol (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>V(acac)₃</td>
<td>1.4</td>
<td>0.20(1)</td>
<td>tr.</td>
<td>14</td>
<td>&gt;99</td>
</tr>
<tr>
<td>2</td>
<td>V(acac)₃</td>
<td>1.4</td>
<td>0.15(2)</td>
<td>tr.</td>
<td>10</td>
<td>&gt;99</td>
</tr>
<tr>
<td>3</td>
<td>V(acac)₃</td>
<td>0.52</td>
<td>0.13(1)</td>
<td>tr.</td>
<td>26</td>
<td>&gt;99</td>
</tr>
<tr>
<td>4</td>
<td>V(acac)₃</td>
<td>0.52</td>
<td>0.10(1)</td>
<td>0.0021(6)</td>
<td>21</td>
<td>99</td>
</tr>
<tr>
<td>5</td>
<td>tris(Dibezoylmethanato)Fe(III)</td>
<td>0.4</td>
<td>0.059(9)</td>
<td>0.0017(2)</td>
<td>4.2</td>
<td>97</td>
</tr>
</tbody>
</table>

**Table 2.2** Conversion and selectivity to phenol using lower initial benzene concentration in situ hydrogen peroxide generation [42].

2.4 **Hydroxylation of benzene with N₂O**

There is considerable interest in a single step oxidation of benzene using the gas phase catalyst for phenol manufacture because it has a potential advantage over the corresponding liquid phase process from an economic point of view. N₂O pollution abatement is an important environmental problem due to the high greenhouse potential of N₂O and its ozone-depleting properties. During the last decades, one of the most interesting new reagents for the selective oxidation has appeared to be N₂O since it contains 36 wt% oxygen and the by-product of an oxidation reaction would be N₂.
N2O was used by Iwamoto et al. for the oxidation of benzene over group 5 and 6 oxides supported on silica gel [43]. This reaction over a vanadium catalyst achieved 70% selectivity at 550°C, which compares well with oxidation by O2. Catalyst preparation methods were improved by many researchers. Yoo et al. [44] reported Fe/Mo/partially deboronated a borosilicate molecular sieve catalyst which was prepared by the Chemical Vapour Deposition (CVD) method and used for the selective hydroxylation of benzene. Two mechanistic paths are postulated based on the reactive oxygen species such as O\(^-\), which can be generated via interaction on N2O with the iron sites or OH\(^+\), which can be generated at the Brønsted site on the catalyst. Gubelmann and Tirel [45] reported a process for the preparation of halophenols with 9.2% conversion and 97.6% selectivity. In their study, a halobenzene is brought into contact with N2O on an acidified zeolite. Matrix composition of the MFI structure catalysts were reported by Panov et al. [46]. It was shown that Fe with different matrix composition such as alominasilicalite, borosilicalite, galosilicalite and titanosilicalite can be used for the preparation of the catalyst.

A new route for producing phenol directly from benzene was based on using N2O as an oxidizing agent in the gas phase and the iron containing zeolites as a catalyst with near 4% and 98% conversion of benzene and selectivity to phenol, respectively. Solutia and the Borescov Institute of Catalysis (BIC) developed this new process jointly [3]. The major hurdles are related to the stability of catalyst, inhibition of side reactions and availability of cheap N2O.

### 2.4.1 Structure and properties of zeolites

The name of zeolite is from the Greek zein (meaning: to boil) and lithos (stone) to describe minerals that frothed when heated. Zeolites are hydrated crystalline materials that are built from a three dimensional framework of (SiAl)O\(_4\) tetrahedra with all four oxygen atoms shared by adjacent tetrahedra. This results in a channel structure with molecular dimensions of 3 to 10 Å. Each AlO\(_4\) tetrahedron in the framework bears a net
negative charge which is balanced by extra-framework exchangeable cations, mainly \( \text{Na}^+, \text{K}^+, \text{Ca}^{2+} \) or \( \text{Mg}^{2+} \). These cations are held within the central cavities and surrounded by water molecules. The cations are mobile and may usually be exchanged by other cations. Zeolite has an empirical formula of:

\[
M_{2n}O \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}
\]

where \( M \) represents the exchangeable cations of valence \( n \). \( M \) is generally a Group I or II ion, although other metal, non-metal, and organic cations may balance the negative charge created by the presence of Al in the structure. Around 40 different framework structures are known in nature and more than 150 synthetic zeolites have been manufactured [47].

There are three properties of zeolites that make them technologically important: (i) they are selective and strong adsorbents, (ii) zeolites are selective ion exchangers, and (iii) they are catalytically active.

Some other characteristic properties that are important for commercial applications, include: (i) a high degree of hydration that is easily dehydrated, (ii) low density and large void volume when dehydrated, (iii) stability of the crystal framework structure when dehydrated, (iv) uniform molecular sized channels in the dehydrated crystals, (v) special electrical properties, (vi) thermally and chemically robust, (vii) chemical composition and structure controlled by synthesis and post-synthesis, (viii) large variety of structures, (ix) strongly acidic and tuneable distribution, and (x) a green catalyst (no waste, recoverable).

The Si/Al ratio is an important characteristic of zeolites. The charge imbalance due to the presence of aluminium in the zeolite framework determines the ion exchange properties of zeolite and induces potential acidic sites. As the Si/Al ratio increases, the cation content decreases. The thermal stability increases and the surface selectivity changes from hydrophilic to hydrophobic.
The various reactions that take place depend primarily on the distribution of acid sites on the matrix and within the zeolite. Brønsted sites are well known as being the important sites for the catalytic reactions [48] and most of these sites reside within the zeolite pore structure. Lewis acid sites play an important role in the formation of coke [49]. Coke formation reactions are quite different from scission reactions since coke requires bond making rather than bond breaking. Strong Lewis acid sites in particular can adsorb unsaturated hydrocarbons for sufficient time for oligomers to form which then end up as coke and hydrogen. Figure 2.17 shows Brønsted and Lewis acid sites on zeolites.

![Figure 2.17 Brønsted and Lewis acid sites on zeolite.](image)

The primary building unit of a molecular sieve is the individual tetrahedral unit. The topology of all known molecular sieve framework types can be described in terms of a finite number of specific combinations of tetrahedral called secondary building units (SBUs). A molecular sieve framework is made up of one type of SBU, although rare, some can have a combination of different SBUs.

![Figure 2.18 Secondary building units (SBUs): a T atom is located at each corner, the oxygen is located near the midpoint between two T atoms [50].](image)
2.4.1.1 *Pentasil zeolites*

There are several types of Pentasil structure according to the ways of connectivity. Figure 2.19 shows seven zeolite structures that contain 5-ring units. The structures are drawn as straight lines connecting adjacent T-sites, in each case are based on reported crystal structures.

*Figure 2.19* Pentasil structures [50].
Based on the pore sizes, zeolites can be classified into small-pore (pore size < 5Å, 8-membraned ring), medium-pore (pore size 5-6 Å, 10-membraned ring), and large-pore (pore size 7-8 Å, 12-membraned ring). Some typical zeolites are listed in Table 2.3.

Table 2.3 Pore dimensions of some typical zeolites [50].

<table>
<thead>
<tr>
<th>Pore size</th>
<th>Code</th>
<th>Abbreviated name</th>
<th>Pore diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Small</td>
<td>LTA</td>
<td>zeolite A</td>
<td>4.1</td>
</tr>
<tr>
<td>Medium</td>
<td>MFI</td>
<td>ZSM-5</td>
<td>5.3 x 5.6</td>
</tr>
<tr>
<td></td>
<td>MEL</td>
<td>ZSM-11</td>
<td>5.3 x 5.6</td>
</tr>
<tr>
<td></td>
<td>MTT</td>
<td>ZSM-33</td>
<td>4.5 x 5.2</td>
</tr>
<tr>
<td></td>
<td>EUO</td>
<td>EU-1</td>
<td>4.1 x 5.7</td>
</tr>
<tr>
<td></td>
<td>AEL</td>
<td>AIPO₄-11</td>
<td>3.9 x 6.3</td>
</tr>
<tr>
<td>Large</td>
<td>MOR</td>
<td>mordenite</td>
<td>6.5 x 7.0</td>
</tr>
<tr>
<td></td>
<td>BEA</td>
<td>zeolite β</td>
<td>7.6 x 6.4</td>
</tr>
<tr>
<td></td>
<td>AFI</td>
<td>AIPO₄-5</td>
<td>7.3</td>
</tr>
<tr>
<td></td>
<td>EMT</td>
<td>hexagonal faujasite</td>
<td>7.4 x 6.4</td>
</tr>
<tr>
<td></td>
<td>FAU</td>
<td>zeolite X or Y</td>
<td>7.4</td>
</tr>
</tbody>
</table>

2.4.1.2 MFI structure

The MFI (ZSM-five, Zeolite Secondary Mobile-five) structure is built up by 5-1 SBU which are link together to form chain and the interconnection of these chains leads to the formation of the channel system in the structure. The MFI structure has a three dimensional pore system consisting of sinusoidal 10-ring channels (5.1 x 5.5 Å) and intersecting straight 10-ring channels (5.3 x 5.6 Å) [50].
Those medium pore size zeolites, like ZSM-5 and ZSM-11, are of great importance since they contain pore size comparable to the size of small organic molecules thereby forming the basis of shape-selective catalysts. Zeolites not only act as shape-selective catalyst, but also act as acid catalysts for chemical reactions if the loosely localized cations in the zeolites are exchanged with protons. Thus, ZSM-5 and silicalite-1 are materials with MFI topology. Silicalite-1 is a pure silica analogue of ZSM-5 (generally, an MFI type material is regarded as ZSM-5 when there is more than one aluminium per unit cell, i.e. a SiO$_2$/Al$_2$O$_3$ ratio less than 190) and strictly it cannot be considered as a zeolite but rather as a silica molecular sieve.

2.4.2 Catalyst preparation methods

Oxygen transfer reactions are very important in catalysis, as they are ion nature. A wide range of transition metals is able to catalyze such reactions. The activity, selectivity and stability of the catalytically active species strongly depend on their structure and local
environments. Zeolites have proven to be good hosts for active species of transition metals. The metal elements can either be introduced during the zeolite synthesis or through post-synthesis treatments.

2.4.2.1 Liquid ion exchange

Typically the iron salt was dissolved in demineralised water and added to the zeolites at once. The suspensions were further diluted by adding additional water up to a solid to liquid (10-15 g solid to 1 l liquid). The exchanges were carried out at 80-85°C and for a period of between 6 and 48 hours while stirring at 500 rpm. The samples were filtered under vacuum and the washing process continued several times and dried overnight at 70°C [51].

2.4.2.2 Chemical vapour deposition

Over-exchanges Fe/ZSM-5 catalysts were prepared via the FeCl₃ Chemical Vapour Deposition (CVD) method describe by Chen and Sachtler [52]. Catalysts were converted into the acidic form by calcination under O₂ at 550°C for three hours. For the CVD exchange a quartz reactor was used. In order to remove absorbed moisture, catalysts were loaded on the reactor and flushed overnight under He at 300°C. The temperature was then lowered to 30°C. Then anhydrous FeCl₃ were loaded on the reactor. After being reconnected to the He line, the reactor was heated to 330°C and kept at this temperature for the period of 5 to 60 minutes. After completion of the iron loading, the temperature was lowered to 30°C. Catalysts were washed with 1000 ml doubly deionised water for 30 min and dried over night in air at 70°C.

2.4.2.3 Solid-state

Solid-state method consisted of grinding the dried zeolite intensely in a mortar together with FeCl₃.6H₂O. Subsequently, the mixture was transferred into a beaker and excess
FeCl₃ was dissolve in water. To reduce the contact time between zeolite and aqueous phase, supernatant solution was poured off after 5-10 minutes even if it was not clear due to incomplete sedimentation, and the dissolution procedure was repeated. Catalyst was washed several times until a test with AgNO₃ did not trace chloride in the supernatant phase [53].

2.4.2.4 Hydrothermal synthesis

Fe/ZSM-5 catalysts were synthesised by controlled hydrolysis of tetraethylorthosilicate (TEOS) in the presence of tetrapropylammonium hydroxide (TPAOH). TEOS was added to TPAOH and mixed for at least one hour. An appreciable amount of this solution was subsequently drop wise added to solution of FeCl₃, Al(NO₃)₃.9H₂O or a mixture of iron and aluminium sources. The mixture was transferred into a teflon lined autoclave and kept at 160-190°C for a period of 100-150 hours. Catalysts were filtered under vacuum and washing process continued several times and dried over the night at 70°C [54].

2.4.3 Techniques for dealumination of zeolites

In the past, many reactions had to be carried out by mixing reactants in the presence of potent mineral acids. In addition to Brønsted and Lewis acid sites of the catalyst, the pore system can be vital in the manipulation of selectivity of acid catalyst reactions. While liquid phase acid catalyzed reactions allow the formation of essentially any transition state, the introduction of a pore system containing the acid site requires the transition state to be able to fit into the pore system.

Aluminium can be removed from the framework by any number of ways, the persistent concerns addressed by each technique are how much the crystal structure is affected and what happens to the aluminium once the framework bonds have been broken. The unique catalytic properties of zeolites are due largely to their porous structures. When framework species are removed, there is always the concern that the crystallinity and hence activity
will be affected. The second major concern is the state of the aluminium once it has left the framework. In the simplest extraction techniques, the aluminium remains in the pore system as an extra framework aluminium oxy-hydroxide. While the creation of extra framework aluminium and the Lewis acidity that accompanies it can be a benefit to some reactions, extraction schemes generally attempt to remove the extra framework aluminium from the crystallite altogether.

2.4.3.1 Acid treatment

Dealumination using mineral acids is by far the easiest method for extracting aluminium from the framework of a zeolite. The reactants are relatively inexpensive, no special equipment is required and the acids are reasonably safe to work with. The downfall is that acid extraction generally results in a significant loss in crystallinity and hence catalytic activity through the addition of a cation capable of assuming the ion exchange position in the zeolite [55]. These additional cations coordinate with the aluminium tetrahedra and allow for more severe acid treatments (lower pH, higher temperature) without a significant degradation in crystallinity. It is also suggested that if a high degree of dealumination is desired, that this be accomplished using a series of treatments in which each subsequent treatment is more severe than the previous. This takes advantage of the enhanced acid stability of the zeolite upon dealumination to remove nearly all of the aluminium without significantly impacting the crystal structure.

Strong organic and inorganic acids have been shown to be reliable dealumination agents; however, treatments using these acids generally result in a significant loss of crystallinity. While some of the structural degradation can be prevented through the addition of structure directing agents during dealumination, the loss in crystallinity is often unacceptable. One family of acids that tend to retain zeolite crystallinity following treatment are the organic sulfonic acids, such as methane sulfonic acid [56]. This patent lays out a procedure for the dealumination of Beta zeolite through contact with 1 to 500 parts of a water soluble organic sulfonic acid per unit of zeolite at temperatures ranging from 0 to 200°C.
2.4.3.2 Removal via soluble aluminium compounds

Chelating agents are essentially any compound that can act as a multidentate ligand to a metal ion. Dealumination occurs by strongly coordinating with the aluminium in the framework while acidity breaks the framework bonds. Once firmly bound to the chelating agent, the extracted metal ion is simply washed out of the zeolite. While there is any number of potential chelating agents, those used for dealumination generally fall into two categories: the dicarboxylic acids and the synthetic amino acids. By far, the most commonly utilized dicarboxylic acid is oxalic acid and the synthetic amino acids are almost exclusively represented by ethylenediaminetetraacetic acid (EDTA) and salts thereof [57].

2.4.3.3 Hydrothermal treatment

Hydrothermal treatments are exactly what the name implies. Aluminium is removed from the framework using a combination of water and heat. While this can take many forms, by far the most common technique is steaming. Steaming is the common term for heating or calcining a zeolite in the presence of steam. The steam in conjunction with the heat ruptures the aluminium to oxygen framework bonds creating an extra framework aluminium hydroxide and a silanol (hydroxyl) nest (Figure 2.22). The problem with steaming is that once the aluminium has been removed from the framework, another
method must be employed to remove the extra framework aluminium from the pore system [58].

Figure 2.22  Illustrated of the mechanism for steam dealumination of zeolite resulting in a silanol (hydroxyl) nest and Al(OH)₃.

2.4.3.4 Removal via volatile aluminium compounds

Hydrothermal treatment has concentrated on washing away aluminium from the framework. Another common technique for the removal of aluminium eliminates the washing step by creating volatile aluminium compounds that can be removed from the solid via evaporation. A number of compounds result in volatile aluminium species upon contact with a zeolite and a good summary of these can be found in Fejes et al. [59]. The family of compounds that result in volatile organic compounds can be further broken down into two groups: acid halides and metal halides. The metal halides are discussed further in the next section, while the acid halides will be used to discuss the general mechanism for dealumination.

Phosgene (carbonyl chloride, COCl₂), thionyl chloride (SOCl₂) and sulfonyl chloride (SO₂Cl₂) are commonly used representative compounds from an extensive list of acid halides that produce volatile aluminum compounds upon contact with a zeolite at elevated temperature. The reaction, as illustrated in Figure 2.23, proceeds via a 3-step
mechanism where during the first step HCl is removed, then CO₂ and finally AlCl₃ [59]. The reaction is said to proceed by abstracting oxygen from the lattice, unfortunately this mechanism does not explain how the resultant silanol nest is formed without the addition of water or another hydrogen and oxygen source.

![Figure 2.23 Illustration of mechanism for dealumination by phosgene.](image)

When milder dealumination conditions are required, it is possible to take advantage of the decomposition of both phosgene and sulfonyl chloride. At elevated temperatures these compounds will break down into chlorine and carbon monoxide or sulphur dioxide. While it would be expected that all dealumination activity would be lost, the reaction does proceed. Furthermore, Fejes et al., were able to dealuminate using a mixture of carbon monoxide and chlorine [59]. While elevated temperatures allow the use of decomposition products, at temperatures above 600°C a concern is the removal of silicon as silicon tetrachloride and a subsequent loss in crystallinity.

2.4.3.5 Selective dealumination

This section concentrates on the selective dealumination of the external surface of a crystallite. Almost any dealumination technique can be adapted to be external surface selective, therefore the following is provided to give an idea of how this can be accomplished.
The selectivity of reactions such as the disproportionation of toluene to para-xylene and benzene over ZSM-5 suffers from the existence of external Brønsted acid sites which unselectively convert toluene to coke. These external Brønsted sites can be eliminated by a combination coking and steamed dealumination [60]. This procedure takes advantage of the coke formation to block internal acid sites from the dealumination agent.

2.4.4 Formation of active sites

Iron loaded zeolites have recently attracted renewed attention due to their outstanding catalytic properties [61-64]. The structure of active sites is less clear. Ione et al. [65] observed three types of iron active sites in the zeolite: (i) Isolated ions in tetrahedral lattice positions, (ii) isolated ions or small complexes inside the channels, and (iii) dispersed oxide particles on the outer surface of the zeolite.

![Figure 2.24 Location of iron in ZSM-5.](image)

In particular, over-exchanged Fe/ZSM-5 (Fe/Al molar ratio>0.7) obtained through the Chemical Vapour Deposition (CVD) of anhydrous FeCl$_3$ has been reported to be very efficient in Selective Catalytic Reaction of nitrogen oxides using Hydro Carbons (HC-
SCR). The high activity of this material has been demonstrated in wide oxygen concentration windows (2-10%) and in the presence of water (10%) when using isobutene as the reductant [52, 66]. A similar performance has been achieved when using n-butane or propane [67]. Furthermore, high activity on Fe/ZSM-5 obtained through CVD of FeCl₃ has been claimed also for the conventional selective catalytic reduction of NO using ammonia [68-70] and for the catalytic decomposition of N₂O [71].

Besides CVD of anhydrous FeCl₃, alternative methods with the aim of synthesizing highly iron loaded ZSM-5 have been reported in the literature. These include aqueous ion-exchange using FeCl₂ [72, 73] FeCl₃ [71, 74], or FeSO₄.7H₂O [75]. The synthesis in a aqueous solution with ferrous oxalate as precursor has led to results comparable to those obtained through the CVD of FeCl₃, with respect to both the iron loading and the catalytic activity towards HC-SCR. Nevertheless, the oxalate technique has shown lack of reproducibility, the reason being the difficulty in preventing the precipitation, during the synthesis, of neutral FeC₂O₄ complexes onto the pore mouths of the zeolite [76, 77]. However, the use of FeCl₃ in its gaseous form has avoided the contact between the ZSM-5 support and the moisture always present in the precursor. It prevents the formation of large iron hydroxide and oxide cluster [74]. The result of the CVD is the highest possible dispersion of extra-framework iron at the acidic exchange positions of the lattice, coupled with a very high reproducibility of the synthesis.

Figure 2.25 shows a possible mechanism of the α-site formation; formation of a binuclear iron complex A via both a synthesis and post-synthesis of the zeolite was suggested [69]. Fe atom was migrated from tetrahedral positions or an external Fe insertion using solid ion exchange, sublimation, CVD. The existence of such complexes was investigated for various structure including Fe/ZSM-5, Fe-silicalite and Fe-β by many authors [78-82]. Then complex A will be transformed into a reduced complex B by oxygen desorption. The process of the α-site formation and Fe²⁺ stabilization appeared to depend on the chemical composition of the matrix and post-treatment methods. The reduced iron atoms of complex B appear to be inert to dioxygen. However, they are readily oxidized at elevated temperatures by nitrous oxide into complex C to give adsorbed O’ species. This
reversible redox transition \( \text{Fe}_a^{2+} \leftrightarrow \text{Fe}_a^{3+} \) between complexes B and C is considered to provide a selective transfer of oxygen atoms from \( \text{N}_2\text{O} \) to hydrocarbon molecules to be oxidized.

\[ \text{complex A} \quad \text{complex B} \quad \text{complex C} \]

A remarkable specificity of \( \text{N}_2\text{O} \) is proved to relate to a particular state of anion radical oxygen species \( \text{O}_a^- \) (called \( \alpha \)-oxygen), which forms on the \( \alpha \)-sites from \( \text{N}_2\text{O} \), but cannot form from \( \text{O}_2 \). A number of thorough studies were devoted to investigation of properties of \( \alpha \)-oxygen including its reactivity tests, IR-spectroscopy isotope labelling, and step-response experiments [82-85].

Among the specific features of \( \alpha \)-oxygen, its very high reactivity seems to be the most remarkable one. For example, it easily oxidizes various organic molecules, including methane, even at room temperature. This allows one to conduct a single turn-over synthesis of, e.g., phenol according to the following scheme. This scheme includes first the \( \alpha \)-oxygen loading (Equation 2.14). Then, after the reactor cooling, the \( \alpha \)-oxygen interaction with benzene is allowed at room temperature (Equation 2.15). The phenol product can be finally extracted from the catalyst surface, e.g., with methanol (Equation 2.16). In all experiments of this type, the extract analysis revealed nearly the theoretical yield of phenol and no other products were detected. These results approve clearly the \( \alpha \)-oxygen participation, which is further confirmed by using the \(^{18}\text{O}_a \) isotope [83, 86].
In view of this situation, Solutia suggested use of waste nitrous oxide for the oxidation of benzene to phenol, incorporating this reaction as a key stage in a new modified adipic acid production scheme [87]. This scheme also starts with benzene which is first oxidized to phenol, and only then is subjected to hydrogenation. Nitrous oxide, produced at the last stage, returns to the front end of the overall process closing the cycle.

The global N₂O emission from adipic acid plants is not sufficient to produce 9 MMT phenol per year. Phenol needs technological processes for the of nitrous oxide synthesis at the unit capacity up to 100 KT/y.

2.4.5 Deactivation of zeolites

The formation of coke deposits leading to catalyst deactivation has been a challenge for catalytic technology in many hydrocarbon processes. Meloni et al. [88] reported catalyst deactivation derived mainly from the decomposition-condensation of phenol onto acid sites, the stronger being the latter, the quicker being the coking rate. In other words, surface acidity was not responsible for activity in the main reaction, but it was heavily involved in catalyst deactivation by coking. Diepen et al. [89] presented different
methods for minimising catalyst deactivation, by tailoring catalyst properties and process operations as well as reactor configurations suitable for the regeneration of deactivated catalysts. Their work showed catalyst deactivation can be caused by (i) decrease in the number of active sites, (ii) decrease in the quality of the active sites, and (iii) decrease of accessibility of the pores space. Panov et al. [90] reported deactivation resulted from decreasing the number of active sites on the catalyst. At the same time, the activity of a single active site was found to remain constant. Perathoner et al. [91] found two possible pathways of carbonaceous species. First through intermediate further hydroxylation of phenol, and then through coupling of phenol with benzene or another phenol molecule. This second pathway is the dominant mechanism of formation of the carbonaceous species, although the relative rate of the two pathways depends on the zeolite characteristics and iron loading. It is also suggested that the second pathway depends on the strong chemisorption of phenol, probably on Lewis acid sites, which hinders the fast back-desorption of phenol out of the zeolite channels and thus favours the formation of carbonaceous species. Regeneration can be done using O₂ and N₂O and a complete restoration of catalytic activity required the removal of 30-35% and 60-65% for N₂O and O₂, respectively [90].

Figure 2.27 Schematic representation of coking and generation of ZSM-5: (A) initial sample before reaction; (B) the coke sample after reaction; (C) the sample after regeneration [90].

The understanding of different issues related to coke, such as formation mechanisms, location, structure, is needed in order to develop catalysts generating less coke and with higher coke tolerance, and to develop more efficient regeneration process.
References

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5. M.A. Cesar, PEP review 97-6 “one-step phenol from benzene by the AlphOx process (1997)”


33. H. Gao, J.Y.S. Lin, Y. Li, and B. Zhang, "Electroless plating synthesis, characterization and permeation properties of Pd–Cu membranes supported on ZrO2 modified porous stainless steel" J. Memb. Sci. 265 (2005) 142-152


3.1 Experimental setup for the catalytic membrane reactor

This work was initially based on reproducing the data of Niwa et al. [1]. Their work was an attempt to produce phenol from benzene in one step using a palladium membrane. This chemistry might be commercial from an industrial point of view if the conversion of benzene to phenol is achievable in one step.

3.1.1 Fabrication of membrane

A porous stainless steel (PSS) membrane was used in this study. The advantages of PSS supports over porous, vycor glass, ceramic, and alumina, are the resistance to cracking, the thermal expansion coefficient of PSS, operability at high pressure, better mechanical strength, and sealability.

Electroplating, electroless plating, chemical vapour deposition and sputtering are major techniques used for the deposition of Pd. Using electroless plating shows more benefit because of uniform deposition and very simple equipment. The thickness of a dense Pd film depends strongly on the morphology, roughness and size of the largest pores of the substrate surface.

3.1.1.1 Porous stainless steel (PSS) supports

Porous 316L stainless steel supports were purchased from Mott Metallurgical Corporation and Fuji Filter Company. Both 0.2 (Mott) and 0.5 (Fuji plate) μm grade supports were used in this work. Since the supports were originally used for filtering proposes, the grade of the support was determined by the rejection particle size. The
supports were called a 0.2 µm grade support, when 95% of the 0.2 µm size particles were rejected by the support during filtration.

Fuji plate is a porous sheet integrated at the micro-structure level. Several protective and back up layers are combined with a fine mesh by vacuum sintering in which pore size is controlled precisely. It has unique properties and is used for many applications in various industrial fields. According to the manufacturer, the grade of the PSS was 0.5 micron with different layers consisting of a supporting layer, a distribution layer, a particle size control layer, and a protective layer. Figure 3.1 shows the schematic and Scanning Electron Micrographs (SEM) pictures of a typical grade 0.5 micron PSS. There are a number of holes on the surface with the dimension around 7 µm.

![Figure 3.1 Scanning electron micrographs of 0.5 micron grade PSS support (Fuji plate).](image)

Figures 3.2 shows SEM images of 0.2 µm grade PSS support. According to manufacturer’s data sheet the average pore size was around 2.1 and 2.5 µm. However, it was observed much larger pores on the surface of support. Therefore, thick layers of
palladium were required to close the large pores on the surface independent of the average pore size of the support.

![Figure 3.2 SEM pictures of 0.2 micron grade PSS support (Mott).](image)

Tube supports were prepared by welding or connecting by fitting to each end of a porous tube, a non-porous stainless steel tube.

![Figure 3.3 Schematic of PSS tube welded to SS tubes.](image)

### 3.1.1.2 Cleaning PSS supports

An important characteristic of plating palladium on the PSS is the strength of the bond that can develop between the base stainless steel and the palladium layer. Metal to metal bonds with high adhesion values require thorough surface preparation to present a clean and optimally rough surface structure. Foreign contaminants (grease, oil, dirt, corrosion products, and others) should be completely removed from the stainless steel surface. This was achieved by mechanical treatment (sandpaper, stainless steel brush, etc.) and cleaning the PSS in an ultrasonic bath with alkaline solution at 60°C followed by rinsing in tap water, deionized water, and isopropanol. The alkaline cleaning solution consisted of a combination of alkaline sodium compounds such as hydroxide, carbonate, phosphate,
and organic detergent. The roughness of the stainless steel surface was increased by a 5 minutes treatment in concentrated hydrochloric acid, followed by water rinsing. Such a treatment also provided the pre-activation of the support surface. The rust on the surface caused by the hydrochloric acid treatment was removed by diluted (40%) phosphoric acid.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Concentration (g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₃PO₄·12H₂O</td>
<td>45-70</td>
</tr>
<tr>
<td>NaOH</td>
<td>45-60</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>65-90</td>
</tr>
<tr>
<td>Anionic and Cationic Detergent</td>
<td>1-5</td>
</tr>
</tbody>
</table>

3.1.1.3 Formation of an oxide barrier layer on PSS

After cleaning, the PSS supports were oxidized in a high temperature furnace. A controlled in situ oxidation of the porous stainless steel prior to plating, produces an oxide layer which acts as a diffusion barrier between the Pd and the PSS. The heating and cooling rate were kept constant at 3°C/min. The supports used in this study were oxidized at 600°C and 900°C for desired amount of time.

3.1.1.4 Surface activation

The membranes went through a surface activation prior to the electroless plating. The purpose of the surface activation was to seed the PSS surface with palladium metal, which during the electroless plating initiated the autocatalytic process of reducing the metastable Pd salt complex on the target surface which is described by Sn⁺² + Pd⁺² → Sn⁺⁴⁴ + Pd⁰. The activation procedure consisted of successive immersion in an acidic bath SnCl₂ (sensitizing) followed by an acidic PdCl₂ bath. After immersion in the SnCl₂ bath,
A gentle rinsing with deionized water was used. Rinsing with 0.01M HCl and then with water was carried out after immersion in the PdCl₂ bath. The 0.01M HCl solution was used to prevent hydrolysis of palladium ions. The typical composition of the activation bath is presented in Table 3.2. During rinsing with deionized water after immersion in the acidic SnCl₂ bath, the partial hydrolysis of tin ions took place from soluble product, Sn(OH)₁.₅Cl₀.₅ and other more complicated hydroxyl chlorides. The composition, structure, and thickness of this layer depended on the ratio HCl/SnCl₂, support surface structure, roughness and shape, and the hydrodynamic regime of rinsing.

An excess of tin ions on the target surface of the porous stainless steel can create a loose (crumbly), easy to peel layer, while a deficiency of tin ions can lead to nonuniform seeding of the palladium nuclei. The distribution of catalytic centres for autocatalytic palladium ion reduction must be dense and uniform at an optimum concentration of tin ions on the surface. If the quality of the activated layer was unsatisfactory, it was removed in an ultrasonic bath with 1M HCl and activation procedure was repeated.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Sn Solution</th>
<th>Pd Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitizing Solution</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SnCl₂·2 H₂O (g/l)</td>
<td>1.0</td>
<td>---</td>
</tr>
<tr>
<td>HCl 37% (ml/l)</td>
<td>1</td>
<td>---</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>20</td>
<td>---</td>
</tr>
<tr>
<td>Duration (min)</td>
<td>5</td>
<td>---</td>
</tr>
<tr>
<td>Activation Solution</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PdCl₂ (g/l)</td>
<td>---</td>
<td>0.1</td>
</tr>
<tr>
<td>HCl 37% (ml/l)</td>
<td>---</td>
<td>1</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>---</td>
<td>20</td>
</tr>
<tr>
<td>Duration (min)</td>
<td>---</td>
<td>3·5</td>
</tr>
</tbody>
</table>
3.1.1.5 Electroless plating of Pd

Figure 3.4 shows that PSS tubes were coated vertically to release gases, which was produced in electroless process, from plated area. The plating solution was prepared according to Table 3.3. The hydrazine, reducing agent was added just prior to plating. The plating solution was renewed every 90 to 120 min. after deposition was completed, then the membrane was left to cool to room temperature and dried. After each drying, the weight and helium flux were measured. The weights gain before and after the plating was used to determine the thickness of the membrane.

<table>
<thead>
<tr>
<th>Table 3.3 Chemical composition of the plating solution.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chemicals</strong></td>
</tr>
<tr>
<td>Pd(NH₃)₄Cl₂.H₂O (g/l)</td>
</tr>
<tr>
<td>AgNO₃ (g/l)</td>
</tr>
<tr>
<td>Na₂EDTA.2H₂O (g/l)</td>
</tr>
<tr>
<td>NH₄OH (28%) (ml/l)</td>
</tr>
<tr>
<td>H₂NNH₂ (1M) (ml/l)</td>
</tr>
<tr>
<td>pH</td>
</tr>
<tr>
<td>Temperature (°C)</td>
</tr>
</tbody>
</table>

A surfactant added to noble metal electroless plating baths. The surfactant is a polyoxyalkylene alkyl ether surfactant and it helps to coat a uniform layer especially in the narrow gaps [2].

\[
\Delta l = \frac{\Delta w \times 10}{A \times \rho}
\]

where \( \Delta l \) is thickness of Pd layer (μm), \( \Delta w \) is weight of coated Pd (mg), \( A \) is plated area (cm²), and \( \rho \) is density of Pd (g/cm³).
Figure 3.4  Electroless plating of PSS.
3.1.2 Experimental setup for Pd membrane system

Figure 3.5 Experimental setup for $H_2$ permeation and hydroxylation reaction.
The support was porous 316L stainless steel tube having an outside diameter 6.35 mm, inside diameter 3.175 mm, and nominal retention size of 0.2 μm. The tube was cut into a 30 mm long segment, and connected to dense stainless steel tubes with 8 mm outside diameter. The porous part of this unit has 6 cm² permeable surface area. The feed gas components were controlled using mass flow controllers (AALBORG, 0-200 ml/min). Benzene feed rate was controlled using a (HARVARD APPARATUS, 0.0004-77 ml/min) syringe dosing system. The reactor was placed in an oven with maximum heating of 300°C and ramp of 0.1°C/min, purchased from RS. The reactor exit gas mixture was sampled and analyzed online. Concentrations of organic compounds were determined via their separation at a capillary column DB-1701 (J&W Scientific) by GC-MS (HEWLETT PACKARD G1800A). The pressure at the H₂ side was controlled using a manual needle valve installed at the exit part of the H₂ line with a pressure gauge (0-10 bar). All the pipes between oven and GC-MS were wrapped in a heating element. All fittings for this system were bought from Swagelok.

A Pd membrane with a different thickness layer was formed on the outer side of the porous tube by electroless plating technique. The quality of the Pd layer was assessed by permeating hydrogen, helium and argon through it. The fluxes of the gases through the Pd membrane were measured by pressurizing of the shell side with the gas under study such that the gas permeated through the palladium membrane from the shell side to the tube side. Flux can be changed by Pressure difference (through the shell and tube side), operating temperature, and properties of the membrane. Permeation measurements for hydrogen, helium, and argon were carried out at 200°C by using the reactor shown in Figure 3.5. The feed gas flowed through the shell side of the membrane and the permeate gas was collected on the tube side. The permeate side pressure 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.

Hydroxylation reaction was carried out in the same system (Figure 3.5) at 150 – 250°C and products were analysed by GC-MS. Benzene, oxygen, and helium were fed at
atmospheric pressure to the tube side. Then, permeated hydrogen was reacted with benzene and oxygen to produce phenol.

3.1.3 Characterization of membranes by SEM and EDX

The morphology of the membrane was observed using scanning electron microscopy equipped with an EDX light element detector for qualitative and quantitative analysis (OXFORD INSTRUMENTS INCA System). SEM specimens of the metal deposited on the PSS supports were cut using a SiC saw and mounted with phenolic powder in a Smithells II mounting press. The resulting samples were ground with SiC papers with increasing grain fineness from 80 to 400 grit. Grinding was performed using a STRUERS grinder-polisher, the STRUERS Tgra Pol-25 automatic polisher was used to polish the samples to 1 μm over a few hours.

3.2 Experimental setup for the plug-flow reactor

3.2.1 Catalyst preparation

Iron zeolites can be prepared by adding different iron salts at the synthesis stage, Hydrothermal Synthesis (HS), or by its post synthetic introduction such as Chemical Vapour Deposition (CVD), Solid State Ion Exchange (SSIE), and Liquid Ion Exchange (LIE) [3]. The samples studied in the present work were prepared by HS, CVD and LIE.

3.2.1.1 Preparing Fe/ZSM-5 by HS

Typically Fe/ZSM-5 with composition of Si/Al ratio of 25 and 0.5 wt% Fe was prepared by using hydrothermal method shown in Figure 3.6. Tetraethylorthosilicate (TEOS) as a Si source, Al(NO₃)₃ and Fe(NO₃)₃ as sources of Al and Fe respectively, and
tetrapropylammonium hydroxide (TPAOH) as a template was used. Solution A was prepared by adding 20.5 g of TEOS drop-wise to a mixture of 0.8 g NaOH, 10.2 g of TPAOH (20% water solution) and 67 g of distilled water while stirring. Solution A, while stirring, was added drop-wise to the Al(NO$_3$)$_3$ and Fe(NO$_3$)$_3$ solution (solution B) prepared by dissolving 0.375 g of Al(NO$_3$)$_3$.9H$_2$O and 0.235 g of Fe(NO$_3$)$_3$.9H$_2$O in 13 g of distilled water. The final solution was kept at 60°C for 2 hours to remove the excess of ethanol formed due to hydrolysis of the TEOS. The gel was then placed into an autoclave with a Teflon lining, and held in a static air oven at a constant temperature of 170°C for 5 days for hydrothermal synthesis. Once the synthesis was completed, the autoclave was cooled, and crystalline material was separated by filtration and washed with abundant quantities of distilled water and dried at 110°C over night. Then the catalyst was calcined in flowing air at 500°C for 10 hours to burn-off the template. The sample was then converted into H-form by three consecutive liquid-ion exchanges with NH$_4$NO$_3$ 0.1M over night and subsequent air calcination at 500°C for 5 hours. Activation was completed in inert gas, oxygen, vacuum or steam at temperatures of 700-900°C during 5 hours.

![Figure 3.6](image-url) *Experimental setup for HS.*

### 3.2.1.2 Preparing Fe/ZSM-5 by CVD

Fe/ZSM-5 was prepared via the FeCl$_3$ CVD method (Figure 3.7) described by Chen and Sachtler [4]. For the CVD exchange a quartz reactor was used. 1.5 g of the HMFI,
purchased from Süd-Chemie, were loaded into the reactor and flushed overnight under He (40 ml/min) at 300°C. The temperature was then lowered to 30°C under the same He flow. Then 0.45 g of anhydrous FeCl₃ was loaded into the reactor. After being reconnected to the He line (30 ml/min), the reactor was heated to 330°C and kept at this temperature for at least half an hour. HCl, formed during the reaction of the sublimed FeCl₃ with the Bronsted sites of the support, was absorbed in 100 ml of 0.05M NaOH solution for titration. After completion of the iron loading, the temperature was lowered to 30°C. Then this catalyst was washed with 1000 ml of double distilled deionised water for 30 minutes and dried for 24 hours in air at 70°C. Samples were heated with an extremely low temperature ramp (0.5°C/min) to 200°C. At this temperature, O₂ were added to He flow while heating was continued to 550°C. After 3 hours at 550°C the temperature was degreased to 30°C.

Commercial zeolite H-MFI was purchased from Süd-Chemie. FeCl₃ solution 0.1M was prepared using double distilled water warmed to 50°C. Then 5 g of catalyst was weighed and added to the stirred FeCl₃ solution over a period of 2-24 hours. Then the zeolites

Figure 3.7 Experimental setup for CVD.
were dried at 120°C over night. The catalyst was placed in a 7 mm diameter stainless steel tube and the temperature increased to 550°C with a ramp of 1°C/min. At 550°C air was fed to the reactor for 4 hours. Then He replaced the air and the temperature was raised to 600°C with the same ramp. The catalyst was treated in a steam atmosphere for 1 hour and then cooled to room temperature with a ramp of 1°C/min. Acid treatment was done in two steps. First the catalyst was reacted with Na₂S₂O₄ for 15 min at 70°C and second with HNO₃ for 30 min at 70°C. The sample was then filtered and washed twice with double distilled water for 30 minutes. Finally, the catalysts were dried at 120°C for 24 hours.

3.2.2 Experimental setup for plug-flow reactor

The experimental setup for evaluating catalyst activity in the decomposition of N₂O and benzene oxidation by N₂O to phenol using a plug-flow reactor is shown in Figure 3.8. The feed gas components were controlled using mass flow controllers (AALBORG, 0-200 ml/min). Benzene and water feed rates were controlled using a (HARVARD APPARATUS, 0.0004-77 ml/min) syringe dosing systems. The reactor was placed in a furnace with maximum heating of 1100°C and ramp of 0.1°C/min, purchased from ELITE THERMAL SYSTEM model TSH12/50/300-2416CG. The reactor exit gas mixture was sampled and analyzed online. Concentrations of organic compounds were determined via their separation in a capillary column DB-1701 (J&W Scientific) by GC-MS (HEWLETT PACKARD G1800A). All the pipes between oven and GC-MS were wrapped by heating element. All fittings for this system were bought from Swagelok. Benzene and N₂O were fed at atmospheric pressure using plug-flow reactor to produce phenol. Reactions were carried out at 350 – 450°C and products were analysed by GC-MS.
Figure 3.8 Experimental setup for hydroxylation of benzene using $N_2O$. 
3.2.3 Characterization of Fe/ZSM-5

In the literature, Fe/ZSM-5 zeolite is comprehensively characterized for the structure of iron sites such as valence and coordination state of iron ions by using EPR, UV/VIS-DRS, XANES and EXAFS, Mössbauer spectroscopy, and XPS. Structural properties and surface acidity were investigated by Solid-state NMR, IR or FT-IR and NH3-TPD measurements. The Fe/ZSM-5 were also investigated by X-Ray Diffraction, Inductivity Coupled Plasma emission spectroscopy (ICP), Atomic absorption spectroscopy (AAS) and Nitrogen adsorption.

3.2.3.1 ICP and AAS

The determination of the bulk elemental composition of zeolites is of importance to verify the synthesis formulations, the bulk Si/Al ratio, the cations concentration, degree of ion exchange and the detection of contaminant elements such as impurities and poisons. The elemental composition of the zeolites was determined by using ICP-AES and AAS VARIAN SPECTRA AA.200. ICP is probably the most widely used technique for the determination for the determination of the elemental composition of zeolites. In general, the sensitivity of ICP is better than that possible with conventional flame AAS for most refractory like metals.

Both conventional ICP-AES and AAS require that the sample be introduced as a liquid, thus decomposition is necessary prior to analysis and similar preparation scheme apply for both techniques. Samples were digested using a sodium peroxide before analysis and for determination of sodium in samples an HF/HNO3/HCL04 was used before analysis.

3.2.3.2 Nitrogen physisorption

Surface area and pore size distribution of the catalyst samples were investigated by nitrogen physisorption. The Brunauer-Emmett-Teller (BET) method, based on multilayer
N₂ adsorption, is inadequate to describe the adsorption process in medium-pore zeolites due to the restricted pore size using Micrometrics ASAP 2010. The measurements were performed at 77 K, in the pressure range 0-1 bars, after degassing the samples in vacuum at -200°C for 16 hours. The first stage in the interpretation of a nitrogen isotherm is the identification of the physisorption mechanism which is monolayer-multilayer adsorption, capillary condensation or micropore filling. Capillary condensation is involved as a secondary process in the filling of mesopores (pore width in the range 2-50 nm). The BET method cannot be used to provide a reliable evaluation of the surface area if the solid contains pores of molecular dimensions such as narrow micropores. Furthermore, with such materials, it is necessary to use different probe molecules to determine the pore size distribution.

3.2.3.3 XRD

The crystalline fingerprint of the zeolite support was compared after each synthesis step to visualize significant lattice damage or formation of large particles of iron oxidic or oxo-hydroxidic crystalline phases. X-Ray Diffraction (XRD) patterns were recorded by means of a Brucker D8 powder diffractometer equipped with a Solex energy dispersive detector. The radiation used was Cu Kα1 (λ=1.5418 Å).

3.2.3.4 FT-IR spectroscopy

Interaction of the iron species with the Brønsted and the Silanol sites of the support was investigated using Fourier Transform Infrared Spectroscopy (FT-IR). The KBr pellet technique is frequently used for investigations of vibration of the framework. Samples, pressed into self-supporting wafers, were heated in situ under He with a temperature ramp of 2°C/min to 350°C. Transmission infrared spectra were recorded under He at 350°C on a Shimatzu 8400 S spectrometer using a DTGS detector. Hydroxyl groups attached to zeolite structures are most important for the chemistry of these materials. Vibrations of the frameworks of zeolite give rise to typical bands in the mid and far
infrared. Also, extra-framework species such as $\text{Al}_x\text{O}_y^{n^+}$, which occur upon dehydroxylation, may be detected by this technique.

### 3.2.3.5 HR-TEM/EDX

Imaging of the samples was obtained through High-Resolution Transmission Electron Microscopy (HR-TEM). For this propose a JOEL EM11020 INCA System electron microscope was used with a field-emission gun operated at 300 kV as a source of electrons. Samples were positioned on a carbon micro grid, supported on copper, by placing a few droplets of a suspension of ground samples in ethanol. The grid was dried at ambient conditions. When possible, identification of visible Fe-containing crystalline aggregates was performed on the basis of the observed lattice d-spacing. These were derived from high-resolution images and compared with literature XRD data. Elemental composition was obtained by Energy Dispersive analysis of X-rays (EDX) performed through a LINK EDX system.

### 3.2.3.6 X-ray Photoelectron Spectroscopy

Oxidation states of iron species in Fe/ZSM-5 zeolite are often investigated by X-ray Photoelectron Spectroscopy (XPS). This technique is surface sensitive and gives information about the external surface region of the material. Thus, it was found that Fe species which are present inside the zeolite pores could not be seen by this technique. In this technique, the binding energies of photoelectrons, liberated from the electronic core shells of Fe-atoms by X-rays are scanned. Depending on the valance state of surface Fe species, the Fe$_{2p3/2}$ peaks appear at different binding energies. The binding energies of the Fe$_{2p3/2}$ usually reported around $\sim$711 eV and $\sim$ 708 eV were attributed to Fe$^{3+}$ and Fe$^{2+}$ ions respectively [5, 6].

The experiments were performed by using an E.S.C.A spectrometer from SCIENTIFIC LTD at room temperature under $10^{-7}$-$10^{-8}$ Torr, using Al $K_a$ radiation.
3.3 Calibration of equipment

In order to determine quality and quantity of reactants and products and also set the flow rate of the gases and liquids at the required values, the GC-MS and MFCs were calibrated. The allocation of these MFCs is shown in Figure 3.5 and 3.8 which give the experimental setups for the hydroxylation of benzene using Pd-membrane system and using N$_2$O in the presence of zeolite as a catalyst, respectively. The GC-MS was calibrated for water, benzene, phenol, catechol, hydroquinone, and resorcinol. A Different concentration of each chemical was made. Then all solutions were introduced to the GC-MS using a 1 μm syringe and these pick areas determined. The experiments were repeated three to five times for each concentration of each solution.
Figure 3.9 Calibration of GC-MS.
MFCs give a reading which indicates how much of the valve inside these controllers is opened and hence how much gas is flowing through this opening. Each gas was allowed to enter to the specified MFC from its source which usually was a gas cylinder. The MFC opening was set at a certain percentage and the exit line from MFC was connected with a digital flow meter. Therefore, in order to obtain the gas flow rate, the MFC was opened at different reading and a specified volume was measured. The time measurements were repeated three to five times at each reading of the MFC.

![Graphs showing gas flow rates](image-url)
Figure 3.10 Calibration of MFCs.
References


CHAPTER 4

RESULTS AND DISCUSSION

PART 1
HYDROXYLATION OF BENZENE USING Pd MEMBRANE

One of the most difficult fields of catalytic chemistry is selective oxidation of hydrocarbons. Niwa and co-workers reported a one step catalytic process to convert benzene to phenol using Pd membrane in the presence of oxygen and hydrogen [1]. This work is an attempt to reproduce Niwa and his group’s data. For efficient generation of active oxygen species, H$_2$ and a mixture of O$_2$ and benzene are separately supplied to both sides of a Pd membrane. The active oxygen species on Pd are reductively produced by the reaction with the active hydrogen species, which permeates into the Pd membrane from the opposite side. Then the adsorbed benzene on the Pd reacts with the active oxygen species, and is thus directly converted into phenol. The advantages of this reactor include (i) no need for expensive oxidizing reagents, such as N$_2$O and H$_2$O$_2$, (ii) avoidance of the risk of explosion, because O$_2$ and H$_2$ are supplied separately rather supplied as a mixture, and (iii) efficient generation of dissociatively activated hydrogen species on the surface of Pd owing to the direct supply through the membrane.

If this Pd membrane reaction system is to be a commercially available system, the stability of the membrane for long reaction periods is crucial. The application and stability of a Pd membrane reactor system at high temperature (>600 K), compared to the application of a Pd membrane at low temperature (<573 K), has been limited because two different palladium hydride phases with different unit cell sizes coexist below 566 K, causing Pd membranes to become brittle.

4.1 Fabrication of membrane

Pd/PSS membranes, welded or connected at both ends to non-porous stainless steel tubes, can be assembled and integrated into a process stream very easily. The long-term stability of the produced composite membranes is limited by the intermetallic diffusion of support elements (i.e. Fe, Cr, and Ni) into the dense membrane layer. In order to prevent
intermetallic diffusion, an additional oxide layer between the metal support and the Pd layer, forms. Pd tubes were then coated by an electroless plating technique on a PSS tube covered with a Pd nuclei layer which provides seeds for electroless plating.

4.1.1 Porous stainless steel support

The grade and pore distribution of the porous supports greatly influence the final membrane thickness and therefore the performance of Pd membranes. Porous 316L stainless steel supports were purchased from Mott Metallurgical Corporation (0.2 μm grade) and Fuji Filter Company (0.5 μm grade).

Fuji plate is a porous sheet integrated at the micro-structure level. Several protective and back up layers are combined with a fine mesh by vacuum sintering in which the pore size is controlled precisely. According to the manufacturer, the grade of the PSS was 0.5 micron with different layers consisting of a supporting layer, a distribution layer, a particle size control layer, and a protective layer. In this study PSS was ordered without the protective layer to give the possibility of a better coating process. Mott porous metal fabrication begins with pregrading metal powders using precise particle size distributions. The powders are then compressed into desired shapes and followed by sintering in control atmosphere furnaces at desired temperatures. The pores and distribution for 0.5 μm grade Fuji plate and 0.2 μm grade Mott are compared in Figure 4.1.
Figure 4.1  SEM micrographs of 0.5 μm grade Fuji plate (A & B) and 0.2 μm Mott (C & D) PSS supports.

There are a number of uniform holes on the surface of Fuji plate with the dimension around 7 μm while different pore diameters were observed in the Mott PSS support. Figure 4.2 shows the pore size distribution of 0.2 μm grade PSS support (according to the manufacturer information). Although the average pore size was around 2.1-2.5 μm, much larger pores could be observed on the surface of the support. Therefore, thick layers of palladium were required to close the large pores on the surface. The final thicknesses of the dense Pd membrane were 23-27 μm on 0.2 μm grade Mott supports and 32-35 μm on 0.5 μm grade Fuji plate supports.
Figure 4.2 Pore size distribution of 0.2 μm grade Mott PSS support.

The main differences between Pd/PSS and other support materials such as ceramic and alumina are the thickness of dense Pd layers that can be achieved and the temperature range at which the membranes can be operated. Indeed the thickness of a dense Pd film depends strongly on the morphology, roughness and size of the largest pores of the substrate surface. Ceramics may be synthesized with a relatively smooth surface layer containing very uniform small pore systems. Therefore very thin dense Pd membranes can be obtained (e.g. 1-6 μm) using ceramic supports. Furthermore, there is no intermetallic diffusion between the ceramic support and the Pd layer. There are a number of advantages for using PSS supports including better mechanical strength, operation at high pressures, resistance to cracking, ease of module fabrication and sealing, and similar thermal expansion coefficients of Pd and PSS result in better mechanical properties of the membrane during temperature cycling. Table 4.1 shows influence of the substrate morphology and pore size on the final thickness of dense Pd/PSS membranes.

| Table 4.1 Comparison of the properties of Fuji plate and Mott PSS supports. |
|---------------------------------|----------------|----------------|
| 0.5 μm grade Fuji plate         | 0.2 μm grade Mott |
| Thickness of PSS (mm)           | 1.8            | 2              |
| Initial He flux (cm³/cm² min)   | 1550           | 701            |
| Final He flux (cm³/cm² min)     | ~ 0            | ~ 0            |
| Final thickness of Pd (μm)      | 32-35          | 23-27          |
4.1.2 Pre-treatment of PSS supports

The PSS supports were cleaned in an ultrasonic bath with alkaline solution at 70°C for 30 minutes. This cleaning procedure was followed by sequentially rinsing in tap water, deionized water and isopropanol. Finally the supports were dried at 120°C over night. The rust on the surface was removed by diluted (40%) phosphoric acid.

![SEM micrographs of the Mott (A) and Fuji plate (B) supports after cleaning.](image)

4.1.3 Intermetallic diffusion barrier

To reduce intermetallic diffusion between the metal support and the Pd layer, and thereby improving the stability of the Pd/PSS composite membrane, Ma et al. [2] used a controlled in situ oxidation of the porous stainless steel prior to plating to produce an oxide layer to act as a diffusion barrier between the Pd and the PSS. Membranes produced by this method have been shown to be stable for over 6000 h in the temperature range of 350-450°C [2, 3]. The objective of this research is to investigate the effects of temperature on the formation of the intermetallic diffusion barrier layer by the controlled in-situ oxidation method for Pd/PSS membranes. The obtained information provided a better understanding of the intermetallic diffusion at the interface between the membrane layer and the metal substrate which is essential for making the Pd/PSS membranes with long term thermal stability. Figure 4.4 shows the SEM pictures of a typical grade 0.2 μm grade Mott PSS after oxidation in 400°C, 600°C, and 900°C.
Figure 4.4 SEM micrographs of Mott PSS supports, (A and a) oxidized at 400°C; (B and b) oxidized at 600°C; (C and c) oxidized at 900°C.
As the oxidation temperature was increased, the weight gain increased indicating the formation of more oxide at higher temperatures. The formation of greater quantities of oxide gave a higher resistance to the He permeation.

Table 4.2 Percent weight gain and flux change after oxidation for Mott PSS supports.

<table>
<thead>
<tr>
<th>Tube</th>
<th>Oxidation (°C)</th>
<th>Δm (%)</th>
<th>Thickness (μm)</th>
<th>Flux, J (cm³/cm²min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>0</td>
<td>0</td>
<td>701</td>
</tr>
<tr>
<td>2</td>
<td>400</td>
<td>0.035</td>
<td>--</td>
<td>700</td>
</tr>
<tr>
<td>3</td>
<td>600</td>
<td>0.78</td>
<td>0.2-0.3</td>
<td>565</td>
</tr>
<tr>
<td>4</td>
<td>900</td>
<td>4.69</td>
<td>1-6</td>
<td>27</td>
</tr>
</tbody>
</table>

Figure 4.5 SEM micrographs Fuji plate PSS supports (A) oxidized at 600 °C; (B) oxidized at 800 °C; (C) cross section oxidized at 600° C; (D) cross section oxidized at 800° C.
Figure 4.5 shows the cross-sectional SEM micrograph of a sample oxidized at 600°C; a dark uniform thin layer was observed throughout the whole support. The EDX spot scan on the surface confirmed that this dark layer was actually the oxide layer. The thickness of this layer was about 0.2-0.3 μm. The SEM micrograph of the sample oxidized at 800°C showed a thicker dark region with a very nonuniform thickness was observed. It could also be observed that the surface of this oxide layer was very crumbly. The thickness of the dark region varied from 1 to 6 μm from spot to spot since the oxide layer was relatively thick.

The oxygen peaks (Figure 4.6) confirm the formation of an oxide layer on the support. It was also observed that the amount of oxygen on the support increased 10 times with higher oxidation temperatures indicating a thicker oxide layer. Among the oxides that can be formed with the elements of stainless steel, Cr₂O₃ 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 H₂ atmosphere. Therefore, it is the most desirable oxide phase for use as a barrier layer to intermetallic diffusion [4].

To check the existence of a Cr-rich oxide on the surface of the samples, EDX spot scan analyse were performed (Table 4.3). The ratio of atomic Cr to atomic Fe on the surface of the supports remained almost constant and essentially the same as the unoxidized sample for the sample oxidized at 600°C, whereas it decreased dramatically for the support oxidized at 800°C indicating an Fe-rich oxide on the outermost layer.
Figure 4.6 Cross sections showing the oxide layer on Fuji plate PSS in (A&B) 600°C, (C&D) 800°C and EDX spot scan in (a&b) 600°C, (c&d) 800°C.
However, it was difficult to determine the compositions of the oxide layers for the samples oxidized at 600°C because the thickness of the oxide layer was too thin to be accurately determined due to limitations of the resolution of the EDX. Cr$_2$O$_3$ was likely formed on the samples at these temperatures due to its Low Gibbs free energy. On the other hand, the enhancement of the diffusion of Fe at higher oxidation temperatures could have led to the growth of iron oxide on the chromium oxide layer during oxidation at 800°C [4].

Table 4.3 Elemental composition in an EDX spot scan at (A & B) 600°C, (C & D) 800°C.

<table>
<thead>
<tr>
<th>Element</th>
<th>Sample A</th>
<th>Sample B</th>
<th>Sample C</th>
<th>Sample D</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wt%</td>
<td>atom%</td>
<td>wt%</td>
<td>atom%</td>
</tr>
<tr>
<td>C</td>
<td>19.77</td>
<td>50.21</td>
<td>26.05</td>
<td>59.48</td>
</tr>
<tr>
<td>O</td>
<td>3.50</td>
<td>6.670</td>
<td>2.48</td>
<td>4.25</td>
</tr>
<tr>
<td>Si</td>
<td>2.42</td>
<td>2.63</td>
<td>1.45</td>
<td>1.50</td>
</tr>
<tr>
<td>Cr</td>
<td>13.80</td>
<td>8.10</td>
<td>13.15</td>
<td>6.94</td>
</tr>
<tr>
<td>Mn</td>
<td>0.94</td>
<td>0.52</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>47.71</td>
<td>26.06</td>
<td>47.34</td>
<td>23.25</td>
</tr>
<tr>
<td>Ni</td>
<td>10.06</td>
<td>5.23</td>
<td>9.02</td>
<td>4.21</td>
</tr>
<tr>
<td>Mo</td>
<td>1.08</td>
<td>0.57</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In general, the oxidation process consists of two main steps, surface oxidation and then the oxide scale formation. During the oxide scale formation there are several mechanisms including the diffusion of elements along their respective gradients, the diffusion of oxygen, and oxidation at the metal oxide interface. All these mechanisms may affect the composition and the thickness of the formed oxide layer [5]. The existence of an oxide layer and the growth of this oxide layer with increasing oxidation temperatures have been reported by many authors [6-9].
4.1.4. Activation of PSS supports

The next step in the membrane preparation was surface activation in order to seed the PSS surface with Pd nuclei to initiate an autocatalytic process of the reduction of a complex on the target surface during electroless plating. The activation procedure consisted of successive immersions in an acidic SnCl$_2$ solution (sensitizing) followed by an acidic PdCl$_2$. The activation layer could be considered as a sandwich structure consisting of a number of thin layers, one after each synthesising/activation cycle, with Pd nuclei on the top of each layer. A thicker activated layer resulted in a higher density of Pd nuclei on the support surface. The optimum activated layer was created after 3-6 cycles.

![Schematic of Pd seeds on PSS.](image)

4.1.5 Deposition of Pd and Pd alloy on PSS support

The deposition of Pd on the outside surface of the activated PSS supports was carried out at 60°C by placing the activation PSS support in an electroless plating cell containing the plating solution. The plating cell was in turn immersed in a constant temperature bath. After about 90 minutes, the deposition rate of Pd decreased with the depletion of Pd ions and hydrazine, with a concomitant decrease in the pH of the plating solution. Because of this, the plating solution was replaced every 90 minutes with a fresh solution in order to maintain a stable, high-deposition rate. The membrane was carefully rinsed with deionized water after each plating cycle. After the substrate was coated with Pd, a dense Pd layer was obtained on the surface. Figure 4.8 shows that the deposited Pd particles were spherical and possessed a range of particle sizes, the particles were still packed together to form a dense layer. It was observed that a sufficient thickness of the Pd film
varied with the different supports and was related to the surface morphology. Figure 4.8 shows 0.2 μm grade Mott PSS support which coated with Pd and formed a dense layer after 24 hours. The thickness of the Pd film was calculated from gravimetric measurements according to Equation 3.1.

Figure 4.9 also shows the Fuji Plate substrate with the uniform pores distribution which was resulted in forming a uniform coating layer. 0.5 μm grade Fuji Plate tubes shows bigger pore diameters than Mott 0.2 μm grade and caused in higher coating thickness (32.5 hours plating duration) to achieve a dense layer.

It is also possible to use 0.1 μm grade Mott PSS support which decrease the cost of coating and fabricating the membranes.
Figure 4.8  SEM photographs of: (A) PSS substrate (Mott 0.2 μm grade); (B) after 13.5 hour plating; (C) after 15 hour plating; and (D) after 24 hour plating.
Figure 4.9 SEM photographs of: (A) PSS substrate (Fuji plate 0.5 μm grade); (B) after 13.5 hour plating; (C) after 21 hour plating; (D) after 32.5 hour plating.
Understanding the structure of the plated film was of key importance when preparing the dense membrane. Figure 4.10 shows that electroless deposition of Ag was initiated by foreign nuclei like Pd. SEM pictures show that the complexing ability of EDTA for Ag\textsuperscript{+} was weak, and thus Ag was likely to have deposited immediately upon reaching an active site without diffusing inside the valleys. But Ag could diffuse inside some of the large pores during plating forming bridges and reducing the effective pore size and the final thickness of the dense layer. A Pd-Ag membrane was prepared by a sequencing method, in which after each Pd layer (90 minutes) Ag was coated and this cycle was repeated until the He flux at room temperature was near zero. The Pd-Ag/PSS support was annealed at 600°C in the presence of He for 10 hours with a ramp of 1 °C/min.
Figure 4.10 SEM photographs of: (A) PSS substrate (Mott 0.2 μm grade); (B) after 6 hour plating; (C) after 9 hour plating; and (D) after 14 hour plating.
The He flux was used to check if the Pd layer was dense. The membrane was deemed “dense” when there was no He flux at room temperature under a pressure difference of 1 atm.

Figure 4.11 He flux at 1 atm. difference pressure at room temperature for membranes formed 0.2 μm grade Mott substrate.

It was discussed in section 2.3.2.4 that the use of pure palladium membranes is hindered by the fact that palladium shows a transition form the α-phase (hydrogen-poor) to the β-phase (hydrogen-rich) at temperatures below 300°C and pressures below 2 MPa, which depends on the hydrogen concentration in the metal. Since the lattice constant of the β-phase is 3% larger than that of the α-phase this transition leads to lattice strain and, consequently, after a few cycles to a distortion of the metal lattice. Figure 4.12 shows distortion of the Pd layer introducing a high concentration of H₂ at room temperature.

Figure 4.12 SEM photographs of distortion of the metal lattice after introducing a high concentration of H₂ at room temperature.
4.2 Permeability of Pd/PSS support

To confirm that the Pd/PSS tube was permeable at temperatures lower than 200°C, which is the reaction temperature for hydroxylation of aromatic compounds, the hydrogen permeance was investigated. Figure 4.13 shows the permeation results for Ar, He and H₂.

![Figure 4.13](image)

Figure 4.13 (○) He, (X) Ar, and H₂ fluxes at 200°C.

Figure 4.13 shows a near linear increase of the H₂ flux with increasing pressure according to Equation 4.1.

\[ y = 4.86x - 0.36 \quad \text{Eq. 4.1} \]

According to Equation 4.1 H₂ flux will be 2.07 cm³cm⁻²min⁻¹atm⁻⁰.⁵ or 1.24 m³m⁻²h⁻¹atm⁻⁰.⁵. The experimental value of Hydrogen permeance at different temperatures has been reported by Rothenberger et al. [10]. Figure 4.14 shows that H₂ flux will be approximately 4.4 cm³cm⁻²min⁻¹atm⁻⁰.⁵ which is higher than our result in this study.
Table 4.4 Hydrogen permeation at different temperature [10].

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>H₂ Permeance (m³ / m² h atm⁰.⁵)</th>
<th>H₂ Permeability ((m³ m / m² h atm⁰.⁵) x 10⁶)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>3.47</td>
<td>127.002</td>
</tr>
<tr>
<td>400</td>
<td>5.97</td>
<td>218.502</td>
</tr>
<tr>
<td>500</td>
<td>8.38</td>
<td>306.708</td>
</tr>
</tbody>
</table>

Table 4.4 was used to estimate the activation energy for hydrogen permeation. Equation 4.2 and 4.3 represent the temperature dependence of hydrogen permeance through the Arrhenius relation.

\[
F = F_0 \exp \left( \frac{-E_A}{RT} \right) \quad \text{Eq. 4.2}
\]

\[
\ln(F) = \ln(F_0) - \left( \frac{E_A}{R} \right) \left( \frac{1}{T} \right) \quad \text{Eq. 4.3}
\]

Figure 4.14 shows the Arrhenius relation between the permeance and the temperature based on Equation 4.3. The activation energy of the Pd membrane was found to be 25.72 kJ/mol, which was close to the previously reported values for pure Pd membranes [11].

Figure 4.14 Arrhenius relations between the hydrogen permeance and temperature; (●) Ma et al. [10], (x) predicted by extrapolation of the line to 200°C, (■) experimentally measured in this work.
4.3 Benzene oxidation to phenol with $H_2$ and $O_2$

A prepared porous Pd membrane tube with 25 mm length and 6.35 mm outside diameter was placed in a solid stainless steel cylindrical housing whose outer diameter was 20 mm. In some experiments a solid stainless steel rod was also placed inside the membrane tube to encourage reactants to flow 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. Table 4.5 presents the different flow rate combinations that were used in this study.

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Tube side (ml/min)</th>
<th>Shell side (ml/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Feed flow condition 1</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>Helium</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Oxygen</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Benzene + helium</td>
<td>10 [benzene 20 mol%, He 80mol%]</td>
<td></td>
</tr>
<tr>
<td><strong>Feed flow condition 2</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>Helium</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>Oxygen</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>Benzene + helium</td>
<td>10 [benzene 20 mol%, He 80mol%]</td>
<td></td>
</tr>
<tr>
<td><strong>Feed flow condition 3</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>Helium</td>
<td>10</td>
<td>40</td>
</tr>
<tr>
<td>Oxygen</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Benzene + helium</td>
<td>10 [benzene 20 mol%, He 80mol%]</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.5 Feed flow conditions in hydroxylation of benzene using membrane reactor.
4.3.1 H₂ fed to the shell side

A mixture of hydrogen and helium was fed to the shell side (SS), and benzene with oxygen and helium was introduced into the tube side (TS), as in Figure 3.5.

Table 4.6 shows the measured productivity of phenol and by-products after 1 hour when the O₂ flow rate and temperature were changed. A sharp decrease in the productivity was observed when lower level of the oxygen was fed into the inlet gas mixture at temperatures below 200°C while slightly increase in the productivity was observed at 250°C. It can be seen with increasing the temperature, at the feed composition TS (He, O₂, (He+C₆H₆) 10, 5, 10 ml/min and SS: (He, H₂) 30, 10 ml/min, productivity and selectivity were shown a decrease from 0.31 mmol/h and 80% to 0.08 mmol/h and 65%, respectively. Although, an increase in productivity and selectivity from 0.06 mmol/h and 33.3% to 0.086 mmol/h and 15.1% at the feed composition TS (He, O₂, (He+C₆H₆)) 10, 2, 10 ml/min and SS: (He, H₂) 30, 10 ml/min was observed. It was resulted the highest productivity of 0.31 mmol/h in this study.

<table>
<thead>
<tr>
<th>TS: He, O₂, (He 80 mol%+C₆H₆ 20 mol%)</th>
<th>SS: He, H₂</th>
<th>Temp.</th>
<th>Phenol</th>
<th>Dihydroxybenzenes</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>(ml/min)</td>
<td>(ml/min)</td>
<td>(°C)</td>
<td>(mmol/h)</td>
<td>(mmol/h)</td>
<td>(%)</td>
</tr>
<tr>
<td>10, 5, 10</td>
<td>30, 10</td>
<td>150</td>
<td>0.31</td>
<td>0.062</td>
<td>80</td>
</tr>
<tr>
<td>10, 5, 10</td>
<td>30, 10</td>
<td>200</td>
<td>0.12</td>
<td>0.036</td>
<td>69</td>
</tr>
<tr>
<td>10, 5, 10</td>
<td>30, 10</td>
<td>250</td>
<td>0.08</td>
<td>0.028</td>
<td>28</td>
</tr>
<tr>
<td>10, 2, 10</td>
<td>30, 10</td>
<td>150</td>
<td>0.06</td>
<td>0.02</td>
<td>21</td>
</tr>
<tr>
<td>10, 2, 10</td>
<td>30, 10</td>
<td>200</td>
<td>0.07</td>
<td>0.019</td>
<td>29</td>
</tr>
<tr>
<td>10, 2, 10</td>
<td>30, 10</td>
<td>250</td>
<td>0.086</td>
<td>0.013</td>
<td>32</td>
</tr>
</tbody>
</table>

Productivity of phenol and the amount of water produced during the reaction was decreased with lower O₂ flow rate or O₂/H₂ ratio. High amount of water in Table 4.6 shows most of oxygen and hydrogen was converted to hydrogen peroxide in the presence
of Pd catalyst. Unstable hydrogen peroxide can produce water and oxygen or hydroxyl radical which consumed in hydroxylation of benzene.

4.3.2 All reactants fed to tube side

Table 4.7 shows the productivity when all reactants were introduced to the tube side at 150°C and 200°C. Using this configuration the phenol production was reduced, so the procedure was not studied further.

<table>
<thead>
<tr>
<th>TS: He, O₂, H₂, (C₆H₆ 20 mol%+He 80 mol%)</th>
<th>SS: H</th>
<th>Temp. (°C)</th>
<th>Phenol (mmol/h)</th>
<th>Dihydroxybenzenes (mmol/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(ml/min)</td>
<td>(ml/min)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10, 2, 10, 10</td>
<td>35</td>
<td>150</td>
<td>0.05</td>
<td>0.17</td>
</tr>
<tr>
<td>10, 2, 10, 10</td>
<td>35</td>
<td>200</td>
<td>0.001</td>
<td>0.003</td>
</tr>
</tbody>
</table>

4.3.3 Using Fe/ZSM-5 as a second catalyst

Influence of using second catalyst in Pd membrane reactor was investigated. The Pd membrane tube was packed with the Fe/ZSM-5. A mixture of gases was introduced to the tube side or shell and tube side at 300°C. Table 4.8 shows that the productivity was not affected by introducing hydrogen in the shell side or in the tube side but, after replacing O₂ and H₂ with N₂O higher productivity (0.32 mmol/h) was observed.
Table 4.8 Using Fe/ZSM-5 as a second catalyst in hydroxylation reaction.

<table>
<thead>
<tr>
<th>TS: He, O₂, H₂, (C₆H₆ 20 mol%+He 80 mol%)</th>
<th>SS: He, H₂</th>
<th>Temp. (°C)</th>
<th>Phenol (mmol/h)</th>
<th>Dihydroxybenzenes (mmol/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(ml/min)</td>
<td>(ml/min)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10, 2, 10, 10</td>
<td>35, 0</td>
<td>300</td>
<td>0.065</td>
<td>0.23</td>
</tr>
<tr>
<td>10, 2, 0, 10</td>
<td>30, 10</td>
<td>300</td>
<td>0.060</td>
<td>0.12</td>
</tr>
<tr>
<td>10, 2 (N₂O), 0, 10</td>
<td>30, 0</td>
<td>300</td>
<td>0.320</td>
<td>0.05</td>
</tr>
</tbody>
</table>

4.3.4 Using Pd membrane coated by Mo

The Pd/PSS membrane coated with Mo by CVD was placed in the stainless steel cylinder. Table 4.9 shows the result of using Mo as a second catalyst in the Pd/PSS tube at 150°C. In a second experiment a stainless steel tube was placed inside the membrane to reduce the flow cross section and thereby promote contact of the catalyst surface by the reactants and increase the reaction area per unit mass of reactants.

Table 4.9 Productivity of phenol using Mo as a second catalyst. A; without stainless steel tube, B; with stainless steel tube.

<table>
<thead>
<tr>
<th>Reactor design</th>
<th>TS: He, O₂, (C₆H₆ 20 mol%+He 80 mol%)</th>
<th>SS: He, H₂ (ml/min)</th>
<th>Phenol (mmol/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>10, 5, 10</td>
<td>30, 10</td>
<td>0.06</td>
</tr>
<tr>
<td>B</td>
<td>10, 5, 10</td>
<td>30, 10</td>
<td>0.09</td>
</tr>
</tbody>
</table>

Compared with the Pd membrane without Mo, low productivity of phenol was obtained, and low conversion of benzene and low percentage of water in the outlet gases were observed. The main reason appears to be that the Pd was covered by Mo on the internal surface of the membrane, reducing the Pd surface area. Mo causes lower hydrogen permeability and lower productivity of phenol compared to the Pd/PSS. Table 4.9 shows productivity was increased by 50% after putting a tube inside of membrane reactor.
4.4 Mechanism for formation phenol and by-products

Based on previous studies for the formation of hydrogen peroxide [12, 13], it is likely that hydrogen peroxide was formed in our system and led to the formation of hydroxyl radicals. Hydrogen is dissociated whilst permeating through the palladium membrane to form H\(^{\circ}\) [14]. Then H\(^{\circ}\) appears on the surface at the opposite side of the membrane and reacts immediately with oxygen to give H\(_2\)O\(_2\) and OOH\(^{\circ}\) hydrogen peroxide then decomposes to OH\(^{\circ}\) water and oxygen [1]. The following reactions summarize the dissociation of H\(_2\):

\[
\begin{align*}
H_2 & \rightarrow 2H^{\circ} \quad \text{Eq. 4.5} \\
4H^{\circ} + 2O_2 & \rightarrow 2H_2O_2 \rightarrow 2OH^{\circ} + H_2O + 1/2 O_2 \quad \text{Eq. 4.6} \\
H^{\circ} + O_2 & \rightarrow OOH^{\circ} \quad \text{Eq. 4.7}
\end{align*}
\]

It was reported [15, 16] that the reaction of OH\(^{\circ}\) with benzene resulted a hydroxycyclohexadienyl, (radical 2 in Figure 4.15), which will reversibly add O\(_2\) to give a hydroxycyclohexadienyl peroxyl (radical 3) and finally reaction 4 is one of the possible reactions that give phenol by direct elimination of OOH\(^{\circ}\) from radical 3. The formation of phenol without involvement of O\(_2\) has been proposed by elimination of a ring bond H\(^{\circ}\) atom from radical 2 (reaction 3). Route 5 forms OOH\(^{\circ}\) through a hydrogen elimination reaction of radical 2 with molecular oxygen.
Figure 4.15  Proposed pathways for the initial steps in the OH$^*$ initiated degradation of benzene in the gas phase [15, 16].

It can be seen from Figure 4.16 that radical 3, which was produced from reaction 2 in Figure 4.15, may react with hydrogen, especially if only dissociated hydrogen (H*) is available on this reaction side to form radical 5. Then this radical will react with oxygen through route 6.

Figure 4.16  Proposed pathways for formation of dihydroxybenzenes [15, 16].


CHAPTER 5

RESULTS AND DISCUSSION

PART 2
The AlphOx technology is based on the vapour phase hydroxylation of benzene with N$_2$O over a ZSM-5 catalyst bed, resulting in phenol and N$_2$. The trade name “AlphOx” refers to a unique form of surface oxygen, known as alpha-oxygen. N$_2$O is a potentially interesting oxidant for selective oxidation of organic substrates since it contains 36 wt% O$_2$ and the by-product of an oxidation reaction would be N$_2$. A new route for producing phenol was reported by Panov et al., based on using N$_2$O and the iron containing zeolites as a catalyst [1]. N$_2$O initially decomposes on the zeolite catalyst surface into alpha-oxygen and nitrogen. Phenol is then obtained by inserting the alpha-oxygen into a C-H bond of the benzene molecule. The hydroxylation reaction takes place at elevated temperatures (300-500°C) and atmospheric pressure, with benzene to phenol selectivity in the range of 95-99%. The main reaction by-products include dihydroxybenzenes such as catechol, resorcinol, and hydroquinone. Some benzene is also decomposed into products of complete oxidation such as CO$_2$ and water. Another undesirable reaction is the formation of coke on the catalyst surface. Deposition of this carbonaceous material (polyaromatic compound) within the zeolite structure leads to catalyst deactivation.

### 5.1 Synthesis strategies of Fe/ZSM-5

Fe/ZSM-5 has been found to be efficient catalyst for direct oxidation of benzene to phenol using nitrous oxide as an oxidant. It is commonly accepted that the preparation method determines the activity of the catalyst in the hydroxylation reaction or N$_2$O decomposition. It is known that Fe/ZSM-5 catalysts may be prepared by Fe addition at the synthesis stage or by its post synthetic introduction. In the present work a range of iron zeolites were prepared by Chemical Vapour Deposition (CVD), Liquid Ion Exchange (LIE), and Hydrothermal Synthesis (HS).

Fe/ZSM-5 was prepared by the CVD method developed by Sachtler et al. which was explained in section 3.2.1.2. Reitzmann et al. [2] reported that FeCl$_3$ exists in the
binuclear form of Fe$_2$Cl$_6$ at 330°C while the monomer form of the FeCl$_3$ was observed at 770°C at atmospheric pressure.

\[
\text{M-OH} + \text{FeCl}_3 \rightarrow [\text{M-O}][\text{FeCl}_2]^+ + \text{HCl} \quad \text{Eq. 5.1}
\]

In relatively Al-rich ZSM-5 zeolites, where the distance between the Al occupying oxygen tetrahedral is small, the reaction may proceed as

\[
2\text{M-OH} + \text{Fe}_2\text{Cl}_6 \rightarrow 2[\text{M-O}][\text{FeCl}_4]^{2+} + 2\text{HCl} \quad \text{Eq. 5.2}
\]

For low Si/Al ratio, the concentration of vicinal protons is low and part of the reaction can be described as

\[
\text{M-OH} + \text{Fe}_2\text{Cl}_6 \rightarrow [\text{M-O}][\text{FeCl}_5]^+ + \text{HCl} \quad \text{Eq. 5.3}
\]

M represents Al or Fe in the framework. This reaction provides a way of introducing two Fe$^{3+}$ for one proton into the zeolite.

The preparation of Fe/ZSM-5 by ion exchange in aqueous solution would have been an attractive route because of its relatively simple experimental conditions, as the redox chemistry of iron in water would not be so complicated. The iron source can be varied from FeCl$_3$ and Fe(NO$_3$)$_3$ for iron (III) to FeSO$_4$, FeCl$_2$, and FeC$_2$O$_4$ for iron (II) salts. The starting material for ion exchange is the Na$^+$ or NH$_4^+$ form of the zeolite. Furthermore, monovalent cations can be exchanged more easily into a zeolite than di- or trivalent cations because the positive charge of multivalent cations has to be balanced by specially separated negative charge of the zeolite matrix. Therefore formation of oxo-ions or hydroxo-ions as Fe(OH)$^+$ is favoured. The exchange degree is in this way also determined by the pH of the solution where at low pH (complex of) Fe ions have to compete with protons. When the pH is above neutral the formation of hydroxylated Fe-species plays a role and precipitation of Fe(OH)$_2$, FeO(OH), and Fe(OH)$_3$ may occur. A difficulty is that Fe(OH)$^+$ can exist only in a narrow pH region and only in equilibrium
with Fe$^{2+}$ and/or Fe(OH)$_2$. Another problem is the control of pH and hence of the presence of Fe(OH)$^+$ species in the zeolite channel. In general, the exchange from solutions containing Fe$^{2+}$ is more efficient than from Fe$^{3+}$. A possibility to stabilize Fe(II) is to start from Fe(II) salts under oxygen free conditions like an inert nitrogen atmosphere, or to use methanol as a solvent instead of water.

The preparation of Fe/ZSM-5 by a hydrothermal synthesis method generally requires extended periods of crystallization, using large crystallization vessels and a precise control of the overall production process to avoid impurities (i.e. different crystalline phases) which harm the end product. The addition of reducing agents was reported not to be successful, at least in the case of using oxalate since that was blocking the zeolite pores [3]. Often, a quaternary ammonium salt in particular a tetrapropyl ammonium (TPA) salt is used in Fe/ZSM-5 synthesis as a template. The disadvantage of using such templates is that they are expensive and that, as a result of decomposition of the organic template, environmentally harmful compounds are released upon heating of the so-prepared zeolites. Hence, efficient preparation of Fe/ZSM-5, using a minimum amount of organic template, is desired. Al$^{3+}$ or Si$^{4+}$ can enter the zeolite framework during synthesis. These include B$^{3+}$, Ga$^{3+}$, Fe$^{3+}$ and Cr$^{3+}$, all of which substitute for Al$^{3+}$; and Ge$^{4+}$ and Ti$^{4+}$ which substitute for Si$^{4+}$. Through modification of synthesis conditions, silicon has been incorporated into many AlPO$_4$ structures. Other ions, such as Mg$^{2+}$, Zn$^{2+}$, Co$^{2+}$, Mn$^{2+}$ may also occupy sites in the AlPO$_{4-n}$ framework. The concentration of Brønsted acid sites in zeolites is inversely proportional to the Si/Al ratio, but the thermal and hydrothermal stability are directly proportional to it. Two theories have been proposed to account for the mechanism of zeolite synthesis. In the solid-solid transformation mechanism, crystallization of the zeolite occurs directly from the amorphous gel to the crystalline phase [4]. In the solution crystallization mechanism, nuclei form and grow in the liquid phase [5]. The latter proposes that equilibrium exists between the solid-gel phase and the solution, and that nucleation occurs in the solution. The gel dissolves continuously, and the dissolved species are transported to the nuclei crystals in the solution. In addition to zeolite formation via either of the two transformations, there is evidence to indicate that both types of transformation can
sometimes occur simultaneously. In some cases zeolites can also be crystallized from a single-solution system containing no secondary solid-gel phase [6]. From the single-phase solution studies, it appears that nucleation and subsequent crystallization can occur readily in the solution phase, leading to the possibility that the presence of a solid-gel phase acts only to supply nutrients to the solution.

The nature of active sites on Fe/ZSM-5 is still unclear. In this study different catalyst preparation and characterization methods was used to find more about catalyst and active sites structure. Then, an efficient catalyst for benzene hydroxylation to phenol was designated.

5.2 Characterization of zeolite prepared by CVD, LIE, and HT

5.2.1 Elemental analysis

Fe/ZSM-5 of different Si/Al ratio may have similar Fe content. Dědecěk et al. [7] reported that the Al distribution in silicon-rich zeolite is not random and depends on the chemical composition and condition of synthesis. Table 5.1 shows the elemental analysis of some samples which were prepared by HT, LIE, and CVD, using ICP-NES and AA techniques.
Table 5.1  Elemental analysis of catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Method</th>
<th>Si/Al</th>
<th>Al (wt%)</th>
<th>Fe/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe/ZSM-5-A</td>
<td>HT</td>
<td>18.4</td>
<td>1.9</td>
<td>0.0081</td>
</tr>
<tr>
<td>Fe/ZSM-5-B</td>
<td>HT</td>
<td>27.7</td>
<td>1.6</td>
<td>0.0062</td>
</tr>
<tr>
<td>Fe/ZSM-5-C</td>
<td>HT</td>
<td>61.1</td>
<td>0.9</td>
<td>0.0077</td>
</tr>
<tr>
<td>Fe/ZSM-5-D</td>
<td>HT</td>
<td>60.8</td>
<td>0.9</td>
<td>0.0297</td>
</tr>
<tr>
<td>Fe/ZSM-5-E</td>
<td>HT</td>
<td>52.1</td>
<td>1.23</td>
<td>0.15</td>
</tr>
<tr>
<td>Fe/ZSM-5-F</td>
<td>LIE</td>
<td>61.0</td>
<td>0.9</td>
<td>0.84</td>
</tr>
<tr>
<td>Fe/ZSM-5-G</td>
<td>LIE</td>
<td>60.8</td>
<td>0.9</td>
<td>0.0391</td>
</tr>
<tr>
<td>Fe/ZSM-5-H</td>
<td>LIE</td>
<td>27.5</td>
<td>1.6</td>
<td>1.25</td>
</tr>
<tr>
<td>Fe/ZSM-5-I</td>
<td>LIE</td>
<td>27.7</td>
<td>1.6</td>
<td>0.0438</td>
</tr>
<tr>
<td>Fe/ZSM-5-J</td>
<td>LIE</td>
<td>18.5</td>
<td>1.9</td>
<td>0.6</td>
</tr>
<tr>
<td>Fe/ZSM-5-K</td>
<td>CVD-770</td>
<td>55.7</td>
<td>1.1</td>
<td>1.61</td>
</tr>
<tr>
<td>Fe/ZSM-5-L</td>
<td>CVD-330</td>
<td>55.7</td>
<td>1.1</td>
<td>1.69</td>
</tr>
</tbody>
</table>

5.2.2 XRD

X-ray diffractograms were measured for catalysts prepared by CVD at 330°C and 770°C before and after post treatment and compared to that of the parent H/ZSM-5 (Figure 5.1). Figure 5.2 also shows XRD patterns of Fe/ZSM-5 prepared by LIE before and after post-treatment and compared with H/ZSM-5.

All patterns appeared to be identical, indicating no detectable damage to the ZSM-5 structure. No indications for the formation of α-Fe₂O₃ (major reflections at 2θ = 33.2°) or any other iron oxide were observed.
Figure 5.1 XRD spectra of the zeolites (CVD); (A) Fe/ZSM-5-L before post-treatment (B) Fe/ZSM-5-L after post-treatment (C) Fe/ZSM-5-K after post-treatment (D) Fe/ZSM-5-K before post-treatment.

Figure 5.2 XRD spectra of the zeolites (LIE); (A) Fe/ZSM-5-H after post-treatment, (B) Fe/ZSM-5-H before post-treatment, (C) Fe/ZSM-5-B after post-treatment, (D) Fe/ZSM-5-B before post-treatment.
5.2.3 Nitrogen adsorption

The textual properties of the catalyst samples were investigated by nitrogen adsorption. The results collected in Table 5.2 for Fe/ZSM-5-B, Fe/ZSM-5-H, and Fe/ZSM-5-I catalysts clearly point to the incorporation of the Fe species into the micropore space which is reflected by the lower surface area and micropore volume. The large decrease is most probably related to some degree of pore blocking.

<table>
<thead>
<tr>
<th></th>
<th>Total BET area (m²/g)</th>
<th>Total pore volume (cm³/g)</th>
<th>Mesopore size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe/ZSM-5-A</td>
<td>364.0312</td>
<td>0.686817</td>
<td>75.4680</td>
</tr>
<tr>
<td>Fe/ZSM-5-B</td>
<td>358.4751</td>
<td>0.578950</td>
<td>67.3618</td>
</tr>
<tr>
<td>Fe/ZSM-5-H</td>
<td>346.1547</td>
<td>0.471184</td>
<td>54.6453</td>
</tr>
<tr>
<td>Fe/ZSM-5-I</td>
<td>349.0030</td>
<td>0.480270</td>
<td>55.0448</td>
</tr>
</tbody>
</table>

Table 5.3 shows a decrease in micropore space which is caused by coke formation on the Fe/ZSM-5-I catalyst. Coke usually forms on mouth of pores and covers active sites which are located on the zeolite channels. In this experiments, lower micropore volumes with increasing reaction time were found, which is consistent with covering of pore mouths.
Table 5.3  Effect of reaction time on total pore volumes, areas, and pore sizes.

<table>
<thead>
<tr>
<th>Reaction time (h)</th>
<th>Total BET area (m²/g)</th>
<th>Total pore volume (cm³/g)</th>
<th>Mesopore size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe/ZSM-5-I</td>
<td>0</td>
<td>349.0030</td>
<td>0.480270</td>
</tr>
<tr>
<td>Fe/ZSM-5-I</td>
<td>1.5</td>
<td>340.0865</td>
<td>0.462478</td>
</tr>
<tr>
<td>Fe/ZSM-5-I</td>
<td>3</td>
<td>335.0025</td>
<td>0.453543</td>
</tr>
<tr>
<td>Fe/ZSM-5-I</td>
<td>5</td>
<td>331.8246</td>
<td>0.441431</td>
</tr>
<tr>
<td>Fe/ZSM-5-I</td>
<td>9</td>
<td>327.6148</td>
<td>0.431755</td>
</tr>
<tr>
<td>Fe/ZSM-5-I</td>
<td>20</td>
<td>321.8714</td>
<td>0.419751</td>
</tr>
</tbody>
</table>

It can be seen from Table 5.4 that the increase in micropore volume for Fe/ZSM-5-J may point to changes in the nature of extra-framework species rather than changes in the pore structure. The latter type of change is not expected since dealumination of Fe/ZSM-5-J upon high temperature calcination appears to be small. Creation of larger pores occurs with removal of aluminium from framework positions. Alternatively, this can be taken as an indication of the migration of small iron species from the micropores to the external surface.

Table 5.4  Effect of calcination temperature on total pore volumes, areas, and pore sizes.

<table>
<thead>
<tr>
<th>Calcination Temp. (°C)</th>
<th>Total BET area (m²/g)</th>
<th>Total pore volume (cm³/g)</th>
<th>Mesopore size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe/ZSM-5-A</td>
<td>-</td>
<td>364.0312</td>
<td>0.686817</td>
</tr>
<tr>
<td>Fe/ZSM-5-J</td>
<td>700</td>
<td>385.1125</td>
<td>0.699649</td>
</tr>
<tr>
<td>Fe/ZSM-5-J</td>
<td>800</td>
<td>381.5188</td>
<td>0.694947</td>
</tr>
<tr>
<td>Fe/ZSM-5-J</td>
<td>900</td>
<td>368.3008</td>
<td>0.662552</td>
</tr>
</tbody>
</table>
5.2.4 FT-IR Spectroscopy

FT-IR spectroscopy is an important and versatile technique to probe hydroxyl stretching and framework vibrations as well as surface acidity of micro and mesoporous materials. Hence, the technique is widely used for in situ studies during catalysis (in the presence of reactants) to probe adsorbed species, active intermediates and the acid base properties of the catalyst surface. The normalized spectra of the hydroxyl stretching regions (4000-2400 cm\(^{-1}\)) are depicted in Figures 5.3 and 5.4. For Fe/ZSM-5-E two intense bands were observed around 3737 cm\(^{-1}\) and 3452 cm\(^{-1}\) which are from terminal Si-OH (silanol) groups and for Brønsted acidic bridging Si-O(H)-Al groups, respectively [8, 9]. Usually, the number of Brønsted sites increase with the decrease of the Si/Al ratio, since each Al atom replacing a Si framework atom creates a Brønsted site. Based on this information one can readily see the lattice arrangement of the zeolite.

![Figure 5.3 FT-IR spectra of Fe/ZSM-5-E before acid treatment.](chart.png)
Figures 5.5 and 5.6 show that thionate acid post treatment does not have any effect on Brønsted and Lewis acidity. Infrared spectroscopy in the framework vibration range 400-1200 cm\(^{-1}\) was also used to probe the framework substitution of iron ions. Due to asymmetric and symmetric stretching vibrations of Si-O-T (T=Al) were shifted to 1200 and 788 cm\(^{-1}\) on isomorphous substitution of Al by Fe atoms in the lattice framework [10].
Figure 5.5 FT-IR spectra of Fe/ZSM-5-E before acid treatment.

Figure 5.6 FT-IR spectra of Fe/ZSM-5-E after acid treatment.
Figure 5.7 shows that following Fe loading and washing, the intensity of the band at 3450 cm\(^{-1}\) decreased significantly, as a result of the exchange of the Bronsted proton by iron, while the signal from the silanol groups remained unchanged. In addition, a new band appeared at 3715 cm\(^{-1}\). This band is ascribable to the stretching vibration of hydrolyzed Fe species formed upon washing of the residual chlorine [11], and disappeared after calcination Fe/ZSM-5.

![FT-IR spectra](image)

**Figure 5.7** FT-IR spectra of; (A) Fe/ZSM-5-L after post-treatment, (B) Fe/ZSM-5-H after post-treatment, (C) Fe/ZSM-5-H before post-treatment, (D) Fe/ZSM-5-B after post-treatment, (E) Fe/ZSM-5-G after post-treatment.

### 5.2.5 X-ray Photoelectron Spectroscopy

Oxidation states of iron species in Fe/ZSM-5 zeolites were investigated by X-ray Photoelectron Spectroscopy (XPS). To understand the surface properties of Fe/ZSM-5 catalysts XPS measurements were performed using an E.S.C.A 5 spectrometer from V.G. SCIENTIFIC LTD at room temperature under 10\(^{-7}\)-10\(^{-8}\) Torr, using Al \(K_\alpha\) radiation. This technique is surface sensitive and gives information about the external surface region of the material. Thus, it was found that Fe species which are present inside the zeolite pores could not be seen by this technique. In this technique, the binding energies of photoelectrons, liberated from the electronic core shells of Fe-atoms by X-rays are
scanned. Depending on the valence state of surface Fe species, the Fe2p\textsubscript{3/2} peaks appear at different binding energies. The binding energies of the Fe2p\textsubscript{3/2} usually reported [12-14] around ≈ 711 eV and ≈ 708 eV were attributed to Fe\textsuperscript{3+} and Fe\textsuperscript{2+} ions which were not observed in this study (Figure 5.8). From the XPS results (Table 5.5) it can be seen that only Fe/ZSM-5-L, prepared by CVD method, shows Fe in the surface. Fe/ZSM-5-B before and after post-treatment, Fe/ZSM-5-H, and Fe/ZSM-5-G samples do not show Fe in the analysis due to migration of the Fe to the channels. Fe/ZSM-5-L with 0.4 atom% Fe centred at 712 eV, which is mainly attributed to Fe\textsubscript{2}O\textsubscript{3} or Fe\textsubscript{3}O\textsubscript{4}. The surface compositions of different Fe/ZSM-5 catalysts are shown in Table 5.5.

### Table 5.5 Surface composition of Fe/ZSM-5 catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C (atom%)</th>
<th>O (atom%)</th>
<th>Si (atom%)</th>
<th>Fe (atom%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeZSM-5-B</td>
<td>4.5</td>
<td>57.8</td>
<td>37.7</td>
<td>0</td>
</tr>
<tr>
<td>FeZSM-5-B</td>
<td>6.5</td>
<td>57.1</td>
<td>36.9</td>
<td>0</td>
</tr>
<tr>
<td>FeZSM-5-G</td>
<td>5.4</td>
<td>58.1</td>
<td>36.5</td>
<td>0</td>
</tr>
<tr>
<td>FeZSM-5-H</td>
<td>5.7</td>
<td>58.4</td>
<td>36.0</td>
<td>0</td>
</tr>
<tr>
<td>FeZSM-5-L</td>
<td>3.5</td>
<td>58.4</td>
<td>37.7</td>
<td>0.4</td>
</tr>
</tbody>
</table>
Figure 5.8 XPS spectrum of (A) Fe/ZSM-5-B, before post-treatment; (B) Fe/ZSM-5-B, after post-treatment; (C) Fe/ZSM-5-H, after post-treatment; (D) Fe/ZSM-5-L, after post-treatment; (E) Fe/ZSM-5-G, after post-treatment.

5.2.6 HR-TEM

High resolution transmission electron micrographs of the Fe/ZSM-5, collected in Figure 5.9, were taken after calcination procedure. As expected, no particles were visible on the Fe/ZSM-5-G and Fe/ZSM-5-E, suggesting that no agglomeration of iron occurred during the LIE and HS methods while darker crystals was observed on the Fe/ZSM-5-L because
of higher level of Fe loaded and probably iron oligomers. XPS results also confirm the existence of iron oxide in the surface of catalyst which prepared by CVD.

Figure 5.9 TEM micrographs; (A and B) Fe/ZSM-5-L, (C and D) Fe/ZSM-5-G, 9E and F) Fe/ZSM-5-E.
5.2.7 Estimation of the nature of the active sites

The nature and distribution of iron species in Fe/ZSM-5 zeolites using Mössbauer spectroscopy has been studied by many researchers. Mössbauer spectroscopy can detect the Fe with different oxidation states (Fe$^{3+}$ and Fe$^{2+}$), coordination states (octahedral and tetrahedral), and aggregation [12, 15, 16]. Although the zeolites used in the present study have not been analysed using Mössbauer spectroscopy, the extensive work of Dobkov et al. [15] was used to guide the catalysts post treatment methods used in this work.

The three different spectral contributions have been assigned to: the isomer shift (IS), the quadrupole splitting (QS), and the magnetic components (MC) or Zeeman splitting. S-electron density at the nucleus and yields information on the oxidation state on the Fe atoms, and are measured by IS. States with IS$<0.3$ mm/s and IS$>0.3$ mm/s are usually assigned to Fe$^{3+}$ ions in the tetrahedral coordination ($Fe_{tn}^{3+}$) and octahedral coordination ($Fe_{oh}^{3+}$) at room temperature, respectively [17].

The QS value for Fe$^{3+}$ ions in ideal tetrahedrons is zero while in distorted tetrahedrons it may attain 1.7 mm/s. The QS values ranging from 0.7 to 2.4 mm/s and QS$<1$ mm/s characterize dinuclear Fe$^{3+}$ complexes and mononuclear high-spin ferric complexes, respectively [18, 19]. With increasing coordination numbers (e.g. upon transition from tetrahedral to octahedral coordination), the QS value for Fe$^{3+}$ions usually decreases, while that for Fe$^{2+}$ ions increases [20].

The magnetic components, or Zeeman splitting, arises from an interaction between nuclear magnetic dipole moments and the magnetic field at the iron nucleus. This hyperfine interaction enables us to probe magnetic properties of Fe-containing materials, such as super paramagnetism or paramagnetism, which in turn provide information on particle size or iron concentration. Dubkov et al. [15] reported that Mössbauer spectra analysis reveals several states of iron. Their parameters and amounts are shown in Figure 5.10 and Table 5.6.
Figure 5.10 Mössbauer spectra of Fe/ZSM-5 after various activation and follow by α-oxygen loading [15].

Table 5.6 Mössbauer Parameters and amount of iron states in Fe/ZSM-5 after activation under various conditions [15].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Subspectrum</th>
<th>Fe state</th>
<th>Spectral parameters (mm/s)</th>
<th>Amount of iron in the state</th>
<th>Fraction (%)</th>
<th>10^{15} Fe/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. A (parent)</td>
<td>MC</td>
<td>Fe^{2+}</td>
<td>0.5</td>
<td></td>
<td>54</td>
<td>8.1</td>
</tr>
<tr>
<td></td>
<td>D1a</td>
<td>Fe^{2+} (Oh)</td>
<td>0.38</td>
<td></td>
<td>39</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>D2</td>
<td>Fe^{3+}</td>
<td>0.76</td>
<td></td>
<td>8</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>D3</td>
<td>Fe^{3+} (Oh)</td>
<td>1.19</td>
<td></td>
<td>8</td>
<td>1.2</td>
</tr>
<tr>
<td>2. A/air 700</td>
<td>MC</td>
<td>Fe^{2+}</td>
<td>0.5</td>
<td></td>
<td>51</td>
<td>7.7</td>
</tr>
<tr>
<td></td>
<td>D1</td>
<td>Fe^{2+} (Oh)</td>
<td>0.49</td>
<td></td>
<td>34</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td>D3</td>
<td>Fe^{3+}</td>
<td>1.19</td>
<td></td>
<td>5</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>D4</td>
<td>Fe^{3+} (Td)</td>
<td>1.04</td>
<td></td>
<td>10</td>
<td>1.5</td>
</tr>
<tr>
<td>3. A/air 900</td>
<td>MC</td>
<td>Fe^{2+}</td>
<td>0.5</td>
<td></td>
<td>52</td>
<td>7.8</td>
</tr>
<tr>
<td></td>
<td>D1</td>
<td>Fe^{2+} (Oh)</td>
<td>0.47</td>
<td></td>
<td>32</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td>D3</td>
<td>Fe^{3+}</td>
<td>1.19</td>
<td></td>
<td>6</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>D4</td>
<td>Fe^{3+} (Td)</td>
<td>1.03</td>
<td></td>
<td>10</td>
<td>1.5</td>
</tr>
<tr>
<td>4. A/vac. 900</td>
<td>MC</td>
<td>Fe^{2+}</td>
<td>0.5</td>
<td></td>
<td>24</td>
<td>3.6</td>
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<tr>
<td></td>
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<td>Fe^{2+} (Oh)</td>
<td>0.58</td>
<td></td>
<td>9</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>D3</td>
<td>Fe^{3+}</td>
<td>1.34</td>
<td></td>
<td>32</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td>D4</td>
<td>Fe^{3+} (Td)</td>
<td>1.02</td>
<td></td>
<td>35</td>
<td>5.2</td>
</tr>
<tr>
<td>5. A/vac. 900 + O2</td>
<td>MC</td>
<td>Fe^{2+}</td>
<td>0.5</td>
<td></td>
<td>39</td>
<td>5.9</td>
</tr>
<tr>
<td></td>
<td>D1</td>
<td>Fe^{2+} (Oh)</td>
<td>1.28</td>
<td></td>
<td>8</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>D3</td>
<td>Fe^{3+}</td>
<td>1.02</td>
<td></td>
<td>12</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>D5</td>
<td>Fe^{3+} (Oh)</td>
<td>0.64</td>
<td></td>
<td>26</td>
<td>3.9</td>
</tr>
<tr>
<td></td>
<td>D6</td>
<td>Fe^{3+} (Th?)</td>
<td>0.39</td>
<td></td>
<td>15</td>
<td>2.3</td>
</tr>
</tbody>
</table>
In the parent sample iron is mainly in a trivalent oxidation state and is represented by a so-called magnetic components (MC=54%), doublet D1a (30%) and also two low-intensive doublet, D2 (8%) and D3 (8%). Dubkov et al. [15] suggested two possibilities for such spectral patterns: first it may be obtained with both a dispersed Fe₂O₃ phase and magnetically isolated Fe³⁺ ions located, for example, in the tetrahedral positions of a crystalline lattice; and secondly such signals may be also caused by the presence of FeO⁺ species in the zeolite channels.

They reported doublet D1a ( IS+0.38 mm/s, QS=2.33 mm/s) relates to the trivalent iron. Such a high QS value indicates that Fe³⁺ ions are present as dinuclear μ-oxocomplexes, e.g., Fe³⁺-O-Fe³⁺.

It was concluded that D3 complexes are formed by Fe²⁺ with coordination numbers of 5 and 6. D2 complexes are formed by iron in an intermediate oxidation state, Fe²⁵⁺. The latter may be particles of mixed valence, such as Fe²⁺-O-Fe³⁺, in which one electron is equally distributed over two iron site.

No changes in magnetic component were observed after post-treatment of the Fe/ZSM-5 in air at 700 and 900°C but other states of iron were affected. State Fe³⁺ presents as doublet D1a changes noticeably and forms a new D1 doublet. Post-treatment in air also resulted in the disappearance of the intermediate valence state D2 and a new reduced-state D4 emerges, which may be assigned to tetrahedral ions Fe²⁺.

Vacuum post-treatment at 900°C was shown an intensive process of iron reduction and to a manifold increase of Fe²⁺ concentration in D3 and D4 states. It was also resulted that The Fe³⁺ ions, which are reduced to Fe²⁺ ions by the thermal treatment, were in isolated extra framework positions and oligonuclear oxo-iron complexes. The hydrothermal treatment was not affected the Fe³⁺ ions in the iron oxide particles of 2 nm.

It was concluded a linear relationship between the concentration of α-sites and active Fe species. Table 5.6 shows that with increasing Cₐ, concentration of D3 and D4 complexes
involving Fe$^{2+}$ linearly increase. Table 5.6 also shows after $\alpha$-oxygen loading on the vacuum-activated zeolite, a strong decrease in D3 and D4 concentrations was observed. Concurrently, new doublets, D5 and D6, of trivalent iron emerge. They concluded that a part of Fe$^{2+}$ which are responsible to create active sites were converted to Fe$^{3+}$. It was seen from their experiments that these $\alpha$-O are instable at temperature more than 300$^\circ$C. It was observed a decrease of concentrations D5 and D6 and an increase of concentrations D3 and D4 in the temperatures more than 300$^\circ$C.

Despite different Mössbauer parameters, two reduced complexes, D3 and D4, on the one hand, and two oxidized complexes, D5 and D6, on the other hand, may have similar structures.

![Figure 5.11 Suggested mechanism of the $\alpha$-O formation.](image)

### 5.3 N$_2$O decomposition

Nitrous oxide has received increasing attention the past decade, due to the growing awareness of its impact on the environment, as it has been identified as an ozone depletion agent and as a greenhouse gas. Identified major sources include adipic acid production, nitric acid and fertilizer plants, fossil fuel and biomass combustion, and de-NO$_x$ treatment techniques, like selective catalytic reduction [21, 22]. For the abatement of N$_2$O emissions one can note much interest in the development of catalysts that decompose nitrous oxide into its elements at rates and conditions that are compatible with the production sources [21, 23].
Catalysts include oxides, mixed oxides, and most published studies deal with Fe-zeolites [21]. The latter, transition metal ion-exchanged zeolites, have been shown to exhibit high activities for the decomposition reaction [24, 25]. Classically the reaction over oxide catalysts is described by adsorption followed by an oxidation of active sites, and a subsequent removal of the deposited oxygen by recombination (Equations 5.5-5.7). The adsorption (Eq. 4.5) and desorption (Eq. 4.7), are generally assumed to be in quasi-equilibrium under decomposition conditions:

\[
2\text{N}_2\text{O} \rightarrow 2\text{N}_2 + \text{O}_2 \quad \text{Eq. 5.4}
\]

\[
\begin{align*}
\text{N}_2\text{O} + * & \rightarrow \text{N}_2\text{O}^* \quad \text{Eq. 5.5} \\
\text{N}_2\text{O}^* & \rightarrow \text{N}_2 + \text{O}^* \quad \text{Eq. 5.6} \\
2\text{O}^* & \rightarrow \text{O}_2 + 2^* \quad \text{Eq. 5.7}
\end{align*}
\]

\[\text{N}_2\text{O}\] decomposition was performed in this study in a stainless steel reactor which was loaded with 300 mg of catalyst. Ar was introduced to the reactor and temperature then was increased to 550°C with the ramp of 3°C/min. After calcination in the presence of air, the reactor was cooled down to 250°C and \text{N}_2\text{O} (5 \text{ mol}%) was added to the feed stream. Then the temperature was increased to 500°C and in different temperature samples was lead to a mass spectrometer for characterization.

Figure 5.12 shows that catalysts which were prepared by the CVD method lead to remarkable performance in decomposition of \text{N}_2\text{O}.
Figure 5.12  \(N_2O\) decomposition vs. temperature at condition (feed gas = 95/5 mol\% (Ar/\(N_2O\)); (Δ) Fe/ZSM-5-L, (○) Fe/ZSM-5-K, (X) Fe/ZSM-5-H; contact time 1.8 s.

It can be seen from Figure 5.12 and Table 5.7 that decomposition of \(N_2O\) increased with increasing reaction temperatures, while concentration of \(N_2O\) in the feed does not affect the decomposition.

### Table 5.7 Influence of the \(N_2O\) concentration and reaction temperature on decomposition of \(N_2O\).

<table>
<thead>
<tr>
<th>Variable</th>
<th>Decomposition (N_2O) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(N_2O) in feed stream (mol%)</td>
<td></td>
</tr>
<tr>
<td>2.9</td>
<td>31</td>
</tr>
<tr>
<td>5</td>
<td>32</td>
</tr>
<tr>
<td>8.2</td>
<td>32</td>
</tr>
<tr>
<td>Reaction temperature (°C)</td>
<td></td>
</tr>
<tr>
<td>380</td>
<td>18</td>
</tr>
<tr>
<td>400</td>
<td>32</td>
</tr>
<tr>
<td>415</td>
<td>45</td>
</tr>
<tr>
<td>425</td>
<td>59</td>
</tr>
</tbody>
</table>
Figure 5.13 shows that impurities such as O\textsubscript{2} and water affect the activity of Fe/ZSM-5-H catalyst. The influences of contaminants are discussed in details on benzene hydroxylation in section 5.5.

\textbf{Figure 5.13} $N_2O$ decomposition vs. temperature at condition (feed gas = 95/5 mol\% (Ar/$N_2O$); (△) Fe/ZSM-5-H + $H_2O$, (○) Fe/ZSM-5-H + $O_2$, (X) Fe/ZSM-5-H; contact time 1.8 s.

The rate of $N_2O$ decomposition can be written as

$$r = kP_{N_2O} \quad \text{Eq. 4.8}$$

$$k = k_0 e^{-E_a/RT} \quad \text{Eq. 4.9}$$

Experimental results (Table 5.7) indicate that the $N_2O$ decomposition is a first order reaction (n=1). Arrhenius plots of the $N_2O$ decomposition over Fe/ZSM-5 catalysts are shown in Figure 5.14. The experiments also show that the apparent activation energy of the Fe/ZSM-5 catalysts is in the range 53-56 kJ/mol, depending on preparation methods.
It was calculated that activation energy for Fe/ZSM-5-L and Fe/ZSM-5-G after high calcination temperatures were 55.78 and 53.05 kJ/mol respectively.

Figure 5.14 Arrhenius plot of N$_2$O decomposition over (O) Fe/ZSM-5-L, (X) Fe/ZSM-5-H.

Yakovlev et al. [26] reported that the structures of the binuclear Fe/ZSM-5 active sites which catalyze N$_2$O decomposition have been determined as a function of temperature and water content. At below 200°C the sites (iron-containing complexes) are fully hydroxylated and above 500°C the sites are completely dehydroxylated, therefore they are not available for reaction. The binuclear sites have predominantly the [OH-Fe-O-Fe-OH]$_2^+$ structure in the range of 200-500°C.

A different degree of hydroxylation results in different reaction mechanisms for N$_2$O decomposition. The low-temperature hydroxylated form may act as a single-ion site since the second Fe ion has a completely saturated first coordination sphere. N$_2$O decomposition on a single ion site proceeds via the Eley-Rideal mechanism. However,
given the activation energies that correspond to this mechanism, the mono centre Fe$^{3+}$ site appears to be inactive at the temperatures of existence of this site, i.e., below 200°C. The other two forms have related mechanisms of N$_2$O decomposition: N$_2$O dissociates on two separate Fe ions followed by oxygen recombination and desorption. The difference between the reaction pathways is that at high temperature the reaction may involve Fe$^{2+} \leftrightarrow$ Fe$^{3+}$ transitions, whereas at lower temperatures it is Fe$^{3+} \Rightarrow$ Fe$^{4+}$. The reaction energy profile for the [OH-Fe-O-Fe-OH]$^{2+}$ site is smoother than that for [Fe-O-Fe]$^{2+}$ suggesting that at the same temperature the former one should be more active. The calculated reaction routes with corresponding energies ($\Delta E = 36$-$38$ kJ/mol) are shown in Figure 5.15.
Figure 5.15 Calculated routes of \( \text{N}_2\text{O} \) decomposition with reaction energies in kJ/mol [26].

5.4 Direct oxidation of benzene using Fe/ZSM-5 catalysts

One-step hydroxylation of aromatics is one of the most difficult problems in the field of organic chemistry. Many attempts to accomplish a direct oxidation of benzene by
molecular oxygen have been unsuccessful. Interaction with oxygen is accompanied by the destruction of the aromatic ring and results in low phenol selectivity. N$_2$O decomposition was studied and the catalytic properties of zeolites were determined by the presence of iron. It was observed that active oxygen, deposited on the catalyst by its reaction with nitrous oxide, can hydroxylate benzene directly to phenol.

5.4.1 The role of iron in benzene hydroxylation

H/ZSM-5 was purchased from Süd-Chemie and was modified with 0.1 M solutions of FeCl$_3$ at 50°C over a period of 2-24, hours followed by drying at 120°C over night. The catalyst was then placed in a 7 mm diameter stainless steel tube and the temperature increased to 550°C with a ramp of 1°C/min in He atmosphere. At 550°C air was fed to the reactor for 4 hours. Then He replaced the air and the catalyst was treated in a steam atmosphere at 600°C followed by cooling to room temperature with a ramp of 1°C/min. The reaction was run at reaction conditions: 55 mol% benzene, 5 mol% N$_2$O, and 40 mol% He at 410°C and 1 second contact time. The sample was collected after 30 and 180 minutes.

The catalytic properties of the different Fe/ZSM-5 samples are shown in Figure 5.14. The experimental data show Fe atoms play an important role for catalytic properties of Fe/ZSM-5. Decomposition of N$_2$O on active sites generates a reactive form of surface oxygen which can not be produced by O$_2$ adsorption. It was observed that productivity, concentration of active sites, and the rate of N$_2$O decomposition depend on iron loaded to catalyst. A detectable activity was observed even for the initial sample containing only <200 ppm of iron. Figure 5.16 shows a nearly linear dependence of the rate of phenol formation on the Fe concentration after 30 minutes of running reaction. Increasing the Fe content up to 2 wt% was accompanied by an increase of the phenol productivity from 3.1 to 32.5 mmol/gh. Figure 5.16 also shows an optimum for iron loaded to the catalyst after 180 minutes of running reaction and higher amount of iron or number of active sites was shown a negative effect on catalyst half-life.
It was observed that increasing Fe wt% in the extra-framework of the zeolite at the same reaction conditions results in higher \( \text{N}_2\text{O} \) decomposition, while a decrease in productivity was observed (Figure 5.16). The main reason could be some \( \alpha \)-oxygen was consumed for converting phenol to dihydroxybenzenes or coke formation.

The location and structure of the Fe sites is important for their redox activity, as revealed by a much higher activity of the catalyst after post-treatment at high temperature. The nature of the Fe in active sites was discussed in section 5.2.7. Based on Mössbauer spectra, Dubkov et al. [15] suggested that the extra-framework dinuclear Fe species, formed by high temperature calcinations, and bearing bridging oxygens, are the active sites for benzene hydroxylation.

Figure 5.16  Productivity of phenol as a function of iron contents in ZSM-5 after; (X) 30 minutes of running the reaction (O) 180 minutes of running reaction.
Conversion of N\textsubscript{2}O via isolated Fe\textsuperscript{3+} sites for different iron loaded catalysts was also studied by Ramírez et al. [27]. Figure 5.17 shows N\textsubscript{2}O conversion and the percentage of isolated Fe\textsuperscript{3+} sites between Fe/ZSM-5 (5 wt\%) > ex-Fe-silicalite (0.68 wt\%) > ex-FeZSM-5 (0.67 wt\%) > Fe-ZSM-5 (1.4 wt\%).

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure5.17.png}
\caption{Correlation between the relative N\textsubscript{2}O conversion at 600 K and the relative fraction of isolated Fe\textsuperscript{3+} sites in the Fe-zeolites investigated [27].}
\end{figure}

The poor catalytic performance of ion exchanged Fe/ZSM-5 can be expected in view of the extensive iron clustering in the form of large inactive Fe-oxide particles. Iron clustering also occurs in the catalyst prepared by sublimation (Fe/ZSM-5), but the high iron content together with a relatively high fraction of iron in intrazeolitic positions makes it the most active formulation in terms of absolute N\textsubscript{2}O conversions. The activity of ex-FeZSM-5 is largely reduced compared to ex-Fe-silicalite, which correlates with the decreased concentration of isolated iron species due to clustering. However, ex-FeZSM-5 was a more effective catalyst than ex-Fe-silicalite in direct N\textsubscript{2}O decomposition. It was found that the presence of Fe is decisive for the redox activity of the zeolites. It was also resulted that not only the amount of iron but also the catalyst structure is important in the creation of an active catalyst.
5.4.2 Influence of contact time

For better understanding of the effect of contact time on hydroxylation of benzene over Fe/ZSM-5 (prepared by LIE), catalyst was loaded into a plug flow reactor with the feed composition of 45 mol% of benzene, 5 mol% of N₂O, and the balance with He at atmospheric pressure and 410°C. It was observed that productivity increased at contact time of 1 second compared with 0.5 second. The optimum contact time to reach higher productivity is different from one to another catalyst and needs to be studied along with the effect of other parameters in the reaction and choose the optimum contact time.

![Graph](image)

*Figure 5.18  Productivity of phenol for Fe/ZSM-5-F at condition: feed gas = 45/5/Balance with He (benzene/N₂O/He); temperature 410°C; at contact time of (X) 0.5 s, and (O) 1 s.*

5.4.3 Effect of acid washing in productivity

Figure 5.19 shows the result for the Fe/ZSM-5-F, which is a zeolite catalyst treated with an aqueous solution containing FeCl₃ and then collected by filtration and washed with water. After a steamed post-treatment at 600°C or calcination at 900°C the catalyst was
then treated with an aqueous solution of sodium dithionate (0.01M) at 70°C for 15 minutes. The amount of ferric ions present in the first solution introduces iron into the catalyst that will be effective to catalyze the hydroxylation reaction. The amount of dithionate ions in the second solution is effective for the removal of iron from the catalyst that would catalyze the formation of undesired by-products. The zeolite was then collected by filtration and washed with water. This was then treated with 0.25M nitric acid at 70°C for 30 minutes. The resulting material was collected by filtration, washed with deionized water and then calcined at 550°C. During the acid treatment hydrogen can exchange with the sodium in the zeolite to enhance the catalytic properties. Benzene oxidation was performed in a plug flow reactor with the inner diameter of 3 mm at 410°C, atmospheric pressure, contact time of 0.5 s, and feed composition of 45 mol% benzene; 5 mol% N₂O; 50 mol% He. Figure 5.20 shows that productivity was decreased by dithionate / acid post-treatment.

Figure 5.19  Productivity of phenol at condition: feed gas = 45/5/Balance with He (benzene/N₂O/He); temperature 410°C; at contact time of 0.5 s; for (X) Fe/ZSM-5-F without dithionate / acid post-treatment (O) Fe/ZSM-5-F with dithionate / acid post-treatment.
5.4.4 Effect of CO in post-treatment

There are many explanations as to why zeolite catalysts are problematic with regard to activation and deactivation for aromatic hydroxylation reactions but no solution has been achieved that provides a noticeable improvement that would lead to an exciting process. Various processes have been used to activate zeolite catalysts, as steamed activation or high temperature calcination does not significantly increase the activation of the catalyst. As described in [28, 29], reducing gases are to be avoided due to the negative impact on such gases to the acidity of the catalyst, which is believed to provide catalyst activity. Table 5.8 shows that 6 mol% CO increases the catalytic activity of the Fe/ZSM-5-F from 11.2 to 14.9 and 9.9 to 13.8 mmol/gh after 30 and 90 minutes of running the reaction, respectively.

Table 5.8 Effect of CO in catalytic activity of zeolite at feed composition of 50 mol% benzene, 5 mol% N₂O, 45 mol% He at 400°C and contact time of 0.5 s.

<table>
<thead>
<tr>
<th></th>
<th>Productivity (mmol/gh)</th>
<th>Productivity (mmol/gh)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30 minutes</td>
<td>90 minutes</td>
</tr>
<tr>
<td>Fe/ZSM-5-F steamed</td>
<td>11.2</td>
<td>9.9</td>
</tr>
<tr>
<td>Fe/ZSM-5-F steamed with CO</td>
<td>14.9</td>
<td>13.8</td>
</tr>
</tbody>
</table>

5.4.5 Effect of production synthesis

Benzene oxidation was performed in a plug flow reactor at 410°C and atmospheric pressure and feed composition of 45 mol% benzene, 5 mol% N₂O, 50 mol% He. It was shown that active sites might be composed of oxygen-bridge, extra-framework, binuclear Fe species, or charge-compensating the framework Fe³⁺ ions, that are able to pick up oxygen from N₂O and to release it to benzene to form phenol, through a Fe³⁺ → Fe²⁺ redox mechanism. Figure 5.20 shows the effect of the introduction of iron ions by LIE Fe/ZSM-5-J, to lead to initial good productivities to phenol comparable to those obtained...
by Fe/ZSM-5-E or Fe/ZSM-5-A samples prepared by hydrothermal synthesis and subsequent partial migration of iron from framework to extra-framework positions due to heat treatment. Centi et al. [30] suggested that in both type of catalysts only very small amounts of iron sites are responsible for the selective oxidation of benzene to phenol and the remaining extra-framework iron species, especially the samples prepared by hydrothermal synthesis, play a role in blocking sites responsible for catalyst deactivation, because catalysts prepared by hydrothermal synthesis show a lower rate of deactivation than those prepared by LIE. It should be noted that an alternative interpretation is the existence of two types of iron sites active in benzene selective hydroxylation, but having different turnover numbers. Figure 5.20 also shows 75%, 81.6%, and 83% decline of initial activity after 30 minutes for Fe/ZSM-5-J, Fe/ZSM-5-E, and Fe/ZSM-5-A, respectively.

![Diagram](image)

**Figure 5.20** Productivity to phenol at condition: feed gas = 4S/5/Balance with He (benzeneN₂O/He); temperature 410 °C; at contact time of 1 s for (Δ) Fe/ZSM-5-A, (O) Fe/ZSM-5-E, (X) Fe/ZSM-5-J.
5.4.6 Effect of temperature on productivity and selectivity

Table 5.9 presents the data on N\textsubscript{2}O decomposition, phenol productivity, and selectivity. The reactor was loaded with Fe/ZSM-5-I and reaction was run at 410\textdegree C, atmospheric pressure and feed composition of 5 mol\% benzene, 20 mol\% N\textsubscript{2}O, 75 mol\% He with contact time of 0.25 second. It can be seen from Table 5.9, that temperature has a positive effect on decomposition of N\textsubscript{2}O and productivity, while it has negative effect on selectivity toward phenol.

<table>
<thead>
<tr>
<th>Reaction temperature (\degree C)</th>
<th>Decomposition N\textsubscript{2}O (%)</th>
<th>Phenol (mol%)/(mmol/gh)</th>
<th>Dihydroxybenzenes (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>380</td>
<td>18</td>
<td>1.61/5.2</td>
<td>0.006</td>
</tr>
<tr>
<td>400</td>
<td>32</td>
<td>2.02/6.5</td>
<td>0.017</td>
</tr>
<tr>
<td>415</td>
<td>45</td>
<td>2.7/8.7</td>
<td>0.031</td>
</tr>
<tr>
<td>425</td>
<td>59</td>
<td>3.19/10.3</td>
<td>0.046</td>
</tr>
</tbody>
</table>

Figure 5.21 shows phenol formation was increased by increasing the temperatures. Comparing the data presented in Table 5.9 it can be seen that rate of N\textsubscript{2}O decomposition and by-products such as dihydroxybenzene were increased.
Figure 5.21 Effect of temperature on productivity and selectivity at condition: feed gas = 5/20/Balance with He (benzene/N₂O/He); at contact time of 0.25 s.

5.4.7 Effect of Si/Al ratio

In section 5.4.1 we have seen a determining role of iron incorporated into the Al/Si matrix. Pirutko et al. [31] reported Fe/ZSM-5 zeolite structure can be synthesised on the Fe-Si base without aluminium or replaced with Ga, B, and Ti. The distinctions in zeolite activity relate to the fact that the formation of Fe-containing active sites strongly depends on the Brønsted acidity and proceeds with different efficiency in various matrices. Finally, the presence of Al, Ga, B, and Ti does not effect the composition and properties of iron containing active sites but increases their concentration due to more favourable distribution of Fe in the zeolite matrix. It was observed that an increase in productivity is obtained for higher amounts of Al in the zeolite matrix (Figure 5.22).
Figure 5.22  Effect of Si/Al ratio on productivity to phenol at condition: feed gas = 45/5/Balance with He (benzene/N₂O/He); temperature 410°C; at contact time of 1 s for (O) Fe/ZSM-5-G, (X) Fe/ZSM-5-I.

5.4.8 Effect of feed composition

A run was conducted to evaluate the effect of N₂O concentration on reaction performance (productivity, N₂O conversion, and by-product yields). During this run, the feed gas mol fraction of N₂O was varied in the following order: 2.9, 5, and 8.2. The key results are given in Table 5.10. It was observed that the N₂O conversion remains virtually constant as N₂O concentration is changed. This indicates that rate of N₂O consumption is first order with respect to N₂O.
Table 5.10 Effect of N$_2$O in feed stream on the reactor performance.

<table>
<thead>
<tr>
<th>N$_2$O in feed stream (mol%)</th>
<th>Decomposition N$_2$O (%)</th>
<th>Phenol (mol%)/(mmol/gh)</th>
<th>Dihydroxybenzenes (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.9</td>
<td>31</td>
<td>0.9/2.8</td>
<td>0.003</td>
</tr>
<tr>
<td>5</td>
<td>32</td>
<td>2.02/6.5</td>
<td>0.017</td>
</tr>
<tr>
<td>8.2</td>
<td>32</td>
<td>2.76/8.9</td>
<td>0.072</td>
</tr>
</tbody>
</table>

It is also observed that as the N$_2$O concentration increases, so phenol productivity was increased while the selectivity to phenol was decreased (Figure 5.23).

![Figure 5.23](image)

Figure 5.23 Effect of N$_2$O in feed stream on productivity and selectivity at condition:
feed gas = 50/5/Balance with He (benzene/N$_2$O/He); temperature 410 °C; at contact time of 1s.

The effect of feed gas benzene concentration on reaction performance was also studied by varying this parameter at 410°C and contact time of 1 second (Table 5.11). As the feed
gas benzene concentration was increased from 30 to 62 mol%, the N₂O conversion was decreased from 36 to 29%, and total by-product concentration was also decreased.

<table>
<thead>
<tr>
<th>C₆H₆ in feed stream (mol%)</th>
<th>Decomposition N₂O (%)</th>
<th>Phenol (mol%)/(mmol/gh)</th>
<th>Dihydroxybenzenes (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>36</td>
<td>1.74/5.6</td>
<td>0.031</td>
</tr>
<tr>
<td>45</td>
<td>32</td>
<td>2.02/6.5</td>
<td>0.016</td>
</tr>
<tr>
<td>62</td>
<td>29</td>
<td>2.54/8.2</td>
<td>0.011</td>
</tr>
</tbody>
</table>

In the absence of N₂O in the feed, benzene does not form carbonaceous deposits by interaction with Fe/ZSM-5-1 catalysts, and therefore it is reasonable to associate the formation of carbonaceous deposits mainly with a secondary transformation of phenol inside the zeolite cavities. Phenol may thus back-diffuse out of the zeolite cavities, be further hydroxylated to di or polyhydroxybenzene, or be converted to behaviour products. Two different feed compositions were applied (Figure 5.24). First, catalytic performances of the zeolite catalyst in the presence of excess of N₂O and lower concentration of benzene. The ratio of benzene to N₂O adjusted from 1 to 4 and diluted with He which resulted the final composition of benzene 5 mol%, N₂O 20 mol%, He 75 mol%. Second, the catalytic tests were made using a large excess of benzene with the feed composition of benzene 50 mol%, N₂O 5 mol%, He 45 mol%.
Figure 5.24  Effect of excess of $C_6H_6$ and excess of $N_2O$ in feed stream on productivity and selectivity: ($\Delta$) and ($\times$): 50 mol% benzene, 5 mol% $N_2O$, balance with He, ($\bigcirc$) and ($\uparrow$)5 mol% benzene, 20 mol% $N_2O$, balance with He.

Figure 5.25 shows some advantages for using excess of benzene in hydroxylation reactions such as minimizing further hydroxylation of phenol, higher selectivity and higher productivity, while lower conversion of benzene was observed which needed a recycling system for benzene removal from the product mixture.
Figure 5.25  Effect of C₆H₆ in feed stream on productivity and selectivity at condition: feed gas = 50/5/Balance with He (benzene/N₂O/He); temperature 410°C; at contact time of 1 s.

The effect of gas-phase phenol concentration on reaction performance was studied by performing a run where phenol was introduced to the feed gas, and the amount of phenol introduced was varied. The data for this run are presented in Table 5.12. As the phenol concentration in the bed was increased, the N₂O conversion and selectivity was decreased.

<table>
<thead>
<tr>
<th>C₆H₅OH in feed stream (mol%)</th>
<th>Decomposition N₂O (%)</th>
<th>Phenol (mol%)/(mmol/gh)</th>
<th>Dihydroxybenzenes (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>29</td>
<td>2.4/7.7</td>
<td>0.022</td>
</tr>
<tr>
<td>2</td>
<td>26</td>
<td>3.3/10.6</td>
<td>0.050</td>
</tr>
<tr>
<td>4</td>
<td>24</td>
<td>5.4/17.4</td>
<td>0.081</td>
</tr>
</tbody>
</table>
It can be seen from Figure 5.26 that the rate of formation of the phenol by-products is higher than productivity to phenol. It is clear that removing phenol from the feed composition will have a positive effect on reaction performance.

![Figure 5.26](image)

**Figure 5.26** Effect of C₆H₅OH in feed stream on productivity and selectivity at condition: feed gas = 50/5/1-4/Balance with He (benzene/N₂O/phenol/He); temperature 410 °C; at contact time of 1 s.

### 5.5 Influence of feed contaminants in hydroxylation of benzene

Producing phenol from N₂O is suggested only if the expensive N₂O is available as an industrial waste product, from for example adipic acid plants. In view of this, Solutia suggested use of purified nitrous oxide for the oxidation of benzene to phenol, incorporating this reaction as a key stage in a new modified adipic acid production scheme [32, 33]. This scheme starts with benzene which is first oxidized to phenol, and only then is subjected to hydrogenation. The cyclohexanol was reacted with cyclohexanone to produce adipic acid and N₂O, and the N₂O returned to the hydroxylation reaction. The global N₂O emission from adipic acid plants is not sufficient to produce 9 MMT phenol per year. Phenol needs technological processes for the nitrous oxide synthesis at the unit capacity up to 100 KT/y. Solutia and BIC recently
developed a new large-scale catalytic process for the synthesis of nitrous oxide via selective oxidation of ammonia over a Mn-Bi-O/α-Al₂O₃ catalyst. The catalyst was found to be active in the temperature range 315-370°C and to provide selectivity up to 90% towards N₂O formation [34].

Depending on the impurities present in the crude N₂O, it can be either cleaned or used directly for the hydroxylation of aromatics. A typical off-gas from adipic acid plants contains N₂O (25-30 vol %), N₂ (60-65 vol %), O₂ (3-8 vol %), CO₂ (3-4 vol %), H₂O (2-3 vol %), NOₓ (1000-5000 ppm), and CO (500-1000 ppm). Studies of the influence of these impurities on the hydroxylation of benzene have revealed that high concentrations of contaminants such as NOₓ and ammonia are catalyst poisons. Others, like CO, although not catalyst poisons, can compete for α-oxygen, thus reducing the selectivity of the process. O₂ was found to lead to complete benzene combustion. Figure 5.27 shows that N₂O stream has to be treated to reduce some of the contaminants that can be detrimental to hydroxylation reaction. Uriarte [33] reported nitrous oxide off-gas could be passed through an SCR reactor in the presence of ammonia to remove NOₓ. The oxygen is eliminated by reaction with H₂ in the presence of a Pd-based catalyst. Pamon et al. reported [34] a new process for production and purification of N₂O via selective oxidation of ammonia over Mn-Bi-O/α-Al₂O₃ catalyst with a low rate of NO. Ammonia was fed in a SCR reactor to remove NOₓ. Again, O₂ was eliminated by introducing H₂ in the presence of a Pd based catalyst.
It has been reported [35] that contaminants and dilutants affect the hydroxylation of benzene. Effects of N-containing compounds, CO, O₂, and water in different concentrations on the behaviour of catalysts in the hydroxylation of benzene were studied below.

Fe/ZSM-5-E catalyst was placed in a 7 mm diameter stainless steel tube and the temperature increased to 550°C with a ramp of 1°C/min. At 550°C air was fed to the reactor for 4 hours. Then He replaced the air and the temperature was raised to 600°C with the same ramp. The catalyst was treated in a steam atmosphere for 1 hour and then cooled to room temperature with a ramp of 1°C/min. Acid treatment was done in two steps. First the catalyst was reacted with Na₂S₂O₄ for 15 min at 70°C. The sample was filtered and washed twice with double distilled water for 30 minutes. Finally, the catalysts were dried at 120°C for 24 hours.

Two major sources of the N₂O were described in Figure 5.27. In both sources, N₂O contains some impurities that show positive or negative effects in hydroxylation of benzene. Depending on the level of impurities in the N₂O different methods were suggested to reduce impurities [36, 37].

Figure 5.27 N₂O sources for hydroxylation of benzene.
5.5.1 Effect of N-containing compounds

Figure 5.28 shows that phenol productivity decreased with introducing 1 and 1.5 mol% NH₃. The reaction was run at 55 mol% benzene, 5.5 mol% N₂O and the balance with He. After five hours NH₃ was introduced with 1 mol% ratio. A sharp decrease in productivity area picks was observed. The NH₃ flow rate was increased to 1.5 mol% and lower productivity resulted. It was also observed that productivity remained very low even after disconnecting the NH₃ line after seven hours. This fact shows N-containing compounds (NOₓ, NH₃, etc.) are catalyst poisons and ideally must be removed from the stream gas inlet. Ma and Grünert [38] reported that a low level of NO contributed to a selective catalytic reduction in the presence of ammonia over the same catalyst with superior catalytic activity and stability in a wide temperature range.

\[
2 \text{NH}_3 + 2 \text{NO} + \frac{1}{2} \text{O}_2 \rightarrow 2 \text{N}_2 + 3\text{H}_2\text{O} \quad \text{Eq. 5.8}
\]

They also observed that the NO conversion increased with increasing reaction temperature. It has been suggested that a very low amount of N-containing compounds (less than 200 ppm or preferably to less than 40 ppm) facilitate the decomposition of N₂O [39]. It is, however, noted that NO is converted to NO₂ according to Equation 5.9.

\[
\text{N}_2\text{O} + \text{NO} \rightarrow \text{N}_2 + \text{NO}_2 \quad \text{Eq. 5.9}
\]
5.5.2 Effect of carbon monoxide

The selective catalytic reduction of N$_2$O with CO was performed over Fe/ZSM-5-E. Reduction of N$_2$O with CO (N$_2$O + CO $\rightarrow$ N$_2$ + CO$_2$) starts at a significantly lower temperature compared to direct N$_2$O decomposition.

Figure 5.29 shows CO can compete with N$_2$O for α-oxygen, thus active sites are contributed in reducing both N$_2$O and CO and result in lower productivity compared with an inlet stream without CO. A 32% reduction in productivity was observed when 1.88 mol% CO was added to the stream line after 3 hours. It can be seen that higher concentrations of CO resulted lower productivity. It was observed that the same N$_2$O decomposition was achieved after 9 hours when CO was removed from the stream line. The same productivity was observed after removing CO from the feed stream.

Figure 5.28  Phenol production vs. time on stream at condition (feed gas = 55/5.5/1.08-5/balance with He mol% (benzene/ N$_2$O/NH$_3$/He); ◆:0 ◆:1, ■:1.5 mol% NH$_3$; contact time 1.8 s; temperature 412°C).
5.5.3 Effect of oxygen

Figure 5.30 shows lower activity of the zeolite after introducing O₂. During the first 5 hours the reaction was run at 55 mol% benzene, 5.5 mol% N₂O and balance with He. Then a 57% reduction in productivity was observed after introducing 2.55 mol% O₂. The experiment was continued with adding 3.25 and 5 mol% O₂ and the results show 60% and 73% reduction in productivity, respectively. It was observed that some of the activity was lost permanently after disconnecting O₂ from inlet stream after 9 hours.

The influence of oxygen in the conversion of benzene can be explained by two effects. First, O₂ was found to lead to complete benzene combustion to CO₂ and H₂O. Panov et al. [32] reported 0.3% benzene conversion at 500°C. Second, oxygen enhances the ionizing properties of acidic sites, which act as a strong oxidant, and aromatic cation
radicals can be formed after oxygen pre-treatment of zeolite catalyst. So the cations formed can be condensed on the outer surface of the zeolite to aromatic polymers, which are precursors of coke deposits.

![Graph showing phenol production vs. time on stream](image)

**Figure 5.30** Phenol production vs. time on stream at condition (feed gas = 55/55/1.08-5/balance with He mol% (benzene/N2O/O2/He); ◊:0, ○:5, +:2.55, •:3.25 mol% O2; contact time 1.8 s; temperature 412 °C).

It is necessary to further decrease the residual O2 in the N2O stream. Figure 5.27 shows in O2 reduction by one or more reductants such as CO, H2, and hydrocarbons which could be introduced into N2O stream.

\[
\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2 \quad \text{Eq. 5.10}
\]

\[
\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} \quad \text{Eq. 5.11}
\]

\[
\text{C}_x\text{H}_y + (x+y/4) \text{O}_2 \rightarrow x \text{CO}_2 + y/2 \text{H}_2\text{O} \quad \text{Eq. 5.12}
\]
5.5.4 Effect of water

Figure 5.31 shows the presence of water which competitively adsorbs on the active centres with N₂O, which explains the lower activity when water is in the feed stream. Lower productivity was observed after introducing 3.3 mol% H₂O after 8 hours. The H₂O flow rate was increased to 10.4 and 12 mol% and lower productivity resulted. Figure 5.31 also shows the same catalyst activity after 11 and 14 hours when H₂O was disconnected from the stream line.

Water is able to reduce significantly the rate of catalyst deactivation. The additional water may keep the ratio of Lewis to Brønsted acid sites low and also displace phenol from the active sites; since phenol is recognized as coke precursors, this may suggest a technique to reduce coke formation.

\[
\text{Brønsted sites} \leftrightarrow \text{Lewis sites} + \text{Water} \quad \text{Eq. 5.13}
\]

Figure 5.31  Phenol production vs. time on stream at condition (feed gas = 55/5.5/3.3-12/balance with He mol% (benzene/ N₂O/H₂O/He); 0:0, ●: 10.4, △: 3.3, +:12 mol% H₂O; contact time 1.8 s; temperature 412 °C).
Figure 5.32 shows the oxidation of benzene to phenol at 55 mol% benzene, 5.5 mol% N₂O, 1.3 mol% H₂O, 0.2 mol% CO and the balance with He over a zeolite catalyst. The activity of the zeolite catalyst shows a 10% decrease after 15 hours.

![Graph](image)

**Figure 5.32** Phenol production vs. time on stream at base condition: feed gas = 55/5.5/1.3/0.2/Balance with He (benzene/N₂O/H₂O/CO/He); contact time 1.8 s; temperature 412°C.

The lifetime of the catalyst, phenol productivity, and selectivity are strongly affected by the presence higher amounts of contaminants in the feed stream. NOₓ and NH₃, for example, are poisons to the catalyst. The presence of O₂ must be limited in order to avoid complete oxidation of benzene and also prevent the speeding up of coke formation on the outer surface of the zeolite. It was observed that CO was in competition with benzene to oxidise on the active sites. Finally, the presence of water which competitively adsorbed on the active centres with N₂O can explain the lower activity but resulted in better stability.
5.6 Coke formation

The formation of coke deposits on catalyst surfaces causes economic and technological problems leading to catalyst deactivation in many hydrocarbon processes. The optimization of such complex processes requires the characterization of the coke deposits in order to understand the effect of the operational variables on these deposits and minimize its formation and develop effective regeneration strategies. Coke formation is strongly dependent on the zeolite structure [40, 41], on the reaction conditions [42-45], and on the nature of the reactants [46, 47]. Catalyst deactivation due to coke formation poses the problem of catalytic activity restoration, which is commonly reached via oxidative treatment of coked catalysts with air or oxygen-containing mixture at high temperatures [48-52]. Such processing may lead to undesirable “side effects”, such as dealumination, zeolite destruction, agglomeration of supported metals, etc. These side-effects decrease the catalyst lifetime and raise the total cost of industrial production.

To understanding the relationship between catalyst characteristics and deactivation of Fe/ZSM-5-J, which was prepared by LIE, catalyst was placed in a 7 mm diameter stainless steel tube and the temperature increased to 550°C with a ramp of 1°C/min. At 550°C air was fed to the reactor for 4 hours. Then He replaced the air and the temperature was raised to 900°C with the same ramp. The catalyst was treated in a vacuum for 1 hour and then cooled to room temperature with a ramp of 1°C/min. Acid treatment was done in two steps. First the catalyst was reacted with Na2S2O4 for 15 min at 70°C. The sample was filtered and washed twice with double distilled water for 30 minutes. Finally, the catalysts were dried at 120°C for 24 hours. The catalytic tests were made using a feed containing a large excess of benzene (benzene:N2O:He, 50:5:45 mol%) at 412°C in order to minimize the possible effect of consecutive reactions of further hydroxylation of the phenol intermediate.

Figures 5.20 and 5.33 show the productivity of phenol during hydroxylation of benzene as a function of the time-on-stream, using a series of Fe/ZSM-5 catalysts prepared by ion exchange or by hydrothermal synthesis and having increasing amounts of iron or Fe/Al.
ratio in the 0.0081 to 0.6 range. The Fe/ZSM-5-A sample shows an initial productivity to phenol of about 2.5 mmol/gh, the productivity of which decreases much faster up to 5 hours on streams and then remained nearly constant over the period 5 to 20 hours. Higher amount of Fe$^{3+}$ ions in samples Fe/ZSM-5-E and Fe/ZSM-5-J significantly increases the initial productivity to phenol, but a lower half-life was observed from the experimental data for these catalysts.

![Graph](image)

**Figure 5.33** Productivity to phenol and coke formation as a function of the time-on-stream in Fe/ZSM-5-J.

To further investigate coke formation the reaction was run for durations of 0, 0.5, 1.5, 5, 9, and 20 hours. Table 5.13 shows the BET results for Fe/ZSM-5-J. The catalysts were weighted before and after regeneration to determine the weight of the coke. It was observed a linear relationship between productivity and coke formation (Figure 5.33).
Table 5.13 Effect of reaction duration on weight of coke, total pore volumes, areas, and pore sizes.

<table>
<thead>
<tr>
<th>Reaction time (h)</th>
<th>Coke (wt%)</th>
<th>Total BET area (m²/g)</th>
<th>Total pore volume (cm³/g)</th>
<th>Mesopore size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe/ZSM-5-J 0</td>
<td>0</td>
<td>349.0030</td>
<td>0.480270</td>
<td>55.0448</td>
</tr>
<tr>
<td>Fe/ZSM-5-J 0.5</td>
<td>2.23</td>
<td>340.0865</td>
<td>0.462478</td>
<td>54.3953</td>
</tr>
<tr>
<td>Fe/ZSM-5-J 1.5</td>
<td>2.63</td>
<td>335.0025</td>
<td>0.453543</td>
<td>53.6820</td>
</tr>
<tr>
<td>Fe/ZSM-5-J 5</td>
<td>3.1</td>
<td>331.8246</td>
<td>0.441431</td>
<td>53.2126</td>
</tr>
<tr>
<td>Fe/ZSM-5-J 9</td>
<td>3.65</td>
<td>327.6148</td>
<td>0.431755</td>
<td>52.1536</td>
</tr>
<tr>
<td>Fe/ZSM-5-J 20</td>
<td>4.47</td>
<td>321.8714</td>
<td>0.419751</td>
<td>50.5920</td>
</tr>
</tbody>
</table>

Figure 5.34 shows that the area of catalyst decreases by linear with weight of coke. As 8% decrease in catalyst area resulted after 20 hours of running the reaction. The surface area decreased more than 2% after 0.5 hour; in the stages of coke formation of catalyst area does not show a linear behaviour with the reaction time.

![Figure 5.34 Effect of coke weight on surface area of Fe/ZSM-5-J.](image-url)
It was observed that coke created and located in the channels resulted in a lower volume after running the reaction. It can be seen from Figures 5.33, 5.35 and Table 5.13 that 10% decrease in volume occurred when the catalyst reached its half-life. Figure 5.36 shows an almost linear relation between volume of catalyst and weight of coke formation while relation between volume and productivity is not linear (Figure 5.33 and Table 5.13).

![Figure 5.35 Effect of coke weight on volume of Fe/ZSM-5-J.](image)

A non-linear relation between pore size and coke formation is shown Figure 5.36, with less than 1% decrease in pore size after 0.5 hour of running the reaction. Table 5.13 shows that after 0.5 hour the rate of decreasing pore size of catalyst was increased sharply while the highest rate of deactivation was accrued in the first hour (Figure 5.33). It was concluded that the most important parameter for deactivating of catalyst in the earlier stages are decreasing of volume and surface of the catalyst via coke formation in channels. It was also observed that a part of coke was formed on the surface of the catalyst and caused the mouths of pores to be blocked by coke.
The amount of coke deposited over the Fe/ZSM-5-J was determined also for different time-on-stream values (Table 5.13). Initially, all the coke formed before 1.5 hour was soluble in methylene chloride, whereas after 1.5 hour on-stream the main part of coke consisted of higher molecular weight polyaromatic compounds which were insoluble. Finally, coke deposited over the Fe/ZSM-5 was characterized by GC-MS.

Figure 5.37 shows the possible mechanism for coke formation over zeolite catalysts. After formation, phenol may back diffuse out of zeolite channels or be further converted. It may be either further hydroxylated and then transformed to heavier products or may be react with benzene or another phenol molecule to give products of coupling, which are then further transformed to carbonaceous species.
Figure 5.37 Possible mechanism for coke formation [45, 47].
5.7 **Kinetics of benzene hydroxylation**

A redox (stepwise) mechanism of phenol and dihydroxybenzenes formation, with different states of $\alpha$-sites, are shown in the following equations. This scheme includes first the $\alpha$-oxygen loading. Then, the $\alpha$-oxygen interaction with benzene and finally phenol can be extracted from the catalyst surface. The oxidation continues with reaction of phenol with $\alpha$-oxygen, and dihydroxybenzenes are extracted from the catalyst surfaces.

\[
\begin{align*}
\text{N}_2\text{O} + \alpha^* & \rightarrow \alpha\cdot\text{O}^* + \text{N}_2 \quad \text{Eq. 5.14} \\
\text{C}_6\text{H}_6 + \alpha\cdot\text{O}^* & \rightarrow \alpha\cdot\text{OHC}_6\text{H}_5 \quad \text{Eq. 5.15} \\
\alpha\cdot\text{OHC}_6\text{H}_5 & \rightarrow \text{HOOC}_6\text{H}_5 + \alpha^* \quad \text{Eq. 5.16} \\
\text{C}_6\text{H}_5\text{OH} + \alpha\cdot\text{O}^* & \rightarrow \alpha\cdot(\text{OH})_2\text{C}_6\text{H}_4 \quad \text{Eq. 5.17} \\
\alpha\cdot(\text{OH})_2\text{C}_6\text{H}_4 & \rightarrow (\text{HO})_2\text{C}_6\text{H}_4 + \alpha^* \quad \text{Eq. 5.18}
\end{align*}
\]

5.7.1 **Influence of the feed composition on the selectivity-conversion behaviour**

The mechanism of the hydroxylation process is based on the decomposition of nitrous oxide forming a monoatomic chemisorbed, oxygen species accompanied by release nitrogen. Then, benzene reacts with the oxygen species to make phenol. The second step not only contains the phenol formation itself, but also the desorption of this product from the active site and the diffusion out of the zeolite channels. These steps are important for the kinetics of the process because of the relatively strong interaction of phenol with the zeolite.

A plug flow reactor was used for investigations of the behaviour of the Fe/ZSM-5-I at 410°C, atmospheric pressure, 1 second contact time, and two different feed compositions. First in the presence of excess of N$_2$O with 5 mol% benzene, 20 mol% N$_2$O, and balance with He resulted in second order behaviour, and second in the presence of excess benzene with 50 mol% benzene, 5 mol% N$_2$O, balance with He resulted in first order behaviour in the hydroxylation reaction. In this study, an excess of benzene feed condition was
applied. The net rate of phenol production is approximately equal to the net rate of N₂O consumption, because the selectivity of N₂O for phenol is >95%. Therefore, the net rate of phenol production is also first order in N₂O concentration. This is illustrated in Figure 5.24 which shows phenol productivity as a function of the feed gas N₂O partial pressure (\(P_{N_2O}^o\)). Productivity increases linearly with feed gas N₂O less than 5 mol%.

Panov et al. [55] also found for Fe/ZSM-5 an absence of oxygen inhibition and pure first order behaviour for nitrous oxide.

The kinetic equation for the rate of N₂O consumption in a plug flow reactor (\(r_{N_2O}\)) with first-order behaviour can be written as

\[
r_{N_2O} = -\frac{dP_{N_2O}}{d\tau} = k_1 P_{N_2O} \quad \text{Eq. 5.19}
\]

If \(\tau = 0\), \(P_{N_2O} = P_{N_2O}^o\) and \(k_1 = \frac{\ln(1-x)}{\tau}\)

The unit of \(r_{N_2O}\) is partial pressure change per unit time. Contact time is also defined as the catalyst bed volume (cm³) divided by the feed gas flow rate (cm³/s).

Tables 5.11 and 5.12 show that an increase of the benzene and phenol mol fractions was decreased N₂O consumption. Therefore, \(r_{N_2O}\) is not constant but varies within the reactor. It was observed that constant \(k_1\) decreases with increasing concentrations of benzene and phenol (Figure 5.38).
Figure 5.38 \( N_2O \) conversion \( (X_{N_2O}) \) as a function of inlet benzene partial pressure \( (P_b^0) \) and inlet phenol partial pressure \( (P_{Ph}^0) \) (reaction conditions: 410°C, atmospheric pressure, 5 mol% \( N_2O \), 1 s contact time).

The Arrhenius plot of apparent rate constant \( k_i \) on temperature is shown in Figure 5.39. The straight line fit between \( \ln(k_i) \) and inverse absolute temperature and the slope of this plot gives a value of the apparent activation energy of 51 kJ/mol.

Figure 5.39 Arrhenius plot rate constants \( (k_i) \) as a function of temperature.
Zeolites have unique properties when compared with conventional heterogeneous catalysts. The micropore structure of the zeolite causes reaction kinetics to depend largely on sorption and diffusion of components within the zeolite structure. The rate of the catalytic reaction depends on the concentration of sorbed components and the concentration of active catalyst sites. The concentration of sorbed components depends on the gas phase concentration and the sorption equilibrium constant, which is temperature dependent. In conventional heterogeneous catalysis, sorption sites and active catalytic sites are the same sites, whereas in zeolite catalysis the sorption sites and active sites are different. These features of zeolite catalysis should be taken into account when interpreting the kinetic data.

For the experimental results obtained in the current study, it has been shown that the overall rate of \( \text{N}_2\text{O} \) consumption is first order with respect to the \( \text{N}_2\text{O} \) gas phase mole fraction. If the rate limiting step is a reaction between sorbed \( \text{N}_2\text{O} \) and \( \alpha \)-sites, it follows that the concentration of sorbed \( \text{N}_2\text{O} \) varies linearly with the gas phase \( \text{N}_2\text{O} \) concentration. In other words, it follows that \( \text{N}_2\text{O} \) sorption in the zeolite obeys Henry's Law and its concentration within the zeolite micropores is expressed by the equation:

\[
\{ \text{N}_2\text{O} \} = \beta_{\text{N}_2\text{O}} P_{\text{N}_2\text{O}} \nu N_0 \quad \text{Eq. 5.20}
\]

In Equation 5.20, \( \beta_{\text{N}_2\text{O}} \) is the Henry's constant; \( N_0 \) the maximum sorption capacity of the zeolite micropores; \( \nu \) is the fraction of free micropore volume not occupied by molecules of benzene and phenol.

The inhibition of the rate of the \( \text{N}_2\text{O} \) consumption observed in the current study, when benzene partial pressure or phenol partial pressure increases, may be explained by a sorption model which predicts a decrease in sorbed \( \text{N}_2\text{O} \) as the amount of sorbed benzene and phenol increases. The literature data imply that large molecules of the size close to the micropore size within ZSM-5 zeolite, such as benzene and phenol, are strongly sorbed on these zeolites at elevated temperature [54]. Small molecules such as \( \text{N}_2\text{O} \), with the exception of substances with alkaline or acidic properties, are strongly sorbed only at
low temperature. Furthermore, Henry’s Law is more likely to be accurate at low sorbed species concentration. So the assumption of \( \text{N}_2\text{O} \) sorption obeying Henry’s Law at the high temperatures of the reaction seems to be reasonable. Under the assumption of equilibrium sorption of benzene and phenol following the Langmuir sorption isotherm, the \( \text{N}_2\text{O} \) concentration in the zeolite may be expressed by equation:

\[
\{ \text{N}_2\text{O} \} = \frac{\beta_{\text{N}_2\text{O}} P_{\text{N}_2\text{O}}}{1 + \beta_{\text{B}} P_{\text{B}} + \beta_{\text{Ph}} P_{\text{Ph}}} N_0 \quad \text{Eq. 5.21}
\]

where \( \beta_{\text{B}} \) and \( \beta_{\text{Ph}} \) are the sorption equilibrium constants for benzene and phenol, respectively.

If the rate limiting step is the reaction between sorbed \( \text{N}_2\text{O} \) and unoccupied \( \alpha \)-sites, and the concentration of unoccupied catalyst active sites is a constant, then the expression for the rate of \( \text{N}_2\text{O} \) consumption is given by the equation:

\[
\text{r}_{\text{N}_2\text{O}} = k_1 P_{\text{N}_2\text{O}} = \frac{k P_{\text{N}_2\text{O}}}{1 + \beta_{\text{B}} P_{\text{B}} + \beta_{\text{Ph}} P_{\text{Ph}}} \quad \text{Eq. 5.22}
\]

In this equation, \( k = k^* \beta_{\text{N}_2\text{O}} N_0 \), where \( k^* \) is the true rate constant for the reaction between sorbed \( \text{N}_2\text{O} \) and unoccupied \( \alpha \)-sites.

### 5.7.2 Kinetic regularities of the formation of dihydroxybenzenes

It is necessary to characterize the kinetics of the formation of dihydroxybenzenes. Figure 5.40 shows plot of the reactor exit gas partial pressures of phenol \( (P_{\text{Ph}}) \) and the sum of the dihydroxybenzenes \( (P_{\text{Di}}) \) as a function of benzene \( (P_{\text{B}}) \) and phenol \( (P_{\text{Ph}}^0) \) concentrations in the feed gas, and is based upon the data in Tables 5.11 and 5.12.
Figure 5.40 Reactor exit partial pressure of phenol ($P_{ph}$) and dihydroxybenzenes ($P_{D}$) vs. inlet partial pressure of benzene ($P_{b}$) and phenol ($P_{ph}$).

Figure 5.40 indicates that with increasing ($P_{b}$) higher ($P_{ph}$) and lower ($P_{D}$) and with increasing ($P_{ph}$) the higher ($P_{ph}$) and ($P_{D}$) was observed. Based upon this fact, it is suspected that dihydroxybenzenes are formed primarily by the oxidation of phenol, according to Equations 5.23 and 5.24.

\[
\begin{align*}
C_6H_6 + N_2O & \rightarrow C_6H_5OH + N_2 \quad \text{Eq. 5.23} \\
C_6H_5OH + N_2O & \rightarrow C_6H_4(OH)_2 + N_2 \quad \text{Eq. 5.24}
\end{align*}
\]

Equations 5.27 and 5.28 show the mechanism of dihydroxybenzene formation.

\[
\begin{align*}
N_2O + *\alpha-OHC_6H_5 & \rightarrow \alpha-O* + N_2 + C_6H_6OH \quad \text{Eq. 5.25} \\
C_6H_6 + \alpha-O* & \rightarrow *\alpha-OHC_6H_5 \quad \text{Eq. 5.26} \\
N_2O + *\alpha-(OH)_2C_6H_4 & \rightarrow \alpha-O* + N_2 + C_6H_6(OH)_2 \quad \text{Eq. 5.27} \\
C_6H_5OH + \alpha-O* & \rightarrow *\alpha-(OH)_2C_6H_4 \quad \text{Eq. 5.28}
\end{align*}
\]

Equations 5.26 and 5.28 have a common intermediate, the oxidized $\alpha$-site. The limiting step of both routes (phenol and dihydroxybenzene formation) is interaction between N$_2$O and $\alpha$-sites occupied by phenol or dihydroxybenzene Equations 5.25 and 5.27.
The rate constant \( k \) of \( \text{N}_2\text{O} \) consumption is presented by Equation 5.19. This Equation is not quite rigorous since it was derived under the assumption that \( \text{N}_2\text{O} \) is consumed by a single route. However, taking into account that the rate of dihydroxybenzene formation (Equation 5.24) is low, its effect on the \( k \) value will be negligible, and \( k= k_1 \) (\( k_1 \) is the rate constant of Equation 5.25).

Applying quasistationary conditions, one may express the rates of phenol and dihydroxybenzenes formation (Equations 5.23 and 5.24) in terms of the rates of benzene and phenol molecules interaction with oxidized \( \alpha \)-sites (Equations 5.26 and 5.28):

\[
\begin{align*}
\text{r}_{\text{ph}} &= k_B \{ B \}[ -O] - k_{\text{ph}} \{ Ph \}[ -O ] \quad \text{Eq. 5.29} \\
\text{r}_{\text{Di}} &= k_{\text{ph}} \{ Ph \}[ -O] \\
\text{Eq. 5.30}
\end{align*}
\]

In Equations 5.29 and 5.30, quantities enclosed in square brackets \([\ ]\) denote concentrations of \( \alpha \)-sites, quantities enclosed in braces \( \{ \} \) are sorbed components in the micropore zeolite volume, \( k_B \) and \( k_{\text{ph}} \) are the rate constants of interaction between the sorbed benzene and phenol molecules and oxidized \( \alpha \)-sites. The concentrations of sorbed components, under the assumption of Langmuir equilibrium, are expressed by equations:

\[
\begin{align*}
\{ B \} &= \frac{\beta_B P_B}{1 + \beta_B P_B + \beta_{\text{ph}} P_{\text{ph}}} N_0 \quad \text{Eq. 5.31} \\
\{ Ph \} &= \frac{\beta_{\text{ph}} P_{\text{ph}}}{1 + \beta_B P_B + \beta_{\text{ph}} P_{\text{ph}}} N_0 \quad \text{Eq. 5.32}
\end{align*}
\]

Where \( \beta_B \) and \( \beta_{\text{ph}} \) are the sorption equilibrium constants for benzene and phenol, respectively. In Equations 5.31 and 5.32, only benzene and phenol concentrations are taken into account since the partial pressure of dihydroxybenzenes is low relative to benzene and phenol, and because \( \text{N}_2\text{O} \) sorption has no effect on the sorption of other components.
Dividing the first equation by the second equation in the system of Equations 5.29 and 5.30 and taking into account Equation 5.31 and 5.32 gives Equation 5.33:

\[
\frac{r_{ph}}{r_{dh}} = b \frac{P_B}{P_{Ph}} - 1 \quad b = \frac{k_B \beta_B}{k_{ph} \beta_{ph}} \quad \text{Eq. 5.33}
\]

Equation 5.33 characterizes the ratio between phenol and dihydroxybenzene formation rates and, in combination with Equation 5.22, characterizes completely the kinetics of the two-step reaction (Equations 5.23 and 5.25) for the chosen conditions of experiment.

In this study, a reaction network of the hydroxylation of benzene to phenol with N\textsubscript{2}O has been derived from kinetic measurements in a plug flow reactor. In the range of conditions evaluated, a first order dependence between the rate of N\textsubscript{2}O consumption and N\textsubscript{2}O concentration and a value of the apparent activation energy of 51 kJ/mol was revealed. An increase on the phenol mol fraction caused an increase in the rate of dihydroxybenzenes formation via phenol oxidation.
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CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER WORK
CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER WORKS

6.1 Conclusions

From the experimental results, we can summarize the conclusions as follow:

- Regarding hydroxylation of benzene using Pd membrane:
  - It is possible to produce phenol using oxygen as an oxidant in a Pd membrane reactor. Permeated hydrogen can react with oxygen to produce active oxygen species which reacts with benzene to produce phenol.
  - Pd membrane showed high hydrogen flux of $1.24 \text{ m}^3 \text{ m}^{-2} \text{ h}^{-1} \text{ atm}^{-0.5}$ at $200^\circ \text{C}$.
  - Table 4.6 shows maximum productivity to phenol and selectivity was $0.31 \text{ mmol/h}$ and $80\%$, respectively.
  - A huge amount of water was produced during the reaction and the $\text{O}_2/\text{H}_2$ ratio is the most important factor to change the amount of water. It was found lower productivity for higher values of the $\text{O}_2/\text{H}_2$ ratio.
  - Lower productivity was observed when a mixture of all reactants introduced to the Pd membrane. This evidence shows more active oxygen was produced when hydrogen permeated from a Pd membrane.
  - Using a second catalyst shows different influences. It was observed slightly increase in productivity using Fe/ZSM-5 while Mo (which coated internal surface of PSS tube using CVD) shows a decrease in productivity.
  - Hydroxylation reaction occurred on the surface of a Pd catalyst and productivity can be improved up to $30\%$ by changing reactor design.

- Regarding hydroxylation of benzene using PFR and zeolite:
• It is possible to produce phenol using N\textsubscript{2}O as an oxidant using catalysts with MFI topology in a PFR.
• Fe is required for formation of extra framework species that are active in selective conversion of benzene to phenol (Figure 5.16).
• A wide range of Fe and Al containing MFI materials, which prepared with LIE, CVD, and HS, were tested to design an effective catalyst in decomposition of N\textsubscript{2}O and hydroxylation of benzene.
• Higher decomposition of N\textsubscript{2}O and productivity toward phenol were achieved by increasing the reaction temperature.
• It was found a higher amount of Fe loaded into the catalyst create higher numbers of the active sites which caused further oxidation of products toward coke.
• It was observed that the rate of coke formation decreased with decreasing reaction temperature and increasing concentration of benzene.
• Figure 5.24 shows that excess of benzene in the feed compositions caused an increase in productivity and selectivity. Productivity can also be increased by lower SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio.
• Lifetime of the catalyst is strongly affected by the presence of contaminants in the feed stream.
• From an economic point of view using N\textsubscript{2}O in the presence of zeolite is expected to offer more advantages than a Pd membrane for oxidation of aromatic compounds.

6.2 Recommendations for future works

The study made recommendation as follow;

  • Regarding hydroxylation of benzene using Pd membrane:
    • Fabrication of Pd alloy membranes using Cu or Ag which are reported higher permeability to hydrogen.
• Using W or Mo (active elements in oxidation using oxygen as an oxidant) in the framework of zeolite.
• Design a Pd membrane reactor which reactants have more chance to contact with the internal surface of Pd/PSS.

Regarding hydroxylation of benzene using PFR and zeolite:

• The nature of active sites is still unclear. Using new techniques such as High Resolution X-ray Absorption Near Edge Spectroscopy (HR-XANES) and Mössbauer Spectroscopy (MS) will lead us to design a more efficient catalyst.
• Using fluidized bed reactor and reproduce our data in this study.
Appendix

JOURNAL PAPERS

- M.H. Sayyar, R.J. Wakeman, "Influence of feed contaminants in hydroxylation of benzene" IChemE (submitted)

CONFERENCE PAPER

- M.H. Sayyar, R.J. Wakeman, "Influence of contaminants in hydroxylation of aromatic compounds using Fe/ZSM-5" III International Conference Catalysis: Fundamentals and Application, July 4-8, 2007 Novosibirsk - Russia

POSTER PRESENTATION

Comparing two new routes for benzene hydroxylation

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\textbf{K E Y W O R D S:}
Benzene hydroxylation
Pd membrane
Hydrogen permeation
Fe/ZSM-5
\N_2\O\ decomposition

\textbf{A B S T R A C T}
The vapour phase hydroxylation of benzene to phenol by two different methods has been investigated. In the first, a mixture of oxygen and hydrogen using a Pd membrane tubular reactor with and without second catalyst was used. Hydrogen dissociated on the palladium layer and reacted with oxygen to give active oxygen species, which reacted with benzene to produce phenol. The slow step in the overall reaction is the formation of usable hydrogen peroxide. Using a second catalyst changed the productivity, and conversion of benzene was increased by changing the length and diameter of porous reactor tubes. Low phenol productivity and selectivity was observed and showed that hydroxylation of benzene using a Pd membrane reactor is a far from economic method. In the second, selective oxidation of benzene with \N_2\O\ on iron zeolite of different SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} composition, with concentration of iron rating from 50 to 2000 ppm was investigated. The effects of temperature, reactant mole ratio, and contact time were investigated. Phenol was formed with near 97% selectivity and average productivity of 5 mmol g\textsuperscript{-1} h\textsuperscript{-1}.

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\textbf{1. 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 alklylation 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 (\textsc{AlCl}_3) at 100–200 °C. 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 60–100 °C. 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 of 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 60-70 °C) 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 (http://acswebcontent.acs.org/home.html) (Bellussi and Perego, 2000; Panov, 2000).

A difficult field of catalytic chemistry is selective oxidation of hydrocarbons. The main difficulty 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\textsubscript{2}, \textsubscript{2}H\O\, O\textsubscript{3}, and \N_2\O\ are used for the

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reaction (Panov, 2000; Dubey and Kannan, 2005; Nomiyama et al., 1998; Takeda et al., 2003; Yanar et al., 2003). Most heterogeneous catalysts contain a transition metal, supply an oxygen species that has a negative charge such as O\(^-\), O\(^2-\), or O\(^3-\), and cause oxidation of benzene via an electrophilic reaction mechanism (Moro-oka and Akita, 1998). It is likely that hydrogen peroxide is formed and leads to the formation of hydroxyl radicals, water, and atomic oxygen (Niwa et al., 2002).

There is considerable interest in use of a gas phase catalytic oxidation for phenol manufacture 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 \(\mathrm{N}_2\mathrm{O}\) 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, Be, Zn, Cu, Sb, As or V (Gabelmann et al., 1991). Kustov et al. (2002) reported the conversion of benzene and the selectivity to phenol 39 and 98%, respectively. In order to achieve these results, \(\mathrm{Zn}/\mathrm{ZSM}-5\) was calcined at 400-950 °C in air or an inert gas. Ribera et al. (2000) reported two isomorphously substituted Fe/ZSM-5 catalysts prepared by hydrothermal synthesis. Samples with a SiO\(_2\)/Al\(_2\)O\(_3\) ratio of \(< 100\) contained 0.5–1 wt% of iron with high selectivity (>99%) and high phenol yield (up to 27%). Pirutko et al. (2002) reported the hydroxyl formation reaction proceeds over the so-called \(\alpha\)-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 (Panov, 2000; Dubkov et al., 2002; Hensen et al., 2004, 2005; Pérez-Ramírez et al., 2003a).

Niwa et al. (2002) 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 \(\alpha\)-alumina tube with a thin layer of palladium by chemical vapour deposition (CVD).

In this paper two different methods for partial oxidation of benzene were investigated. In the first method, two kinds of membranes were developed. In the first, a Pd/PSS (palladium/porous stainless steel) membrane in which the intermetallic diffusion barrier layer was formed by controlled oxidation, and Pd was deposited by an electroless technique onto the outer surface of a PSS tube. Then the internal surface of a Pd/PSS membrane was coated using CVD with Mo as a second catalyst. A stainless steel tube was placed inside the Pd/PSS to give an annular flow section to promote the reactants, present near the catalyst surface. In the second, a Fe/ZSM-5 catalyst was made and used for the hydroxylation reaction. Catalytic experiments were performed using a plug flow reactor. Reaction conditions were studied and their effects on conversion, productivity, and selectivity are reported. The reaction path and mechanism are discussed.

### Table 1 - Composition of the solutions for preparation and plating of the stainless steel tubes

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Temperature (°C)</th>
<th>pH</th>
<th>Duration (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cleaning solution</td>
<td>(\mathrm{Na}_3 \mathrm{PO}_4 \cdot 12 \mathrm{H}_2 \mathrm{O} ) (g/l)</td>
<td>45-70</td>
<td>5-10</td>
</tr>
<tr>
<td></td>
<td>(\mathrm{NaOH} ) (g/l)</td>
<td>45-60</td>
<td>5-10</td>
</tr>
<tr>
<td></td>
<td>(\mathrm{Na}_2 \mathrm{CO}_3 ) (g/l)</td>
<td>65-90</td>
<td>5-10</td>
</tr>
<tr>
<td></td>
<td>Detergent (BEH100) (g/l)</td>
<td>1-5</td>
<td>5-10</td>
</tr>
<tr>
<td>Pd plating solution</td>
<td>(\mathrm{Pd(NH}_3)_4 \mathrm{Cl}_2 \cdot \mathrm{H}_2 \mathrm{O} ) (g/l)</td>
<td>4-6</td>
<td>5-10</td>
</tr>
<tr>
<td></td>
<td>(\mathrm{Na}_2 \mathrm{EDTA} \cdot 2 \mathrm{H}_2 \mathrm{O} ) (g/l)</td>
<td>40-80</td>
<td>5-10</td>
</tr>
<tr>
<td></td>
<td>(\mathrm{NH}_4 \mathrm{OH} ) (28%) (ml/l)</td>
<td>190-400</td>
<td>5-10</td>
</tr>
<tr>
<td></td>
<td>(\mathrm{H}_2 \mathrm{NNH}_2 \cdot 1 \mathrm{~M} ) (ml/l)</td>
<td>5-10</td>
<td>5-10</td>
</tr>
<tr>
<td></td>
<td>Polyoxyalkylene alky1 ether (ml/l)</td>
<td>0.1-0.5</td>
<td>5-10</td>
</tr>
<tr>
<td>Sensitizing solution</td>
<td>HCl (37%) (ml/l)</td>
<td>1.0</td>
<td>5-10</td>
</tr>
<tr>
<td></td>
<td>Temperature (°C)</td>
<td>20</td>
<td>5-10</td>
</tr>
<tr>
<td></td>
<td>Duration (min)</td>
<td>5</td>
<td>5-10</td>
</tr>
<tr>
<td>Activation solution</td>
<td>(\mathrm{FeCl}_3 ) (g/l)</td>
<td>0.1</td>
<td>5-10</td>
</tr>
<tr>
<td></td>
<td>HCl (37%) (ml/l)</td>
<td>1.0</td>
<td>5-10</td>
</tr>
<tr>
<td></td>
<td>Temperature (°C)</td>
<td>20</td>
<td>5-10</td>
</tr>
<tr>
<td></td>
<td>Duration (min)</td>
<td>3-5</td>
<td>5-10</td>
</tr>
</tbody>
</table>

Palladium is used as a catalyst, and the second route was based on using \(\mathrm{N}_2\mathrm{O}\) as an oxidizing agent and the Fe/ZSM-5 as a catalyst.

#### 2.1. Hydroxylation with \(\mathrm{O}_2\) and \(\mathrm{H}_2\) using Pd membrane reactor

##### 2.1.1. 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 30–60 min; the composition of the alkaline solution is given in Table 1. The tubes were then thoroughly washed with deionized water in an ultrasonic bath to remove the alkaline solution trapped in the pores. The cleaning process was repeated twice to ensure that all dirt and grease were removed from the surface. The tubes were then immersed in 2-propanol for 10 min to aid their complete drying.

Two of the support tubes were then oxidized in air at 600 and 800 °C for 2 h, with heating and cooling rates of 3 °C/min. The oxidation layer formed acts as a diffusion barrier between the PSS substrate and the Pd catalyst. The substrate was then activated by pre-seeding with finely divided Pd nuclei. The activation procedure consisted of successive immersion in a SnCl\(_2\) bath (sensitizing), followed by immersion in an acidic PdCl\(_2\) and rinsing with 0.01 M HCl solution to prevent hydrolysis of Pd\(^{2+}\) ions. The typical composition of the sensitizing and the activation bath is presented in Table 1.

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 90–120 min. After deposition was completed the membrane was left to cool to room temperature and dried. After each drying, the weight of the tube and the flux of helium through it were measured.
The weight gains before and after the plating were used to determine the thickness of the membrane.

One of the Pd/PSS tubes was used for the second step of the coating process; MoO2Cl2 was used to coat the internal surface of the tube by CVD. For the CVD exchange the tube was connected to a quartz reactor which contains a very thin layer of Mo on the internal surface of the tube by CVD. A very thin layer of Mo was formed on the internal surface of the tube by CVD. The reactor was heated to 330 °C and kept at this temperature for at least 30 min. Finally, the temperature was lowered to 30 °C under the same He flow. A very thin layer of Mo was formed on the internal surface of the Pd/PSS tube.

The morphology of the membrane was observed using scanning electron microscopy equipped with an EDS light element detector for qualitative and quantitative analysis (INCA Scientific). Table 2 presents the different flow rate combinations that were used in this reaction. During the reaction, the shell-side gas pressure was 2 atm and a trans-membrane pressure of 1 atm was used.

Fermentation measurements for hydrogen, helium, and argon were carried out at 200 °C using the reactor shown schematically in Fig. 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 analyzed by GC-MS.

### 2.2. Hydroxylation with N₂O using plug flow reactor

#### 2.2.1. Catalyst preparation

Zeolites containing a-sites can be prepared by adding FeCl₃ at the synthesis stage (Hydrothermal Synthesis) or by its post-synthetic introduction such as chemical vapour deposition, solid state ion exchange (SSIE), and liquid ion exchange (LIE) (Kharitonov et al., 1992). The samples studied in the present work were prepared by CVD and LIE.

Fe/ZSM-5 was prepared using the FeCl₃ CVD method described by Chen and Sachtler (1998). For the CVD exchange a quartz reactor was used. 1.5 g of the H/ZSM-5 was loaded into the reactor and flushed overnight under He (40 ml min⁻¹) at 300 °C. The temperature was then lowered to 30 °C under the same He flow. 0.45 g of anhydrous FeCl₃ was then loaded into the reactor. After being reconnected to the He line (30 ml min⁻¹), the reactor was heated to 330 °C and kept at 30 °C under the same He flow. 0.45 g of anhydrous FeCl₃ was then loaded into the reactor. After being reconnected to the He line (30 ml min⁻¹), the reactor was heated to 330 °C and kept at 330 °C.

### Table 2 - Productivity of phenol using Pd as a catalyst at various reaction temperatures and feed flow conditions

<table>
<thead>
<tr>
<th>Tube side He, O₂, H₂, (He + C₆H₆) (ml/min)</th>
<th>Shell side He, H₂ (ml/min)</th>
<th>Temperature (°C)</th>
<th>Phenol (mmol h⁻¹)</th>
<th>Dihydroxybenzenes (mmol h⁻¹)</th>
<th>H₂O in outlet gas (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10, 5, 0, 10</td>
<td>30, 10</td>
<td>150</td>
<td>0.31</td>
<td>0.062</td>
<td>80</td>
</tr>
<tr>
<td>10, 5, 0, 10</td>
<td>30, 10</td>
<td>200</td>
<td>0.12</td>
<td>0.036</td>
<td>69</td>
</tr>
<tr>
<td>10, 5, 0, 10</td>
<td>30, 10</td>
<td>250</td>
<td>0.08</td>
<td>0.028</td>
<td>28</td>
</tr>
<tr>
<td>10, 2, 0, 10</td>
<td>30, 10</td>
<td>150</td>
<td>0.06</td>
<td>0.02</td>
<td>21</td>
</tr>
<tr>
<td>10, 2, 0, 10</td>
<td>30, 10</td>
<td>200</td>
<td>0.07</td>
<td>0.019</td>
<td>29</td>
</tr>
<tr>
<td>10, 2, 0, 10</td>
<td>30, 10</td>
<td>250</td>
<td>0.086</td>
<td>0.013</td>
<td>32</td>
</tr>
<tr>
<td>All reactants fed on the tube side</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10, 2, 10, 10</td>
<td>35, 0</td>
<td>150</td>
<td>0.05</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td>10, 2, 10, 10</td>
<td>35, 0</td>
<td>200</td>
<td>0.001</td>
<td>0.003</td>
<td></td>
</tr>
<tr>
<td>Using Fe/ZSM-5 as a second catalyst</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10, 2, 10, 10</td>
<td>35, 0</td>
<td>300</td>
<td>0.065</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td>10, 2, 0, 10</td>
<td>30, 10</td>
<td>300</td>
<td>0.060</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>10 (He), 2 (N₂O), 10</td>
<td>30, 0</td>
<td>300</td>
<td>0.320</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>Using Mo as a second catalyst</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10, 5, 0, 10</td>
<td>30, 10</td>
<td>150</td>
<td>0.06</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>10, 5, 0, 10, 10</td>
<td>30, 10</td>
<td>150</td>
<td>0.09</td>
<td>0.03</td>
<td></td>
</tr>
</tbody>
</table>

* The tube side cross-section of this reactor was reduced by insertion of a stainless steel rod.

---

#### Fig. 1 - Schematic of Pd membrane reactor.
this temperature for at least 30 min. HCl, formed during the reaction of the sublimed FeCl₃ with the Brønsted sites of the support, was absorbed in 100 ml of 0.05 M NaOH solution for titration. After completion of the iron loading, the temperature was lowered to 30 °C. Then this catalyst was washed with 1000 ml of double distilled deionised water for 30 min and dried for 24 h in air at 70 °C.

For later comparisons, catalysts were also prepared from commercial zeolites H/ZSM-5 by modifying them by liquid ion exchange with 0.01 M FeCl₃ solution. The exchange was carried out at 80 °C for 12 h whilst stirring at 500 rpm. The samples were filtered and washed twice with double distilled deionised water for 30 min. Finally, the catalysts were dried at 70 °C for 24 h.

The chemical composition of the catalysts was determined by ICP-AES. XRD analysis was performed in the range 5° < 2θ < 50° using Cu Kα radiation with the scanning speed of 0.1° min⁻¹. The pore size and surface catalyst area were measured by nitrogen adsorption at 77 K using a Micrometrics ASAP 2010 analyzer. For transmission electron microscopy (TEM) examination, a catalyst sample was suspended by a few drops of acetone, followed by drying at ambient conditions. Transmission electron microscopy was carried out in a JEOL JEM-1011 microscope operated at 80 kV and equipped with a SIS Megaview III CCD camera. For this visualization, a few droplets of the sample suspended in acetone were placed on a carbon-coated copper grid followed by evaporation at ambient conditions.

2.2.2. Reactor construction and reaction conditions

Catalytic experiments were performed using a plug flow reactor. For each experiment, 200 mg of 0.1–0.2 mm diameter catalyst particles were placed into a stainless steel reactor with an inner diameter 3 mm. The feed gas components were controlled using mass flow controllers. The benzene feed rate was controlled using a syringe dosing system (Harvard apparatus, 0.00044–77 ml min⁻¹). The reactor exit gas mixture was sampled and analyzed online. Concentrations of products were determined by GC-MS and separating them using capillary columns DB-1701.

The experiments were carried at 370–450 °C with a feed gas containing 5–80 mol% benzene, 3–20 mol% N₂O, and the balance made up with He.

3. Results and discussion

Selective oxidation of hydrocarbons is recognized as a difficult field of catalyst chemistry, although new process routes are under investigation. For example, a one-step catalytic process to convert benzene to phenol using a Pd membrane in the presence of oxygen and hydrogen has been reported, and a new route for producing phenol based on using N₂O and iron containing zeolite as a catalyst has been proposed (Panov, 2002; Chen et al., 2002). In the following paragraphs, the results from experiments on benzene oxidation by O₂ and N₂O are discussed separately.

3.1. Benzene oxidation with H₂ and O₂

3.1.1. Effect of oxidation temperature on oxide barrier layer

After cleaning, the tubes were oxidized in air in a high temperature furnace at constant temperature. Fig. 2 shows the change of the properties of the 0.5 μm grade Fuji Filter PSS tubes following oxidation of the cleaned tubes. The oxygen peaks confirm the formation of oxide layers on the supports. 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, Cr₂O₃ 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 H₂ atmosphere. Therefore, it is the most desirable oxide phase for use as a barrier layer to minimize intermetallic diffusion.

To check the existence of a Cr-rich oxide on the surface of the...
samples, EDS spot scan analyses were performed (Samsanov, 1973). From the SEM micrograph of the samples oxidized at 600 °C, a dark uniform thin layer was observed. The EDS spot scan on the surface confirmed that this dark layer was actually the oxide layer, and its thickness was 0.2-0.3 μm. The SEM micrograph of the PSS oxidized at 800 °C shows a thicker dark region, but its thickness is nonuniform. It was also observed that the surface of this oxide layer was crumbly. The thickness of the dark oxide region varied from 1 to 6 μm from spot-to-spot.

In general, the oxidation process consists of two main steps, surface oxidation and then oxide scale formation. During the oxide scale formation there are several mechanisms including the diffusion of elements along their respective gradients, the diffusion of oxygen and oxidation at the metal oxide interface. All these mechanisms may affect the composition and the thickness of the formed oxide layer (Shackelford, 1996).

3.1.2. Surface morphological changes during membrane synthesis

Fig. 3 shows SEM photographs of the stainless steel substrate and the surface morphology of the Pd/PSS composite membrane. 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. It is also noted that although the deposited Pd particles were spherical and possessed a range of particle size, the particles were still packed together to form a dense layer. When a sufficient thickness (23-27 μm) had formed, after 24 h of plating, the Pd film was continuous and apparently defect free.

To confirm that the Pd/PSS tube was permeable at temperatures lower than 200°C, which is the reaction temperature for hydroxylation of aromatic compounds, the hydrogen permeance was investigated. The permeability of the tube to H₂ 1.24 m³ m⁻² h⁻¹ atm⁻⁰.⁵; its permeability to Ar and He was 0.045 and 0.11 m³ m⁻² h⁻¹ atm⁻¹, respectively.

The different units for H₂ permeation through the membrane arise from the transport mechanism. The transport equation for H₂ flux (J) is (Holleck, 1970):

\[ J = -K \left( \frac{P_{\text{feed}}^{\text{H}_2} - P_{\text{permeate}}^{\text{H}_2}}{L} \right) \]

where \( K \) is the permeability (related to the hydrogen diffusion coefficient and its solubility), \( P_{\text{feed}} \) and \( P_{\text{permeate}} \) are the hydrogen pressures on the upstream and downstream sides of the membrane, respectively, and \( L \) is the membrane thickness. The index on the pressure, \( n \), is related to the atomic ratio of hydrogen to palladium and has values that vary between 0.5 and 1.0 (Zhao et al., 1998). For a thick palladium film, as used in this work, bulk diffusion is the rate determining step for hydrogen permeation and \( n = 0.5 \). For thin membranes, hydrogen transport is thought to be controlled by a surface process involving adsorption and dissociation of molecular hydrogen, for which \( n \to 1 \).

### 3.1.3. Direct hydroxylation of benzene

The results of hydroxylation experiments are summarized in Table 2. When a mixture of hydrogen and helium was fed to the shell side, and benzene with oxygen and helium to the tube side, the productivity of phenol and amount of water produced during the reaction decreased with lower O₂ flow rate (or O₂/H₂ ratio). At the higher O₂/H₂ ratio, water production was reduced by higher reaction temperatures. These conditions coincided with lower production rate of phenol. When all reactants were introduced to the tube side the phenol production was reduced, making this an unattractive arrangement so the procedure was not studied further. Attempts were made to use Fe/ZSM-5 (2.1, 40, CVD-330) as a second catalyst by packing a Pd membrane tube with it. A mixture of gases was introduced to the tube side at 300°C but the productivity decreased; however, by replacing O₂ and H₂ with N₂O a much higher productivity was obtained.

The Pd/PSS membrane coated with Mo as a second catalyst was used in a further set of experiments. Compared with the Pd membrane without Mo the productivity of phenol was low, and the conversion of benzene was low (a low percentage of water in the outlet gases was also observed). The main reason appears to be that the Pd was covered by Mo on the internal surface of the membrane, reducing the Pd surface area, and that Mo caused lower hydrogen permeability. In a further experiment a stainless steel rod with 2 mm diameter was placed coaxially inside the membrane tube to reduce the flow cross-section and thereby promote contact of the catalyst surface by the reactants and increase the reaction area per unit mass of reactants. This configuration increased the productivity by 50%.

### 3.1.4. Mechanism for formation phenol

Based on previous studies for the formation of hydrogen peroxide, it is likely that hydrogen peroxide was formed in our system and led to the formation of hydroxyl radicals (Clerici and Ingallina, 1998; Tatsumi et al., 1992). Hydrogen is dissociated whilst permeating through the palladium membrane to form H⁺ (Niwa et al., 2002). Then H⁺ appears on the surface of opposite side of the membrane and reacts immediately with oxygen to give H₂O₂ and •OOH. Hydrogen peroxide then decomposes to •OH, water and atomic oxygen (Herron and Tolman, 1987). The following reactions summarize the dissociation of H₂:

\[
\begin{align*}
2\text{H}^+ & \rightarrow \text{H}_2 \\
\text{H}^+ + \text{O}_2 & \rightarrow \text{H}_2\text{O}_2 \rightarrow \cdot\text{OH} + (1/2)\text{H}_2\text{O} + (1/2)\text{O}_2 \\
\text{H}^+ + \text{O}_2 & \rightarrow •\text{OOH}
\end{align*}
\]

It is well established that the reaction of •OH with benzene proceeds by the addition of the aromatic ring giving a hydroxycyclohexadienyl (radical 2 in reaction 1 in Fig. 4), which will reversibly add O₂ to give a hydroxycyclohexadienyl peroxy (radical 3) (Alzueta et al., 2000; Brezinsky et al., 1998; Volkamer et al., 2002). This equilibrium adjusts rapidly and a multitude of subsequent reaction channels have been proposed; reaction 4 is one of the possible reactions that gives phenol. Route 5 forms •OOH through a hydrogen abstraction reaction of radical 2 with molecular oxygen. Route 4 in principle yields those same products through the direct elimination of OOH from radical 3. The formation of phenol without involvement of O₂ has been proposed by elimination of a ring bond H⁺ atom from radical 2 (reaction 3). It can be seen from Fig. 4 that radical 3, produced from reaction 2, may react with hydrogen, especially if only dissociated hydrogen (H⁺) is available on this reaction site to form radical 5. Then this radical will react with oxygen through route 7 and will form dihydroxybenzenes.

#### 3.2. Benzene oxidation with N₂O

Iron loaded zeolites have recently attracted renewed attention due to their outstanding catalytic properties. The main reactions catalyzed by Fe/ZSM-5 catalysts have been reported to be very efficient in selective catalytic reduction of nitrogen oxides using hydrocarbons (HC-SCR) (Brezinsky et al., 1998), selective oxidation of methane and benzene to methanol and phenol (Meloni et al., 2003; Wood et al., 2004), alkane conversion to alkene (Weckhuysen et al., 1998), and catalytic decomposition of N₂O (Pérez-Ramírez et al., 2003b; Wood et al., 2002).

![Fig. 4 - Proposed pathways for the initial steps in the •OH initiated degradation of benzene in the gas phase.](image-url)
Zeolite structures are determined by their SiO₂/Al₂O₃ ratio. Increasing the ratio improves acidity and thermal stability, increases the extent of cation exchange and atomic radius, and improves their hydrophilic specifications. Samples with different ratios were digested using a sodium peroxide fusion before analysis by ICP-AES; the elemental compositions of the various zeolite samples are given in Table 3.

The textual properties of the catalyst samples were investigated by nitrogen adsorption. The total surface area, the pore volume, and mean pore size for the H/ZSM-5 (0.01, 45) catalyst were measured to be 462 m² g⁻¹, 0.764 cm³ g⁻¹ and 66 Å, respectively, and for the Fe/ZSM-5 (1.95, 45, LIE) catalyst 445 m² g⁻¹, 0.746 cm³ g⁻¹ and 67 Å. The X-ray diffractograms of various samples are shown in Fig. 5; all samples display the typical diffraction pattern of the ZSM-5 framework. No indications were observed of the formation of Q-Fe₂O₃ (major reflections at 2θ = 33.2° and 35.7°) or any other iron oxide. TEM examination of Fe/ZSM-5 and its high temperature calcined and steamed counterparts showed no iron oxide particles on the external surface of the zeolite (Fig. 6).

3.2.2. Effect of reaction parameters on reactor performance

Catalytic experiments were performed at 400 °C using Fe/ZSM-5 (0.18, 45) with a feed gas containing 5.5 mol% N₂O, 50 mol% benzene, and 44.5 mol% He, and the results suggested that only a small fraction of the Fe is active in the selective oxidation of benzene to phenol. An excess of active sites promote coke formation which is resulted coupling of phenol with benzene or another by-products presence in reaction area. More active sites show more productivity to phenol during the first hour of the reaction operation but very quickly coke was formed and cover the active sites and a sharp decreasing in productivity to phenol was observed. Fig. 7 also indicates that the liquid ion exchange membrane yields a higher productivity than either the hydrothermally synthesised or CVD formed membranes.

Firutko et al. (2002) reported that the concentration of active sites increased with increasing amounts of Fe in Fe/ZSM-5. Fig. 7 shows the effects of the amount of iron on productivity with the feed composition 5.5 mol% N₂O, 50 mol% benzene, and 44.5 mol% He, and the results suggested that only a small fraction of the Fe is active in the selective oxidation of benzene to phenol. An excess of active sites promote coke formation which is resulted coupling of phenol with benzene or another by-products presence in reaction area. More active sites show more productivity to phenol during the first hour of the reaction operation but very quickly coke was formed and cover the active sites and a sharp decreasing in productivity to phenol was observed. Fig. 7 also indicates that the liquid ion exchange membrane yields a higher productivity than either the hydrothermally synthesised or CVD formed membranes.

Brønsted sites are well known as being the important sites for the catalytic reactions. Lower SiO₂/Al₂O₃ ratios provide higher Brønsted acid sites in which the H replaces with Fe during preparation of catalyst. Fig. 8 also shows that the productivity to phenol can be increased by decreasing the SiO₂/Al₂O₃ ratio.

Farmon et al. (2005) reported a possible mechanism of the active site formation by Fe atom migration from tetrahedral positions of zeolite lattice, or by insertion of external iron to
form a binuclear iron complex. A new stable state of reduced iron atoms are able to oxidize at high temperature calcination. The reduced iron zeolite has more advantages than the Pd membrane. Its average productivity was 5 mmol g$^{-1}$ h$^{-1}$ using Fe/ZSM-5 (0.18, 45) at 400 °C with a feed gas containing 5.5 mol% N$_2$O, 50 mol% benzene, with the balance made up by He, which is at the top end of the best industrial catalysts for selective oxidation reactions. Panov (2000) reported 4 mmol g$^{-1}$ h$^{-1}$ productivity and 97-98% selectivity toward phenol. In our experiments two dihydroxybenzenes, catechol and hydroquinone, were detected while Panov reported all three dihydroxybenzenes (catechol, hydroquinone, and benzoquinone) as by-products.

Niwa et al. (2002) reported 13% conversion of benzene and 85% selectivity to phenol using Pd membrane reactor. According to their work the selectivity can increase to 96% but with only 1% conversion of benzene. We also observed 0.31 mmol h$^{-1}$ productivity to phenol and low selectivity around 80% at 150 °C and feed gases containing He 10 ml min$^{-1}$, O$_2$ 5 ml min$^{-1}$, (He+ benzene) 10 ml min$^{-1}$ in the tube side, and He 30 ml min$^{-1}$, H$_2$ 10 ml min$^{-1}$ on the shell side. Water and catechol were the main by-products detected, although in some cases benzoquinone and cyclohexanone were detected but their presence was not reproducible.

The iron zeolite has better productivity and selectivity but lower stability which was caused by coke formation and resulted in a lower half-life for the catalyst. Zeolite, which was deactivated by coke formation on the active sites, was very easily regenerated using O$_2$ or N$_2$O without losing performance (Ivanov et al., 2003).

### Table 4 - Effect of reaction variables on the reactor performance

<table>
<thead>
<tr>
<th>Variable</th>
<th>Decomposition N$_2$O (%)</th>
<th>Phenol (mmol g$^{-1}$ h$^{-1}$)</th>
<th>Dihydroxybenzenes (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$O in feed stream (mol%)</td>
<td>31</td>
<td>3.8</td>
<td>0.003</td>
</tr>
<tr>
<td>2.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>32</td>
<td>6.5</td>
<td>0.017</td>
</tr>
<tr>
<td>8.2</td>
<td>32</td>
<td>6.9</td>
<td>0.072</td>
</tr>
<tr>
<td>C$_2$H$_6$ in feed stream (mol%)</td>
<td>30</td>
<td>5.6</td>
<td>0.031</td>
</tr>
<tr>
<td>36</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>32</td>
<td>6.5</td>
<td>0.016</td>
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</tr>
<tr>
<td>29</td>
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<td></td>
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</tr>
<tr>
<td>Reaction temperature (°C)</td>
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<td>5.2</td>
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</tr>
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<td>18</td>
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<tr>
<td>400</td>
<td>32</td>
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<td>0.017</td>
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<td>45</td>
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<td>425</td>
<td>59</td>
<td>10.3</td>
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</tr>
</tbody>
</table>

3.2.3. Comparing productivity and selectivity using Pd membrane and iron zeolite

Hydroxylation of benzene to phenol was performed using two different methods; our experiments show that using iron zeolite has more advantages than the Pd membrane. Its average productivity was 5 mmol g$^{-1}$ h$^{-1}$ using Fe/ZSM-5 (0.18, 45) at 400 °C with a feed gas containing 5.5 mol% N$_2$O, 50 mol% benzene, with the balance made up by He, which is at the top end of the best industrial catalysts for selective oxidation reactions. Panov (2000) reported 4 mmol g$^{-1}$ h$^{-1}$ productivity and 97-98% selectivity toward phenol. In our experiments two dihydroxybenzenes, catechol and hydroquinone, were detected while Panov reported all three dihydroxybenzenes (catechol, hydroquinone, and benzoquinone) as by-products.

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The iron zeolite has better productivity and selectivity but lower stability which was caused by coke formation and resulted in a lower half-life for the catalyst. Zeolite, which was deactivated by coke formation on the active sites, was very easily regenerated using O$_2$ or N$_2$O without losing performance (Ivanov et al., 2003).

### 4. Conclusions

Direct oxidation of benzene to phenol with two different routes was investigated. In the first method permeated hydrogen can react with oxygen to produce active oxygen species. A membrane was fabricated by a dense layer of Pd on PSS support and showed high hydrogen permeability at 200 °C. Our experiments show phenol productivity was decreased by increasing the temperature from 150 to 250 °C. We also observed low productivity for high values of the O$_2$/H$_2$ ratio. A huge amount of water was produced during the reaction and the O$_2$/H$_2$ ratio is the most important factor to change the amount of water. Low productivity was the result of entering a mixture of all reactants inside the membrane tube.
This evidence shows more active oxygen was produced when hydrogen permeated from the Pd membrane and reacted with oxygen in the other side of membrane comparing all reactants to put in the same side. By using this Pd membrane, the maximum productivity was 0.31 mmol h\(^{-1}\) at 150°C with an O\(_2\)/H\(_2\) ratio 0.5.

In the second method a comparison of a wide range of iron and aluminium containing MFI materials provides further strong indications that iron is required for formation of extra framework species that are active in selective conversion of benzene to phenol. Our experiments show a higher amount of iron loaded into the catalyst create more active sites that cause further oxidation of products and coke formation. We also observed that the rate of coke formation decreased with decreasing reaction temperature and increasing concentration of benzene. Higher reaction temperature affects decomposition of nitrous oxide and shows better productivity. Productivity can also be increased with decreasing the SiO\(_2\)/Al\(_2\)O\(_3\) ratio. By using zeolite, the average productivity was 5 mmol g\(^{-1}\) h\(^{-1}\).

In this work, two different methods were used to improve productivity in Pd/PSS membrane. First, changing design of the reactor: the experimental results show higher productivity using a solid tube inside the membrane to reduce the feed volume and promote reactant contact with the catalyst. Second, productivity was decreased when using Mo as a second catalyst, but we observed higher productivity when we packed the reactor tube with Fe/ZSM-5 and used N\(_2\)O.

From an economic point of view using N\(_2\)O in the presence of zeolite is expected to offer more advantages than Pd membrane for oxidation of aromatic compounds.

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References


INFLUENCE OF FEED CONTAMINANTS IN HYDROXYLATION OF BENZENE

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Abstract

\(\text{N}_2\text{O}\) obtained from the adipic acid process as a waste by-product or synthesised via selective oxidation of ammonia is used as feedstock for single-step technology of benzene hydroxylation. Conversion of benzene in the presence of N-containing compounds, \(\text{CO}, \text{O}_2, \text{and } \text{H}_2\text{O}\) was studied. Phenol productivity and resistance to coke formation of zeolite catalysts were affected by contaminants in different ways. Some of them such as N-containing compounds were shown poison the catalyst. \(\text{CO}\) was found in competition with \(\text{N}_2\text{O}\) to reduce the number of active sites and \(\text{H}_2\text{O}\) had a negative effect on productivity. Complete Oxidation of benzene to \(\text{CO}_2\) and \(\text{H}_2\text{O}\) occurred in the presence of \(\text{O}_2\). As the result, phenol was formed with near 97% selectivity and average productivity of 5 mmol/gh while \(\text{H}_2\text{O}\) and \(\text{CO}\) exerted a promoting effect on prolonging activity of the zeolite catalyst.

Keywords: Benzene hydroxylation; Contaminants; Catalyst stability; Fe/ZSM-5

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INTRODUCTION

Phenol is an important intermediate for the synthesis of petrochemicals, agrochemicals, and plastics. Nearly 90% of global phenol capacity (9 MMT in 2006) is based on oxidation of cumene to form cumene peroxide, which is then cleaved into phenol and
acetone. The cumene process shows several disadvantages: in particular, it uses three reaction steps, requires high capital investment, it produces acetone as a by-product in the same molar quantity to phenol, and it generates highly reactive intermediates.

The efficient production of active oxygen species on a catalyst remains difficult. Active oxygen can be produced by different sources such as H$_2$O$_2$, N$_2$O, O$_2$, and O$_3$. The direct oxidation of benzene to phenol applying H$_2$O$_2$ has been studied [1-4]. The experiments show the benzene conversion and selectivity to phenol is lower than using N$_2$O and the cost of using H$_2$O$_2$ is also higher than for N$_2$O.

Some researchers reported that using O$_2$ has advantage for partial oxidation of aromatic compounds when a membrane reactor is used [5-8]. However, cheaper H$_2$O$_2$ can be produced with a Pd membrane but conversion of benzene and selectivity to phenol remains lower than using N$_2$O.

A new route for producing phenol directly from benzene is based on using N$_2$O as an oxidizing agent in the gas phase and the iron containing zeolites as a catalyst. Solutia and the Boreskov Institute of Catalysis (BIC) have developed this new process jointly [9]. The new phenol process (AlphOx) uses a Fe-containing zeolite catalyst. Several research groups have prepared different structures of zeolites loaded one or more metals such as Fe, Cu, Zn, Mo, V, Ag, and Pt in synthesis or post synthesis methods [10-12]. The nature of Fe active sites in Fe/ZSM-5 zeolites has been investigated [13-21].

Producing phenol from N$_2$O is suggested only if the expensive N$_2$O is available as an industrial waste product, from for example adipic acid plants. In view of this, Solutia suggested use of purified nitrous oxide for the oxidation of benzene to phenol, incorporating this reaction as a key stage in a new modified adipic acid production scheme [22, 23]. This scheme starts with benzene which is first oxidized to phenol, and only then is subjected to hydrogenation. The cyclohexanol was reacted with cyclohexanone to produce adipic acid and N$_2$O, and the N$_2$O returned to the hydroxylation reaction. The global N$_2$O emission from adipic acid plants is not sufficient
to produce 9 MMT phenol per year. Phenol requires technological processes for the synthesis of nitrous oxide at the unit capacity up to 100 KT/y. Solutia and BIC recently developed a new large-scale catalytic process for the synthesis of nitrous oxide via selective oxidation of ammonia over a Mn-Bi-O/α-Al₂O₃ catalyst. The catalyst was found to be active in the temperature range 315-370°C and to provide selectivity up to 90% towards N₂O formation [24].

Depending on the impurities present in the crude N₂O, it can be either cleaned or used directly for the hydroxylation of aromatics. A typical off-gas from adipic acid plants contains N₂O (25-30 vol %), N₂ (60-65 vol %), O₂ (3-8 vol %), CO₂ (3-4 vol %), H₂O (2-3 vol %), NOₓ (1000-5000 ppm), and CO (500-1000 ppm). Studies of the influence of these impurities on the hydroxylation of benzene have revealed that high concentrations of contaminants such as NOₓ and ammonia are catalyst poisons. Others, like CO, although not catalyst poisons, can compete for α-oxygen, thus reducing the selectivity of the process. O₂ was found to lead to complete benzene oxidation. Figure 1 shows that the N₂O stream has to be treated to reduce some of the contaminants that can be detrimental to hydroxylation reaction. Uriarte [23] reported nitrous oxide off-gas could be passed through an SCR reactor in the presence of ammonia to remove NOₓ. The oxygen is eliminated by reaction with H₂ in the presence of a Pd-based catalyst. Parmon et al. reported [24] a new process for production and purification of N₂O via selective oxidation of ammonia over a Mn-Bi-O/α-Al₂O₃ catalyst with a low rate of NO. Ammonia was fed in a SCR reactor to remove NOₓ. Again, O₂ was eliminated by introducing H₂ in the presence of a Pd based catalyst.

It has been reported that contaminants and diluents affect the hydroxylation of benzene, though not in detail [25]. In this work, we will discuss in detail the effects of N-containing compounds, CO, H₂O, and O₂ in different concentrations on the behaviour of catalysts in hydroxylation of benzene.
EXPERIMENTAL

Catalyst preparation

Fe/ZSM-5 with a Si/Al ratio of 52.1 and Fe/Al 0.15 was prepared as follows. Tetraethylorthosilicate (TEOS) was used as Si source, Al(NO₃)₃ and Fe(NO₃)₃ as sources of Al and Fe respectively, and tetrapropylammonium hydroxide (TPAOH) as a template. 20.5 g of TEOS was added drop-wise to a mixture of 0.8 g NaOH, 10.2 g of TPAOH (20% water solution) and 67 g of distilled water while stirring. Solution A, while stirring, was added drop-wise to the Al(NO₃)₃ and Fe(NO₃)₃ solution (solution B) prepared by dissolving 0.75 g of Al(NO₃)₃·9H₂O and 0.094 g of Fe(NO₃)₃·9H₂O in 13 g of distilled water. The final solution was kept at 60°C for 2 hours to remove the excess of ethanol formed due to hydrolysis of the TEOS. The gel was then placed into an autoclave with a Teflon lining, and held in a static air oven at a constant temperature of 170°C for 5 days for to synthesise hydrothermally. Once the synthesis was completed, the autoclave was cooled, and crystalline material was separated by filtration and abundantly washed with distilled water and dried at 110°C overnight. Then the catalyst was calcined in flowing air at 550°C for 6 hours to burn-off the template. The sample was then converted into H-form by three consecutive liquid ion exchanges with NH₄NO₃ 0.1M overnight and subsequent air calcination at 500°C for 5 hours. Activation was completed in inert gas, oxygen, vacuum or steamed at temperatures of 700-900°C over 5 hours.

Catalyst characterization

The chemical composition of the samples was determined by an ICP-AES method. XRD analysis was performed in the range 5°<2θ<50° using Cu Kα radiation with a scanning speed of 0.1°min⁻¹. The pore volume was measured by nitrogen adsorption at 77 K was carried out in a Micrometrics ASAP 2010 apparatus. Transmission Electron Microscopy (TEM) was carried out in a JEOL JEM-1011 microscope operated at 80kV and equipped with a SIS Megaview III CCD camera. A few droplets of the sample suspended in acetone were placed on a carbon-coated copper grid followed by evaporation at ambient conditions.
The results in Table 1 for Fe/ZSM-5 point to the incorporation of Fe species into the micropore space, which results in a lowered surface area and micropore volume. The x-ray diffractograms of samples are shown to be 100% crystalline. The samples also displayed the typical diffraction pattern of the MFI framework. TEM micrographs of Fe/ZSM-5 clearly show there are no iron oxide particles on the external zeolite surface.

**Catalytic properties**

Catalytic experiments were performed using a plug flow reactor. For each experiment, 200 mg of 0.1-0.3 mm diameter catalyst particles were placed into a stainless steel reactor with an inner diameter of 3 mm. The feed gas components were controlled using mass flow controllers. Benzene and water feed rates were controlled using a syringe dosing system (Harvard Apparatus, 0.00044-77 ml/min). The reactor exit gas mixture was sampled and analyzed online. Concentrations of products were determined via their separation in a capillary column DB-1701 by GC-MS. The experiments were carried out at 410°C with a base feed gas containing 55 mol% benzene, 5.5 mol% N₂O, and the balance made up with He. Contaminants with different concentrations were fed to the base feed gas.

**RESULT AND DISCUSSION**

To demonstrate a baseline from which to compare subsequent experimental results, an extended experiment was carried out on the oxidation of benzene to phenol with a feed stream of 55 mol% benzene, 5.5 mol% N₂O, 1.3 mol% H₂O, 0.2 mol% CO and the balance with He mol% over a zeolite catalyst. The small quantities of H₂O and CO were incorporated into the feed for this experiment to represent what might reasonably be expected from the source feeds shown in Figure 1. The results are shown in Figure 2. The activity of the zeolite catalyst shows a 10% decrease after 15 hours. The results shown below indicate how the productivity of phenol is reduced by inclusion of greater amounts of N-containing compounds, CO, O₂, or H₂O in the feed stream.
Two major sources of the N\textsubscript{2}O were described in Figure 1. In both sources, N\textsubscript{2}O contains some impurities that show positive or negative effects during hydroxylation of benzene. Depending on the level of impurities in the N\textsubscript{2}O different methods have been suggested to reduce impurities \cite{26,27}.

Effect of N-containing compounds

Figure 3 shows that phenol productivity was decreased when 1.08 and 1.5 mol\% NH\textsubscript{3} were added to the feed gas. The reaction was initially started with a feed gas composed of 55 mol\% benzene, 5.5 mol\% N\textsubscript{2}O and 39.5 mol\% He. After 5 hours NH\textsubscript{3} was introduced into the feed stream at 1.08 mol\% (replacing part of the He) and which time a sharp decrease in productivity of the phenol was observed. A further increase of the NH\textsubscript{3} concentration to 1.5 mol\% led to a further small reduction in phenol productivity. It was also observed that productivity remained very low after removing the NH\textsubscript{3} from the feed. This demonstrates that N-containing compounds (NO\textsubscript{x}, NH\textsubscript{3}, etc.) are catalyst poisons and ideally must be removed from the gas inlet stream.

In the reaction

\[2 \text{NH}_3 + 2 \text{NO} + \frac{1}{2} \text{O}_2 \rightarrow 2 \text{N}_2 + 3\text{H}_2\text{O}\]

Grüner \cite{28} reported that a low level of NO contributed to a selective catalytic reduction in the presence of ammonia over the same catalyst, with superior catalytic activity and stability over a wide temperature range. It was also observed that the NO conversion increased with increasing reaction temperature. It has been suggested that a very low amount of N-containing compounds (less than 200 ppm or preferably to less than 40 ppm) facilitate the decomposition of N\textsubscript{2}O \cite{29}.

Effect of carbon monoxide

The selective catalytic reduction of N\textsubscript{2}O with CO was performed over the Fe/ZSM-5 catalyst. Reduction of N\textsubscript{2}O with CO (N\textsubscript{2}O + CO → N\textsubscript{2} + CO\textsubscript{2}) starts at a significantly lower temperature when compared to direct N\textsubscript{2}O decomposition.
Figure 4 shows that CO can compete with N₂O for α-oxygen, thus active sites contribute to reducing both N₂O and CO and result in lower productivity when compared with the inlet stream without CO. A 32% reduction in productivity was observed when 1.88 mol% CO was added to the feed stream after 3 hours. Higher concentrations of CO also resulted lower productivities. Upon removal of CO from the feed stream the N₂O decomposition returned almost to the level that it was before CO was introduced, leading to a restoration of the phenol productivity. The CO is not only a catalyst poison, but it also improves the stability of the catalyst.

**Effect of oxygen**

Figure 5 shows lower activity of the zeolite after introducing O₂. During the first 5.5 hours the reaction was run at 55 mol% benzene, 5.5 mol% N₂O, and 39.5 mol% He. When 2.55 mol% O₂ was introduced into the feed stream, the phenol productivity reduced by about 57%. The experiments were continued by adding 3.25 and then 5 mol% O₂ and the results showed 60% and 73% reductions in productivity, respectively. It was observed that some part of the activity was lost after disconnecting O₂ from the inlet stream after 8.5 hours.

The influence of oxygen in the conversion of benzene can be explained by two effects. Firstly, O₂ was found to lead to complete benzene oxidation to CO₂ and H₂O. Panov et al. [24] reported 0.3% benzene conversion at 500°C. Secondly, oxygen enhances the ionizing properties of acidic sites, which act as a strong oxidant, and aromatic cation radicals can be formed after oxygen pre-treatment of zeolite catalyst. So the cations formed can be condensed on the outer surface of the zeolite to aromatic polymers, which are precursors of coke deposits.

It is necessary to further decrease the residual O₂ in N₂O stream. For the O₂ reduction, Figure 1 shows that one or more reductants such as CO, H₂, and hydrocarbons are likely to be introduced into the remaining portion of N₂O and cause the residual O₂ content to be reduced according to:

\[
CO + \frac{1}{2} O₂ \rightarrow CO₂
\]
Effect of water

Figure 6 shows the effects of the presence of water which competes with N₂O to adsorb onto the active centres, which explains the lower activity. The reaction was initially run at 55 mol% benzene, 5.5 mol% N₂O and 39.5 mol% He. Lower productivity was observed after introducing 3.3 mol% H₂O into the feed gas (replacing part of the He) after 7 hours. The H₂O content of the feed stream was increased to 10.4 and then to 12 mol%, which resulted in lower productivities. Figure 6 also shows a recovery of the catalyst activity after 11.5 and 14 hours when H₂O was disconnected from the feed stream.

The results illustrate how water is able to reduce significantly the rate of catalyst deactivation. The Lewis acid sites are recognised as coke precursors, so keeping the ratio of the Lewis to Brönsted acid sites low has practical advantages. Addition of water to the feed encourages the Brönsted sites

\[(\text{Brönsted sites} \leftrightarrow \text{Lewis sites} + \text{Water})\]

and displaces phenol from the active sites.

CONCLUSION

The lifetime of the catalyst, phenol productivity and selectivity are strongly affected by the presence of contaminants in the feed stream. NO and NH₃, for example, are poison to the catalyst. The presence of O₂ must be limited in order to avoid complete oxidation of benzene and also prevent the speeding up of coke formation on the outer surface of the zeolite. It was observed that CO was in competition with benzene to oxidise on the active sites. Finally, the presence of water which competes with N₂O to adsorb onto the active centres can explain the lower activity but resulted in better stability.
ACKNOWLEDGMENT

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REFERENCES


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Figure 1  N$_2$O sources for hydroxylation of benzene.

Figure 2  Phenol production related to reaction time when processing the base feed composition (contact time 1.8 s; temperature 412°C).
Figure 3  Phenol production related to reaction time when NH₃ replaces part of the He in the base feed (contact time 1.8 s; temperature 412°C).

Figure 4  Phenol production related to reaction time when CO replaces part of the He in the base feed (contact time 1.8 s; temperature 412°C).
Figure 5  Phenol production related to reaction time when $O_2$ replaces part of the He in the base feed (contact time 1.8 s; temperature 412°C).

Figure 6  Phenol production related to reaction time when $H_2O$ replaces part of the He in the base feed (contact time 1.8 s; temperature 412°C).