Aula TU Delft

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De bus moet er minder dan 10 minuten over.

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einde afrit naar rechts (Schoenmakerstraat),
3e afslag (na bouwplaats) links, na 200 m Aula aan de
linkerkant. Er is parkeergelegenheid voor de aula.
Stellingen

behorende bij het proefschrift

The partial hydrogenation of aromatics

van

Matthijs Soede

26 november 1996
1. Onder hydrogeneringscondities speelt dehydrogenering vaak een rol.

   *B. Coughlan and M.A. Keane, Zeolites 11 (1991) 486*
   *Zie dit proefschrift, Hoofdstuk 4*

2. De wijze van wassen, welke gepropageerd wordt door Richard *et al.*, garandeert geen zout-vrij reactiesysteem voor de partiële hydrogenering van benzeen.

   *M.A. Richard, J.C. de Deken, and D.K. Yee, Catalytica Inc.,
   International Patent, WO 93/16972*

3. Wanneer men doelstellingen van chemisch onderzoek met elkaar vergelijk met een glimlach soms niet te onderdrukken.

   *A novel method for the conversion of benzyl alcohols to benzaldehydes by lactase-catalyzed oxidation.*


   Selective hydrogenation of benzaldehyde *to benzyl alcohol* over a monolithic nickel catalyst.


4. Chemici zijn creatief!
5. Bij het gebruik van composietmaterialen in auto's dient men ervoor te zorgen dat de kooi van Faraday intact blijft, zodat bij onweer de veiligheid gewaarborgd blijft.

6. Bij een verschil van mening, waarvan de standpunten sterk uiteenlopen, wordt vaak ten onrechte gezegd dat de waarheid ergens in het midden ligt.


8. Het geloof in de wetenschap is sterker naarmate de onwetendheid groter is.

9. De drijvende kracht voor het beoefenen van wetenschap is onwetendheid.

10. Sport is emotie. Het strekt echter tot aanbeveling dat spelers en coaches zich trainen op de beheersing van negatieve emoties.

11. Gebrekkige (spelregel-)kennis leidt vaak tot conflicten.

12. Om een goede helicopterview op het eigen vakgebied te kunnen krijgen, is het aan te bevelen dat tijdens de opleiding aandacht besteed wordt aan wetenschapsfilosofie en ethiek.


14. Door meer mensen op contract-basis in dienst te nemen, zal het wij-gevoel binnen een bedrijf afnemen.
The partial hydrogenation of aromatics

PROEFSCHRIFT

ter verkrijging van de graad van doctor
aan de Technische Universiteit in Delft,
op gezag van de Rector Magnificus Prof. ir. K.F. Wakker
in het openbaar te verdedigen ten overstaan van een commissie,
door het College van Dekanen aangewezen,
op dinsdag 26 november 1996 te 16.00 uur

door

Matthijs SOEDE

scheikundig ingenieur
geboren te De Bilt
The research reported in this thesis has been carried out at the Delft University of Technology, Faculty of Chemical Technology and Materials Science (Julianalaan 136, 2628 BL Delft, The Netherlands). The research was financially supported by DSM Research (Geleen, The Netherlands).

Soede, Matthijs
The partial hydrogenation of aromatics

Proefschrift, Technische Universiteit Delft
- met samenvatting in het Nederlands

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Ter nagedachtenis aan mama
(† 10 juni 1994)

Voor papa
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Introduction

CATALYTIC HYDROGENATION

Catalytic hydrogenation is one of the instruments for the organic and industrial chemist; most functional groups can be readily reduced catalytically, often under mild conditions, and frequently with high chemo-, regio-, and stereoselectivity.

Hydrogenation catalysts are of two types: homogeneous and heterogeneous ones. Heterogeneous catalysts are solids, which form a distinct phase in a gas or liquid environment and as a consequence the catalysts can be separated very easily by filtration or by centrifugation. The great majority of hydrogenations are performed with such a type of catalyst; the technical application was already reported at the end of the 19th century by Sabatier, who hydrogenated ethene and ethyne over a reduced nickel catalyst [1].

Homogeneous catalysts mostly dissolve in a liquid environment, forming a single phase with the solvent, the reactants, and the products. Catalysts of this type are of relatively recent origin; the first example was reported by Calvin in 1939 [2]. Cuprous acetate in an aqueous solution was used as a catalyst to hydrogenate quinoline [3]. The main problem in the development of a process based on a homogeneous catalyst is the isolation of the catalyst from the product stream.

Sabatier was also the first who hydrogenated benzene to cyclohexane [4]. Berthelot had already attempted to obtain cyclohexane from benzene by
hydrogenation in a concentrated solution of hydrogen iodide at a temperature of 523 K, but only the isomer methylcyclopentane was formed [4]. Sabatier led a mixture of gaseous benzene and hydrogen in excess over a bundle of reduced nickel, maintained at a temperature of 473 K, which resulted in total conversion to cyclohexane.

For the gas- or liquid-phase hydrogenation of aromatics, for instance of benzene to cyclohexane, often nickel or platinum catalysts are employed. The reaction is performed over such catalysts under mild conditions, viz. at a pressure of 2.0-4.0 MPa and at a temperature between 440-600 K [5a]. Two aspects of the catalytic hydrogenation of benzene are still investigated: the activity and stability of the catalysts on the one hand, and the partial hydrogenation of benzene to cyclohexene on the other hand. The latter is the subject which is of our interest.

It is generally accepted that benzene is hydrogenated to cyclohexane via the formation of cyclohexadiene and cyclohexene [6]. Therefore, in the partial hydrogenation of benzene to cyclohexene a catalyst should be used, which does not adsorb the intermediate cyclohexene too strongly, and in many partial hydrogenation reactions ruthenium is used for this purpose [7].

INDUSTRIAL APPLICATIONS OF AROMATICS

From an industrial point of view important aromatics are benzene, toluene, and the xylenes, the total production being over 32 million tons a year (Worldwide production in 1989 [8]) and this production is for more than 90% petroleum-based [9]. In Figure 1 the main routes from petroleum to the aromatics are shown.

In the polymer industry 31% of the products is based on aromatics and in the chemical industry more than 70%. Ethylbenzene (±50%), cumene (±20%) and cyclohexane (±15%) are the main products made from benzene. This indicates that the alkylation of benzene to ethylbenzene and to cumene, both intermediates in the styrene and phenol production, respectively, and the hydrogenation of benzene to cyclohexane, an intermediate in the production of cyclohexanol and cyclohexanone, are important reactions in the processing of benzene. Other products manufactured from benzene are aniline, chlorobenzene, maleic anhydride, nitrobenzene, and the alkylbenzenes. Styrene is the monomer of polystyrene and phenol is used for the production of phenolic resins and bisphenol-A. Phenol is also hydrogenated to cyclohexanone, an intermediate leading to ε-caprolactam [5c].
As already mentioned benzene can be hydrogenated to cyclohexane over a nickel or platinum catalyst at mild conditions and the reaction is performed in both the liquid or gas phase.

The industry uses nickel or platinum based catalysts, and at moderate pressure (2.5-3.0 MPa) and temperatures up to 473 K a cyclohexane selectivity of up to 100% is reached at complete conversion. Cyclohexane is oxidized with air to cyclohexanol and cyclohexanone over a Mn- or Co-catalyst in the liquid phase at 400-440 K and 0.8-1.5 MPa. The so-called KA-oil (keton-alcohol-mixture) is dehydrogenated over a copper/zinc oxide or iron/zinc catalyst to yield cyclohexanone. Subsequently, cyclohexanone can be converted into cyclohexanone oxime with hydroxylamine sulfate. This oxime is converted to ε-caprolactam, the precursor of Nylon-6, via a

Introduction
Beckmann rearrangement with sulfuric acid. The reactions described above are schematically represented in Figure 2.

The KA-oil can also be oxidized to adipic acid with HNO₃ over an NH₄-metavanadate/Cu-nitrate catalyst or with air over a Cu-Mn-acetate catalyst. Adipic acid is mainly used for the production of Nylon-6.6 [5d].

Toluene is oxidized in the liquid phase to benzoic acid with air at 400-450 K and at 0.2-10 MPa in the presence of Co-salts. Benzoic acid can be further oxidized to phenol with a copper salt as a catalyst. The copper catalyst is reoxidized by air, which is saturated with water and led through the benzoic acid melt. Finally, phenol can be hydrogenated to cyclohexanone over a palladium catalyst [5c].

The different routes to manufacture ε-caprolactam (via cyclohexane, phenol or benzoic acid), have each some disadvantages. A disadvantage of the route via benzoic acid/phenol, for instance, is the formation of carbon dioxide as a by-product.

Figure 2: Industrial applications of benzene and toluene; the production of Nylon-6.
In all routes a large number of process steps are necessary, in which always one oxidation step is involved. Oxidations are hazardous processes. The conversion per pass has to be kept low (<10%) in order to obtain selectivities higher than 90%. The oxidation of cyclohexane and of cumene are free radical chain processes. In general, radicals are very reactive catalysts, but not selective; however, under moderate conditions and low conversion per pass (~10%) high selectivities can be reached. The major drawback of low conversion per pass is that large recycles are needed.

It is the aim of many research programmes to tackle the problems mentioned above. Safety, environment, shortage of raw materials (in future), and a lowering of the process costs are stimulating factors to search for new routes and methods to manufacture products of economic value.

APPLICATIONS OF CYCLOHEXENE AND METHYLCYCLOHEXENES

From cyclohexene to cyclohexanone

In future, the production of ε-caprolactam via cyclohexene can become possible if an attractive method becomes feasible to oxidize cyclohexene to cyclohexanone. Such oxidation can be performed stepwise by the oxidative acetoxylation of cyclohexene to 1-cyclohexenyl acetate [10,11], followed by hydrolysis (see route 1 in Figure 3). A direct route to cyclohexanone could be the Wacker oxidation of cyclohexene, which can be performed homogeneously [12-15], as well as heterogeneously [16-18], but the activity and selectivity of the catalysts are not high enough to develop a process based on this reaction (see route 2 in Figure 3). At present, the most recommended route will be the one via cyclohexanol. Cyclohexanol can be obtained through hydration of cyclohexene over strong acidic solids [19-23]. Subsequently, the gas-phase dehydrogenation of cyclohexanol over Cu/ZnO or Fe/Zn catalysts has to be carried out (see route 3 in Figure 3) [24].

![Figure 3: Present and future industrial processing of cyclohexene to cyclohexanone.](image-url)
Chapter 1

Other products from cyclohexene

Cyclohexene is a chemical which can be used for the production of other chemicals besides cyclohexanone; an overview is presented in Figure 4. For instance, cyclohexene can be oxidized to adipic acid, precursor for the synthesis of Nylon-6,6. Cyclohexanediol can be prepared directly by reaction of cyclohexene with hydroperoxide or indirectly via cyclohexene oxide production followed by hydrolysis. Epoxidation to cyclohexene oxide can be performed by using hydrogen peroxide [25].

To introduce a second functional group in the ring, cyclohexene is oxidized to cyclohex-2-en-1-ol with a metalloporphyrine [26]. With cobalt chloride in an ether solution cyclohexene is oxidized to a mixture of 2-cyclohexen-1-ol and 2-cyclohexen-1-one [27]. Acetoxylation with copper or palladium complexes in acetic acid yields 3-acetoxy-1-cyclohexene [28,29].

Another possibility is to hydroformylate cyclohexene with heterogenized rhodium phosphine complexes, but complexes of ruthenium or of platinum are used as well [30,31]. In industrial processes cobalt and rhodium complexes are used [32,33]. Carbonylation with [Ru(EDTA-H)(CO)] gives a mixture of cyclohexene-1-carboxaldehyde and cyclohexene-3-carboxaldehyde [30]. Reduction of this mixture with hydrogen yields cyclohexanecarboxaldehyde.

Cyclo-olefin copolymers (COC’s) can be produced by ring-opening polymerization [34]. The COC’s are highly transparent, heat-resistant engineering plastics. The free energy of ring-opening polymerization is usually sufficiently negative for cycloolefins, but with cyclohexene the low strain energy of the rings results in a heat of polymerization (-ΔH), which is rather low or even negative (endothermic). The ΔG° for cyclohexene polymerization is positive at 323 K, which is the reason that it cannot be polymerized by ring opening [35,36]. However, at 190-230 K, where ΔG for cyclohexene polymerization is less positive, up to 14% of cyclohexene is converted to oligomeric products (degree of polymerization P<6) in the presence of WCl6/(CH3)4Sn [37]. These cyclic oligomers depolymerize to the monomer when warmed to room temperature.

Direct use of cyclohexene in the production of polymers is only found in the manufacture of olefin-sulfur dioxide copolymers. These are obtained by the free-radical reaction of olefins, e.g. cyclohexene, with sulfur dioxide. Poly(cyclohexene sulphone) melts at 473 K, and is thermally instable around this temperature. Due to this instability the copolymers are not used as bulk thermoplastics; certain specialty uses have been developed [38].

The list of described reactions can be further completed; reactions with trimethylbenzene, 1-cyclohexenylacetyl chloride, ozone and many other chemicals can
provide useful fine chemicals for the (pharmaceutical) industry [39-42]. However, the economics of cyclohexene production via the partial hydrogenation of benzene have to be improved before the above-mentioned possibilities will be realized.

Also for the methylycyclohexenes, products of the partial hydrogenation of toluene, several applications are possible. Oxidation with permanganate of methylycyclohexene gives 1-methylycyclohexane-1,2-diol [43]. Addition of carbon monoxide (Koch reaction) or water yields 1-methylycyclohexanecarboxylic acid and methylycyclohexanol, respectively, see Figure 5. Undoubtedly, many other applications can be found when the possibilities of cyclohexene will be translated to methylycyclohexene.

Figure 4: Possible applications of cyclohexene.  

Figure 5: Possible applications of 1-methylycyclohexene.
Chapter 1

MECHANISM OF THE CATALYTIC HYDROGENATION OF BENZENE

The mechanism of heterogeneous catalytic benzene hydrogenation over metals like nickel, platinum, and ruthenium is complex and many details are still unknown. In 1924 Zelinsky and Pavlov observed no cyclohexadiene and cyclohexene as intermediates in the benzene hydrogenation reaction [44], but when cyclohexene was led over a palladium catalyst both benzene and cyclohexane were found. Later, Zelinsky proposed that the hydrogenation of benzene is not a one-step reaction [45]. Indeed, from a kinetic point of view, it is difficult to accept that in one elementary reaction step six hydrogen atoms and one benzene molecule react via one transition state forming cyclohexane. Based on the observation mentioned above, he proposed a mechanism, in which chemisorbed benzene reacts first with hydrogen to cyclohexadiene. Subsequently, cyclohexadiene disproportionates to benzene and cyclohexene in a bimolecular reaction, and the formed cyclohexene disproportionates to cyclohexadiene and cyclohexane. Overall, the benzene is converted to cyclohexane.

The mechanism proposed by Horiuti and Polanyi in 1934 is more in agreement with modern insights [46]. Hydrogen is adsorbed dissociatively on two vacant catalyst sites, indicated by asterisks.

$$2 \ast + H_2 \rightleftharpoons 2 H\ast$$

The aromatic compound or olefin is di-adsorbed on two adjacent sites, presumably as an overlayer on the hydrogenated metal surface.

$$2 \ast + \text{-CH}_2\text{-CH=CH-CH}_2\ast \rightleftharpoons \text{-CH}_2\text{-CH-CH-CH}_2\ast$$

Next, a chemisorbed hydrogen atom, supplied via surface migration adds to one carbon, leaving a mono-adsorbed species, often referred to as a half-hydrogenated state.

$$H\ast + \text{-CH}_2\text{-CH-CH-CH}_2\ast \rightleftharpoons \text{-CH}_2\text{-CH}_2\text{-CH-CH}_2\ast + 2 \ast$$

Addition of a second hydrogen atom leads to a saturated C-C-bond. In the benzene hydrogenation an olefin is formed, in the case of an olefin a paraffin is formed. The products will desorb from the catalyst. All steps, except the last one, are proposed to be reversible.

$$H\ast + \text{-CH}_2\text{-CH}_2\text{-CH-CH}_2\ast \rightleftharpoons \text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\ast + 2 \ast$$
If the half-hydrogenated state undergoes a configurational change, before reverting to an olefin, cis-trans isomerization may take place. Double-bond migration will occur if the half-hydrogenated state returns to a di-adsorbed species different than the original.

\[
\text{-CH}_2\text{-CH}_2\text{-CH-CH}_2\text{-} + 2 \ast \iff \text{H-}\ast + \text{-CH}_2\text{-CH}_2\text{-CH-CH-}\ast
\]

The extent of migration and isomerization is related to the rate at which the half-hydrogenated species reacts in reverse order to the di-adsorbed form relative to the rate, at which it adds a second hydrogen. Migration and isomerization are favoured by a low hydrogen coverage at the surface, and diminished by high hydrogen availability at the surface. It has been suggested that under conditions of low hydrogen availability on palladium the mechanism changes, that hydrogen is lost to give a syn- or anti-\(\pi\)-allyl species, and that then, through addition of hydrogen, either the initial \(\pi\)-species or an isomer is formed [2].

A schematic representation of the Horiuti-Polanyi mechanism for the catalytic hydrogenation of benzene is given in Figure 6. Experimentally it has been found that during the hydrogenation of benzene besides cyclohexane, also cyclohexene is formed [47]. When cyclohexadiene is hydrogenated, cyclohexene, cyclohexane as well as benzene are formed [48]. These reactions support the mechanism of Horiuti and Polanyi.

It is usually assumed that the mechanisms of the hydrogenation of other aromatics, alkenes and their substituted derivatives proceed likewise. However, Siegel, van Bekkum, and others conclude that for a given catalyst the reactivity of a double bond is influenced by the electron donating or withdrawing properties of the substituents and by the spatial conformation of the molecule with respect to the catalytic surface [49-58]. Generally, the conformational effects dominate the electronic effects, especially if the substituents are bulky and if the degree of substitution is high.

\[
\begin{align*}
\text{H}_2 & \quad \text{H}_2 & \quad \text{H}_2 & \quad \text{H}_2 \\
\\downarrow & \quad \downarrow & \quad \downarrow & \quad \downarrow \\
\text{a} + 2 \text{H}_a & \iff \text{a} + 2 \text{H}_a & \iff \text{a} + 2 \text{H}_a & \iff \text{a} \\
\end{align*}
\]

**Figure 6:** Schematic representation of the Horiuti-Polanyi mechanism for the catalytic hydrogenation of benzene (\(a=\)adsorbed).

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**Introduction**

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Chapter 1

THERMODYNAMICS OF THE HYDROGENATION OF BENZENE

An approximate diagram representing the change of the standard reaction free enthalpy in the hydrogenation of benzene as a function of the extension of the reaction is given in Figure 7. The data are taken from Janz [59] and from Schoenmaker-Stolk [48]. The free enthalpy levels of the intermediates \( \text{C}_6\text{H}_7 \), \( \text{C}_6\text{H}_9 \), and \( \text{C}_6\text{H}_{11} \) are not included in the figure, because from a theoretical point of view it can be stated that they are the most unstable partially hydrogenated species; the most stable species are 1,3- or 1,4-cyclohexadiene and cyclohexene.

From the diagram it can be concluded that thermodynamically the partial hydrogenation of benzene to cyclohexene is very unfavourable; at equilibrium the cyclohexene yield is expected to be less than 0.1%. Optimization of the process by a change in the temperature and pressure will only result in a small increase of the yield to cyclohexene. For this reason a kinetic solution has to be found to obtain a high cyclohexene yield. This implicates that the hydrogenation rate of cyclohexene has to be lowered and/or that the desorption rate from the catalyst surface has to be increased.

\[
\begin{align*}
\Delta G^\circ & \text{ (kJ/mol)} \\
\text{Extent of the reaction} & \rightarrow \\
\text{C}_6\text{H}_6 + 2 \text{H}_2 & \quad \text{C}_6\text{H}_6 + 3 \text{H}_2 \\
\text{C}_6\text{H}_6(a) + 4 \text{H}(a) & \quad \text{C}_6\text{H}_6(a) + 6 \text{H}(a) \\
\text{C}_6\text{H}_6 + \text{H}_2 & \quad \text{C}_6\text{H}_{10} + \text{H}_2 \\
\text{C}_6\text{H}_{12} + 2 \text{H}(a) & \quad \text{C}_6\text{H}_{12(a)} \\
\end{align*}
\]

Figure 7: The change of the standard reaction free enthalpy in the hydrogenation of benzene as a function of the extension of the reaction. For the \( \text{H}_2/\text{C}_6\text{H}_6 \) mixture in the gas phase, \( \Delta G^\circ \) is taken zero as a reference point. Upper levels: gas phase hydrogenation. Lower levels: catalytic hydrogenation over ruthenium. Temperature around 300 K. Data are taken from Schoenmaker-Stolk [48].

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THE PARTIAL HYDROGENATION OF BENZENE TO CYCLOHEXENE

The formation of cyclohexene from benzene has been of interest to many researchers. The results published about the catalytic hydrogenation of aromatics can be divided in four groups [60]: i) hydrogenation reactions in the gas phase, ii) homogeneous catalytic hydrogenations in the liquid phase, iii) heterogeneous catalytic hydrogenation in the liquid phase at low pressure and low temperature, and iv) heterogeneous catalytic hydrogenation in the liquid phase at high pressures and temperatures. For clarity, the yield is defined as the total conversion of the aromatic times the selectivity to the desired product.

Catalytic hydrogenation in the gas phase.

The gas-phase hydrogenation has been studied extensively by Teichner et al. [61,62], Galvagno et al. [63], and Scholten et al. [64-66]. Teichner studied the gas-phase hydrogenation over polyamide-supported Pt-, Pd-, and Rh-catalysts. Teichner puts forward the idea that the polyamide support functions as an electron donor, which alters the catalytic properties of the active metal crystallites in such a way that the desorption of intermediate cyclohexene is stimulated. Galvagno studied Rh/Nylon catalysts and suggested that electron deficient metal sites are responsible for cycloolefin formation. Scholten et al. studied the benzene hydrogenation with non-supported ruthenium catalysts. Addition of reaction modifiers, like water, alcohols, and ε-caprolactam, to the feed enhances the selectivity to cyclohexene. The increase in selectivity has been explained by the adsorbate-adsorbate interaction between modifier and cyclohexene. The occurrence of hydrogen bonding between modifier and cyclohexene has been demonstrated in a FT-IR-study by Struijk et al. [67].

Very high selectivities in the hydrogenation of benzene to cyclohexene have been obtained by Imamura et al. [68]. Ytterbium catalysts immobilized on SiO₂ or Al₂O₃, which are formed by the reaction of the support with the lanthanide dissolved in liquid ammonia, are used without any modifiers. The selectivity to cyclohexene is 100%, but the activity of the 15 w% Yb/SiO₂-catalyst is extremely low, viz. 0.18 μmol benzene/min/gcat (WHSV=0.001). The catalyst shows zero activity during the hydrogenation of cyclohexene and Imamura et al. state, that this is the reason, why the catalyst shows a high selectivity to cyclohexene.

The study of the catalytic gas-phase hydrogenation assists in the elucidation of the mechanism of the liquid-phase catalytic hydrogenation. Despite all efforts to further increase the selectivity to cyclohexene, the maximum cyclohexene yield did not exceed 4% and this makes industrial application on a large scale unattractive.
Chapter 1

**Homogeneous catalytic hydrogenations in the liquid phase**

High cyclohexene selectivities are obtained in the homogeneous hydrogenation of benzene. Bleek and Muettarties investigated the hydrogenation with D₂ and used a Co-complex [69]. When aromatics were hydrogenated in the presence of olefins such as 1-hexene, a variety of isomeric alkylcyclohexenes were observed. 1-Hexene will be cohydrogenated. Cyclohexene selectivities up to 90% were achieved, but the activity is low.

Ru- and Co-complex catalysts were used by Johnson and Muettarties [70]. The cobalt catalysts fail in a practical sense because of their relatively short lifetimes. A maximum cyclohexene yield of 5% was obtained. A pentaammineosmium (II) complex is also active, at a pressure of 0.1 MPa and a temperature of 23 K, and with addition of a Pd₀-on-carbon catalyst, small amounts of cyclohexene are observed [71].

The results in the homogeneous catalytic hydrogenation carried out in the liquid phase are promising, but the activities are too low and in the literature the stability of the complexes is not reported.

**Solid catalyzed liquid-phase hydrogenation at low pressure and low temperature**

Horiuti and Polanyi [46] hydrogenated benzene in the liquid phase at ambient temperature and pressure over platinum and nickel catalysts. The amount of cyclohexene observed during the hydrogenation reaction was close to zero. Hartog et al. achieved better results with the usage of ruthenium catalysts [56,72,73], but the maximum cyclohexene yield achieved was only 2% in the presence of methanol.

Hydrides of the early transition metals, like ZrH₂ and HfH₂, have been used by Pez and Criskey [74]. The yields were up to 7%; this yield could be attained by the addition of amines or ethers.

Struijk obtained a maximum yield of 11% when a ruthenium catalyst was used dispersed in n-hexane, to which benzene was added, and using modifiers, like methanol and ethanol; without adding modifier a yield of 2% was observed [75].

Recently, Kluson et al. observed the formation of both cyclohexadiene and cyclohexene in the hydrogenation of benzene over a 5% Ru/C catalyst [76]. The support was not washed, and it was claimed that the sodium ions on the surface of the catalyst play an important role in the promotion of the cyclohexadiene and cyclohexene formation; the alkali metal causing electron donation to the ruthenium metal. Over a 2.5 w% Ru/TiO₂, but also over other supported catalysts, not cyclohexene as an intermediate product, but exclusively 1,3-cyclohexadiene was claimed, the maximum yield in the case of Ru/TiO₂ mounting to 60%. The reaction
was carried out in isopropanol as a solvent at 303 K and at atmospheric pressure. However, as mentioned above the formation of dienes is very unlikely both from a thermodynamic and a kinetic point of view. Therefore, the results of Kluson et al. are questionable.

It is evident that in the liquid-phase hydrogenation higher cyclohexene yields can be obtained than in the gas-phase hydrogenation, and the addition of modifier appears to be essential. Up to now, the reason why a modifier is necessary during the reaction has not been fully elucidated. The beneficial effect of the modifier can be explained by the electron donation of the modifier to the catalyst surface, and by which the ruthenium-cyclohexene interaction is weakened. Another possibility is the occurrence of an interaction between the modifier and the cyclohexene molecules, which weakens the ruthenium-cyclohexene interaction. A third explanation might be that the modifiers adsorb preferentially on strongly bonding ruthenium sites, leaving the weaker bonding sites available for benzene hydrogenation [67,77].

**Catalytic hydrogenation in the liquid phase at high pressure and temperature.**

Very good results are achieved in the catalytic hydrogenation at high pressure and high temperatures in stirred autoclaves. Drinkard, from Du Pont de Nemours, carried out the benzene hydrogenation reaction in an autoclave containing an emulsion of benzene in an aqueous salt solution, in which finely divided hydrogen and ruthenium particles are dispersed [78]. The reaction was carried out at temperatures around 450 K and at hydrogen pressures of about 7.0 MPa; a maximum yield of 32.5% at a benzene conversion of 50% could be obtained. The aqueous salt solution contained large amounts of NaOH, ZnCl₂, W(NO₃)₆, and TiCl₃. The pH of the solution was >13, which means that strong corrosion of the inner wall of the autoclave could take place.

A large number of patents, based on the mode of operation claimed by Du Pont de Nemours, have been published later on by other companies; a summary of the patents is listed in Table 1. As can be seen from this table several types of catalysts can be used: alloys, non-supported, and supported catalysts. The best result so far is obtained by Asahi Chem. Ind. [82], for a non-supported ruthenium catalyst, consisting of metallic ruthenium particles having an average crystallite size of 20 nm or less. Asahi uses zinc sulfate as a promoter in the aqueous phase. To inhibit the agglomeration of the catalyst particles and adhesion of the particles to the metallic surface of the reactor wall metal oxides, hydroxides and/or hydrates are added.

The use of supported catalysts gives also promising results, but still additives like zinc or cobalt sulfate are necessary [79,80,84,86]. Catalytica claims that after pre-adsorption of cobalt sulfate on the catalyst and washing the catalyst with distilled water, the performance of the catalyst in a benzene/water emulsion without additives

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**Introduction**

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can be compared with the performance of the catalyst in a benzene/water emulsion with additives [85].

Also in the technical literature the partial hydrogenation of benzene to cyclohexene at high pressures and high temperatures is described. Odenbrand et al., for instance, performed the reaction in a slurry reactor [87-90]. The reaction was performed in an alkaline aqueous phase in a stirred stainless-steel autoclave and the influence of reaction parameters, e.g. hydrogen pressure, alkali concentration, amount of catalyst and temperature was determined. Odenbrand proposed that hydrogen mass-transfer during the reaction is a good explanation for the increased yield to cyclohexene. A second reason for the increased yield has been suggested to be the blockage of the consecutive reaction to cyclohexene through poisoning of the catalyst by cations originating from the wall of the autoclave.

Niwa et al. prepared a supported ruthenium catalyst in different alcohols by chemical mixing of two catalyst precursors, ruthenium trichloride and tetraethoxysilane [91,92].

Table 1: Summary of the conditions and results of batch-wise preparation of cyclohexene from benzene in stirred autoclaves, according to the patent literature. The cyclohexene yield is the maximum reported yield.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Additives</th>
<th>volume ratio (\text{C}_6\text{H}_6/\text{H}_2\text{O})</th>
<th>Conditions</th>
<th>Benzene conversion (%)</th>
<th>(\text{C}<em>6\text{H}</em>{10}) yield (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru, Pd, Rh</td>
<td>NaOH, ZnCl_2, W(CO)\text{6}, TiCl_3</td>
<td>0.25</td>
<td>448 K</td>
<td>50</td>
<td>33</td>
<td>Du Pont [78]</td>
</tr>
<tr>
<td>Ru-XY/BaSO\text{4} (X = \text{Co}, \text{Fe}, \text{Zn}), Y = Cu, Ag</td>
<td>sulfate of (\text{Co}, \text{Fe}, \text{Zn})</td>
<td>1.00</td>
<td>453 K</td>
<td>76</td>
<td>41</td>
<td>Sumitomo [79,80]</td>
</tr>
<tr>
<td>Ru, Ru-Zn, Ru-Fe</td>
<td>ZnSO\text{4}, Zn(OH)\text{2}, ZrO\text{2}</td>
<td>0.25</td>
<td>423 K 5.0 MPa</td>
<td>60</td>
<td>48</td>
<td>Asahi Chem. Ind. [81,82,83]</td>
</tr>
<tr>
<td>Ru</td>
<td>as above</td>
<td>0.50</td>
<td>423 K 9.0 MPa</td>
<td>70</td>
<td>56</td>
<td>Asahi Chem. Ind. [82]</td>
</tr>
<tr>
<td>Ru/SiO\text{2}/La\text{2}O\text{3}/La\text{ONO}_3</td>
<td>CoSO\text{4}</td>
<td>1.67</td>
<td>423 K 4.4 MPa</td>
<td>80</td>
<td>40</td>
<td>Catalytica [84,85]</td>
</tr>
<tr>
<td>Ru/Ni alloy</td>
<td>ZnSO\text{4}</td>
<td>2.1</td>
<td>423 K 5.0 MPa</td>
<td>69</td>
<td>40</td>
<td>BASF [86]</td>
</tr>
</tbody>
</table>
The highest yield achieved by Niwa et al. is 31%, not as high as found with the non-supported catalysts listed in Table 1, but the addition of any additive seems to be unnecessary. According to Niwa et al., strong interaction between the ruthenium and the support increases the cyclohexene yield.

High yields to cyclohexene have also been found by Struijk et al. [93,94]. In the hydrogenation of benzene over a ruthenium catalyst in the presence of an aqueous solution of zinc sulfate, a yield of 46% was reached. They reported that the surface of the catalyst is partly covered by chemisorbed zinc sulfate. Because of this the catalyst particles, initially hydrophobic, become hydrophilic and hence are surrounded by a stagnant water layer. With the formation of a stagnant water layer around the catalyst a diffusion barrier is built up. The benzene and hydrogen molecules have to diffuse through the water layer and on the surface they react to cyclohexene and cyclohexane. The rate of the hydrogenation steps is diminished strongly by the presence of the water layer. The suppression of the cyclohexene hydrogenation rate, will result in enhancement of the cyclohexene selectivity. According to Struijk et al., the most important factor determining the yield of cyclohexene is the low solubility of cyclohexene in water [93]. Due to this low solubility the rate of diffusion of cyclohexene is slow, and consequently, the rate of readsoption is extremely low, and accumulation of cyclohexene in the organic phase will occur. Struijk et al. also conclude that the performance of the catalyst during the hydrogenation reaction is strongly influenced by iron, originating from the reactor wall [94].

Table 2: Summary of the conditions and results of batch-wise preparation of cyclohexene from benzene, published in the technical literature. The cyclohexene yield is the maximum reported yield.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Additives</th>
<th>Volume ratio C₆H₆/H₂O (-)</th>
<th>Conditions</th>
<th>Benzene conversion (%)</th>
<th>C₆H₁₀ yield (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru</td>
<td>NaOH, Fe, Ni, Cr, TiCl₃, FeCl₃</td>
<td>0.25</td>
<td>T (K)</td>
<td>P₁₂ (MPa)</td>
<td>pH</td>
<td>70 - 80</td>
</tr>
<tr>
<td>Ru-M/SiO₂</td>
<td>none</td>
<td>1.60</td>
<td>T (K)</td>
<td>P₁₂ (MPa)</td>
<td>pH</td>
<td>453 K</td>
</tr>
<tr>
<td>Ru</td>
<td>ZnSO₄</td>
<td>2.67</td>
<td>T (K)</td>
<td>P₁₂ (MPa)</td>
<td>pH</td>
<td>423 K</td>
</tr>
</tbody>
</table>

Introduction
SCOPE OF THE THESIS

The objectives of the research described in this thesis is to obtain more insight in the mechanism of the benzene hydrogenation carried out in a four-phase system. The thermodynamics of the benzene reaction are very unfavourable to achieve high cyclohexene selectivities. The presence of an aqueous salt solution showed to be inevitable to obtain high selectivities, and, therefore, it seems to be crucial to understand the real function of the aqueous salt solution.

Firstly, in Chapter 2, the preparation of non-supported ruthenium catalysts will be discussed. The reproducibility of the catalyst showed to be poor, and, therefore, a good description of all steps in catalyst manufacturing is necessary. Also, methods to prevent catalyst poisoning by ions originating from the experimental equipment will be described. The ruthenium catalyst has been characterized with different techniques and the results will be described in Chapter 3. The influence of the salt addition on the performance of the catalyst during the benzene hydrogenation will also be discussed.

In Chapter 4 an overview will be given of the performance of the ruthenium catalysts in the partial benzene hydrogenation. The mechanism of the reaction will be investigated in more detail. For this reason the influence of pressure and temperature on the overall hydrogenation rate and selectivity to cyclohexene will be studied. Also, the (de-)hydrogenation of cyclohexene at reaction conditions analogously to the benzene hydrogenation has been studied. It is clear that the consecutive hydrogenation of cyclohexene to cyclohexane is the most important reaction, which influences the cyclohexene selectivity in a negative way. More details about the cyclohexene hydrogenation can offer opportunities to develop better catalysts for the partial benzene hydrogenation.

The kinetics of the partial hydrogenation of benzene depend on physical as well as on chemical parameters. Using toluene or p-xylene instead of benzene will change these parameters, but the reaction mechanism might remain virtually the same. For this purpose the hydrogenation of benzene, toluene, an p-xylene will be compared in Chapter 5.

A major drawback of the use of an aqueous salt solution, especially when the reaction process has to be scaled up, are the technical complications arising during separation of reactants and products, and controlling of the salt concentration. Therefore, the synthesis of a catalyst which is intrinsically hydrophilic would be of great interest. A hydrophilic support is easily hydrated, and the water shell formed will possibly also wet the supported ruthenium particles. In Chapter 6 the results of the benzene hydrogenation with ruthenium on conventional supports, like silica and
alumina, will be described. In Chapter 7 the results are presented with ruthenium on SiC, prepared by Chemical Vapour Deposition (CVD). CVD is a powerful method to develop a high surface SiC support with, in principle, a tuneable hydrophilic character.

In the description of the kinetics of the benzene hydrogenation, not only the chemical reaction, but also the mass-transfer processes, should be involved. A quantitative description of the chemical reaction and mass transfer for this four-phase system will be presented in Chapter 8. An overview will be given of the rate equations of every individual step by using results of separate hydrogenation experiments and literature data. Calculations and modelling will be carried out by varying several parameters to obtain more insight in the optimum conditions for the partial hydrogenation of benzene.

Finally, the main aspects, which will be of importance when a process is developed on base of the partial hydrogenation of benzene, will be discussed in Chapter 9. Recommendations for further research will also be given.

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*Introduction*
Chapter 1


Trial and error in the preparation and testing of ruthenium catalysts

ABSTRACT

The preparation procedure of unsupported ruthenium catalysts for the partial hydrogenation of benzene has been studied. The catalyst was prepared by reduction of ruthenium hydroxide, formed by adding a sodium hydroxide solution to a ruthenium trichloride solution. The reproducibility of the preparation showed to be difficult. One of the reasons might be the high pH-value during the preparation and reduction of the catalyst, causing irregularities due to corrosion. A new method has been developed by which the reduction of the ruthenium catalyst could be performed at lower pH-values.

The ruthenium catalyst has been tested in the partial hydrogenation of aromatics. The reproducibility of the testing procedure was poor due to external effects, like corrosion of the autoclave and dissolution of plasticizers from the gaskets. A TiN coating on the inner wall of the autoclave and on the internals, and adaptation of the gaskets shows to be adequate to prevent poisoning of the catalyst and leads to a better reproducibility of the testing method.

The vapour pressure of several benzene/water mixtures have been measured in the autoclave at 423 K and showed to be a function of the stirring rate.
INTRODUCTION

For the production of cyclohexanone, the route via cyclohexene can be an alternative for the routes currently used, see Figure 1. Cyclohexene can be produced by partial hydrogenation of benzene in the gas phase using a ruthenium catalyst, but high selectivities at high conversion without strong deactivation have not been accomplished (max. selectivity 42% at conversion levels of 20% [1,2]).

\[
\begin{align*}
\text{\textcircled{C}} & \hspace{1cm} 2\text{H}_2 \quad \text{Ru} \\
\text{\textcircled{C}} & \rightarrow \begin{array}{c}
\text{H/}H_2O \\
\end{array} \\
\text{\textcircled{C}} & \rightarrow \hspace{1cm} \text{H}_2 \\
\end{align*}
\]

*Figure 1: Alternative route for the production of cyclohexanone.*

Excellent results in the partial benzene hydrogenation have been achieved at high pressure and high temperatures in a multi-phase system, comprising two liquid phases; selectivities up to 80% and yields exceeding 50% have been reported. An unsupported ruthenium catalyst, suspended in an aqueous zinc sulfate solution, showed a good catalytic performance [3-6]. For this reason, as a starting point, reproduction of the methods presented in this literature was tried. Despite several attempts, completely satisfactory reproducibility has not been realized. Reproduction of own results was even sometimes difficult. Due to lack of clarity in reported recipes, the use of different equipment, and the occurrence of catalyst poisoning, close reproduction of the catalyst performance seems to be theoretical.

It is the aim of this chapter to present a good description of all steps in catalyst preparation and catalyst testing. Also, methods to prevent catalyst poisoning by iron, originating from the technical equipment, will be described. Because optimization of catalyst preparation and testing is a continuous process of making improvements, testing and evaluation, the experiments and results will be described chronically.

EXPERIMENTAL

**Chemicals**

Benzene was obtained from Fluka and Janssen Chimica; the benzene was thiophene free and reagent grade (purity >99.5%). Ruthenium trichloride, *spec. pure*, 42.0-42.3 wt% Ru, was supplied by Johnson Matthey. Sodium hydroxide and iron
sulfate (FeSO₄·6H₂O), both pro analyse, were obtained from J.T. Baker. Zinc sulfate (ZnSO₄·7H₂O), pro analyse, was obtained from Merck. Hydrogen, purity >99.95% (oxygen content <5 ppm), was obtained from Air Products. For catalyst preparation and hydrogenation experiments distilled water has been used.

**Catalyst preparation**

Initially, the method of preparation of the ruthenium catalyst was essentially identical to the method of Struijk [1]. The preparation is schematically depicted in Figure 2. An aqueous 0.04 M ruthenium trichloride (pH=1.0) solution was heated to 353 K under vigorous stirring. Next, a 1 M sodium hydroxide solution was added instantaneously (ratio Ru³⁺ : OH⁻ ≈ 1 : 25). The resulting black coloured suspension (pH≈13.6) was kept at 353 K for 3 hours. Subsequently, the mixture was cooled to room temperature, and transferred to a measuring cylinder and the black colloidal ruthenium hydroxide was left to precipitate. The supernatant was decanted and the precipitate was transferred into an autoclave with a glass insert. After purging with nitrogen and hydrogen, the autoclave was pressurized to 2.0 MPa with hydrogen and the temperature was raised. At the point where the appropriate temperature of 423 K was reached the total pressure was adjusted with hydrogen to 4.0-5.0 MPa, whereupon further reduction of the ruthenium hydroxide was performed under vigorous stirring for 5 hours. The autoclave was cooled down and subsequently opened. The reaction mixture (pH≈13.5) was transferred into a glass vessel in the open air. The ruthenium catalyst was allowed to passivate further overnight by slow reaction with air dissolving in the water with slow agitation at ambient temperature. Finally, the passivated catalyst was filtered off, washed with distilled water until neutrality and dried at 298-350 K.

![Figure 2: Schematic representation of ruthenium catalyst preparation.](image)

*Trial and error in the preparation and testing of ruthenium catalysts* 23
**Characterization methods**

Dried ruthenium hydroxide particles were analyzed by scanning electron microscopy (SEM) on the JEOL JSM-35 to investigate the morphology. An acceleration current of 15 to 20 keV has been applied.

Diffuse Reflectance Infra-red Fourier Transform spectrometry (DRIFT) has been used on a Magna IR 500 spectrometer from Nicolet for detection of hydroxide groups in the dried ruthenium hydroxide particles.

X-ray photoelectron spectroscopy, XPS, has been performed on the PHI-5400 XPS spectrophotometer from Philips, equipped with a hemispherical analyzer.

The water phase has been analyzed by optical emission spectrometry with the use of inductive coupled plasma (ICP-OES). For these measurements a Perkin-Elmer spectrophotometer, type 2380, was used.

BET-surface area and free-metal surface area determinations will be dealt with in Chapter 3.

**Description experimental set-up for catalyst testing**

The hydrogenation equipment is represented schematically in Figure 3. Hydrogenation and catalyst reduction were carried out in two nearly identical autoclaves: a 500 ml Zipperclave from Autoclave Engineers, and a home-made 400 ml autoclave. The autoclaves were constructed from AISI 316 stainless steel (17 wt% chromium, 13 wt% nickel, 2 wt% molybdenum, 2 wt% manganese, 0.1 wt% carbon, and balance iron) and equipped with a magne-drive, removable baffle bars, a thermowell, a cooling coil, and a pressure relief valve. The temperature was measured by means of a chromel-alumel thermocouple and regulated by a temperature controller, type 815P, from Eurotherm, actuating a heating jacket. The pressure was regulated by means of an electronic pressure controller, an EPC 612 from Inacom Instruments.

Stirring was performed by means of a Rushton type turbine. The hollow shaft of the turbine, combined with the small holes in the shaft between the blades, provided a gas-bubble dispersion at rotational speeds above 800 rpm. The stirring speed was monitored by means of a Hall-effect reader.

The progress of the hydrogenation reaction was monitored by taking small samples of the reaction mixture at periodic intervals, followed by gas chromatographic analysis. For this purpose a sampling tube was positioned in the organic upper liquid layer, which is formed by breaking of the water-benzene emulsion as soon as stirring is ceased. Breaking of the water-benzene emulsion causes immediate interruption of the progress of the reaction. The sampling tube was led, via a 2 or 10 μm filter, to a
pneumatically actuated liquid sample injection valve, a P7410 from Rheodyne. The complete sampling procedure took two minutes and had no effect on the further course of the reaction.

A Packard 429 gas chromatograph equipped with a 50 m CB 52 Carbowax WCOT column from Chrompack (outer diameter 0.25 mm, waxcoat thickness 0.25 μm) was used for the analysis at a constant temperature of 353 K. The peak areas were recorded and integrated with use of the software programme Mosaic® from Chrompack.

![Figure 3: Experimental set-up for batch-wise liquid phase hydrogenation. GC = Gas chromatograph, P = Pressure controller, T = Temperature controller.](image)

**Catalyst testing**

An amount of ruthenium catalyst, aromatic compound, distilled water, and zinc sulfate or iron sulfate were introduced into the autoclave. For details of the reaction conditions, see figures in the following text. After purging with nitrogen and hydrogen, the pressure was elevated to 2.0 MPa with hydrogen. When the desired reaction temperature was reached, the total pressure was adjusted to 5.0 MPa with hydrogen. The hydrogenation reaction was started by switching on the stirrer (stirring speed 1500 rpm). Nearly all hydrogenation runs described in this thesis were carried out in the Zipperclave. When a hydrogenation run was performed in the home-made autoclave this will be mentioned separately. Disadvantage of the home-made autoclave is that the maximum stirring speed, which could be reached, was only 1200 rpm. Of course, the stirring rate is not the only parameter determining the mixing

*Trial and error in the preparation and testing of ruthenium catalysts*
behaviour, because the configuration of the reactor strongly determines the effect of stirring. The design of the reactor is given in Figure 4. In preliminary experiments the influence of the stirring rate on the apparent rate of reaction was checked. Stirring rates above 1000 rpm gave satisfactory results.

Consecutive experiments have been carried out by removing the organic phase with a pipette. The remaining water phase and catalyst, which was suspended in the water phase, were used for a consecutive hydrogenation experiment.

To determine the autogenic pressures of the benzene/water mixture at elevated temperatures, the reactor was partly filled with water and benzene in different ratios. The autoclave was heated to the desired temperature and after 15 minutes of stirring the pressure was determined.

RESULTS AND DISCUSSION

Catalyst preparation

Reproducibility is very important in catalyst preparation. Aim is to attain catalyst particles with equal mean diameters, surface areas, pore size distributions, and performance in the catalytic reaction. So, in the ruthenium catalyst preparation control of the ruthenium hydroxide crystals is an important step. When sodium hydroxide is added instantaneously to the ruthenium chloride solution, no control of the crystal growth can be expected. This step can be improved by the drop-wise addition of the sodium hydroxide solution under vigorous stirring. Ultimate control of crystal growth by gradual raising of the pH by homogeneous decomposition of urea at 363 K [7], using a solution of ruthenium chloride and urea, was not successful. The pH of the solution after decomposition of the urea was only 9 and no deposition of ruthenium hydroxide particles was observed. For ruthenium hydroxide deposition higher pH values are required. The preferred pH is >12.

The reduction of the hydroxide particles was performed in an autoclave. To prevent poisoning of the catalyst by iron, originating from the inner reactor wall and the internals, a glass insert was used. After a reduction experiment, in which the ruthenium hydroxide suspension was not stirred during the reduction step, white crystal were deposited at the bottom of the glass insert. The glass insert seemed to be affected. The composition of these crystals was analyzed with EDX. The elements detected in the crystals were oxygen, sodium, aluminium, and silicium; the crystals originated from the glass insert. The corrosion of glass is also reported in Perry’s Chemical Engineers Handbook [8]. From the reported data it can be estimated that the
corrosion of the glass insert would exceed 1 mm per year, when a 23 w% sodium hydroxide solution would be used at a temperature of 373 K. At 423 K it can be expected that the corrosion rate is even higher.

To prevent this corrosion, either the reduction temperature or the sodium hydroxide concentration could be lowered. A lower reduction temperature is out of question, because the reaction has to be carried out at temperatures around 423 K and activation of the catalyst, at conditions applied during the reaction, is inevitable. Therefore, a procedure was chosen in which the pH was kept as low as possible. Before the suspension is reduced in the autoclave, the supernatant was decanted and fresh distilled water was added. This procedure of precipitation, decantation and adding water was repeated twice. The pH after these treatments was around 12, which means that the hydroxide concentration is now 40 times lower than of that in the previous procedure. At this low concentration the corrosion effect could be expected to be lower. Disadvantage of lowering the pH was that the ruthenium particles settled down very slowly. The mean particle size of the crystals could be smaller at lower pH values, but a change in electrostatic effects is more likely.

Isolation of the ruthenium hydroxide particles to measure the mean particle size did not succeed. The particles were filtered off, washed with distilled water, and dried at 353 K. During the drying process the small particles fused together to large clusters. The particles were crushed for analysis with Scanning Electron Microscopy (SEM) and Diffuse Reflectance Infra-red Fourier Transform spectrometry (DRIFT). SEM micrographs showed that some planes of the particles were smooth and other rough, see Figure 5. At both types of planes no pores were visible. The DRIFT-spectrum showed no hydroxide vibration band at 3600 cm\(^{-1}\). The DRIFT-spectrum of the ruthenium hydroxide corresponded to the spectrum of passivated ruthenium catalyst. A passivated ruthenium catalyst consists of an inner nucleus of metallic ruthenium with a surface layer of ruthenium oxide, see Chapter 3. The conclusion can be drawn that ruthenium hydroxide transferred into ruthenium oxide during the drying process at a temperature of 353 K.

--- 50 µm

Figure 5: SEM micrograph of ruthenium hydroxide particles.

_Trial and error in the preparation and testing of ruthenium catalysts_
As mentioned above, at pH values lower than 12 the ruthenium hydroxide particles settled down very slowly during precipitation. This problem could be eliminated when a gas mixture of hydrogen in nitrogen (H₂/N₂-ratio 1:3) was led through the solution. The particles were reduced at low temperature (353 K) and low pressure (0.1 MPa). When the stirring was stopped the particles settled down very quickly and the particles could be washed several times with distilled water until neutrality. Following this way the particles settled down quickly even at pH values lower than 12.

Afterwards the particles could be reduced further in a non-basic solution at 423 K and at a hydrogen pressure of 4.5 MPa under vigorous stirring (1200 rpm). Advantage of this procedure is that it will lead to less corrosion of the reactor.

After reduction the catalyst particles were transferred in the open air into a glass vessel. The catalyst was passivated overnight by slow reaction with air dissolving in the water with slow agitation. Finally, the passivated catalyst was filtered off, washed with distilled water until neutrality, dried at room temperature and subsequently at 353 K. Drying has to be performed at room temperature, because when the drying is performed at higher temperatures, spontaneous ignition of the catalyst is possible. Like other small metal particles, very small ruthenium particles are pyrophoric.

A schematic representation of the adapted ruthenium catalyst manufacturing is given in Figure 6.
Catalyst testing

Influence of corrosion on the catalyst performance

The ruthenium catalysts have been tested at temperatures around 423 K and pressures ranging from 3.0-7.0 MPa. The catalysts were active in the hydrogenation of benzene and toluene and showed selectivity to (methyl)-cyclohexene, but the stability was poor: in a successive run the activity of the catalysts showed to be considerably lower or even no activity at all was observed. In Figure 7 the catalyst poisoning is illustrated; toluene was not converted totally when a non-coated stainless-steel autoclave was used. Due to erosion and corrosion of the autoclave, cations of the autoclave wall could dissolve in the water phase and can adsorb on the surface of the catalyst. The stainless-steel autoclave contains mainly iron (66 wt%) and chromium (17 wt%). Detailed corrosion data show that stainless steel corrodes in an aqueous zinc sulfate solution at temperatures above 373 K [8]. Experiments showed that the higher the temperature, the higher the influence of corrosion on the activity of the catalyst.

The ICP-OES analysis, see Table 1, showed indeed that the aqueous phase contained elements originating of the reactor wall after an experiment: iron, chromium, manganese, molybdenum, nickel, and tungsten. As mentioned above a point of concern was that the

**Figure 7: Typical course of the toluene hydrogenation with a ruthenium catalyst in a stainless steel autoclave. Reaction conditions: 0.2 g ruthenium catalyst, 75 ml water, 200 ml toluene, 3.5 g zinc sulfate, total pressure 5.0 MPa, temperature 443 K.**

**Table 1: Composition of stainless steel, AISI 316ss, and results of the ICP-OES analysis of the aqueous phase after hydrogenation of benzene in the autoclave before and after coating with TiN.**

<table>
<thead>
<tr>
<th>Elements</th>
<th>Composition autoclave (w%)</th>
<th>Composition aqueous phase before coating (mg/kg)</th>
<th>Composition aqueous phase after coating (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>-</td>
<td>1.1</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Cr</td>
<td>17</td>
<td>traces</td>
<td>&lt;0.025</td>
</tr>
<tr>
<td>Fe</td>
<td>66</td>
<td>&gt;175</td>
<td>0.165</td>
</tr>
<tr>
<td>Mn</td>
<td>2</td>
<td>10</td>
<td>0.04</td>
</tr>
<tr>
<td>Mo</td>
<td>2</td>
<td>0.1</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Ni</td>
<td>13</td>
<td>28</td>
<td>0.065</td>
</tr>
<tr>
<td>W</td>
<td>-</td>
<td>100</td>
<td>&lt;0.1</td>
</tr>
</tbody>
</table>

_Trial and error in the preparation and testing of ruthenium catalysts_
catalyst could be poisoned by one of these elements during the catalyst testing in the autoclave. XPS-measurements showed indeed that the catalyst was covered among others with iron and chromium, which originate from corrosion of the reactor wall. Some of the elements, like cobalt, molybdenum, or nickel, could also have a positive effect on the cyclohexene selectivity according to Struijk et al. [2], but it is very likely that one of the elements, originating of the autoclave, poisons the catalyst. Elimination of the corrosion effects is, therefore, a prerequisite.

Elimination of the effects of corrosion on the catalytic activity of the catalyst, is possible when the autoclave and all internals are manufactured from a corrosion-free material. In laboratory equipment usually a Teflon® coating is used, but at high temperatures creep can occur and as a consequence this material is not suitable. Moreover, the low heat-transfer coefficient of Teflon will result in poor control of the reaction temperature.

An unusual, but effective way, showed to be total coating of the reactor with titanium nitride (TiN) by Chemical Vapour Deposition (CVD). The autoclave and internals have been coated doubly, each coating layer had a thickness of 3 μm. ICP-analysis of the water phase, after a hydrogenation experiment in the coated autoclave, confirmed that corrosion was negligible, see Figure 8.

![Diagram of corrosion mitigation](image)

*Figure 8: Due to TiN-coating the corrosion of the stainless-steel autoclave wall and internals is negligible. X^n+ = other cations originating from stainless steel.*

**Influence of plasticizers from the gaskets on the catalyst performance**

After coating of the reactor the reaction rate still altered in successive hydrogenation experiments. The rate of benzene consumption did not decrease this time, but increased, whereas the cyclohexene selectivity decreased. The increase of the reaction rate can be explained from the change in hydrophilicity of the catalyst due to adsorption of grease and plasticizers. The autoclave was sealed by a Viton® O-ring, see Figure 9. For a leakproof closing the ring was greased. Due to the benzene which condensed at the top of the autoclave and slid down via the walls to the bulk fluids, some parts of the grease, but also plasticizers from the O-ring dissolved, and partly
adsorbed on the surface of the catalyst. The catalyst particles then turned from hydrophilic into hydrophobic by the organophilic character of plasticizers and of the grease. As a consequence, the contact between the organic phase and hydrogen and the catalyst increased and the reaction rate increased, while the cyclohexene selectivity decreased. So, for a good testing procedure an alternative had to be found. Adaptation of the reactor, whereby use of O-rings was not necessary anymore, seemed to be impossible. The use of a Kalrez® O-ring, which is resistant to benzene and distilled water, showed not to be a good solution. Kalrez® is resistant, but due to the minimization of the use of plasticizers the material is rigid, and for this reason not practical under non-static conditions. Due to frequent closing and opening of the reactor the Kalrez® O-ring could be easily damaged. The use of a Teflex® O-ring, a Viton® O-ring enclosed by Teflon®, showed to be a more convenient option. Advantage of this type of O-ring is the good resistance to benzene and water; a disadvantage is the poor flexibility of the ring at room temperature.

After coating of the reactor and adaptation of the O-rings, successive hydrogenation runs showed the same behaviour in terms of activity and cyclohexene selectivity. The performance of the catalyst seemed not to be influenced by external factors.

Successive runs now showed minor variations in reactivity and selectivity. In Figure 10 the course of two consecutive benzene hydrogenation runs is shown. In the first hydrogenation run the hydrogen consumption rate showed to be 4.5 mmol/s, and a maximum cyclohexene yield of 21% was obtained. In the second run the consumption rate showed to be 4.7 mmol/s and a maximum yield of 20% was
obtained. Furthermore, in all hydrogenation runs total conversion of the aromatics could be reached.

For measuring the stability of the catalyst a batch reactor shows not to be the optimal choice. During removal of the organic phase, small amounts of the catalyst are lost. Also, a small amount of the water phase is dissolved in the organic phase. This means that in consecutive reactions the amount of water (and thereby the salt concentration) and the amount of catalyst could not be kept constant. For measurement of the stability of a catalyst a continuous flow reactor is preferable.

**Applied reaction conditions**

In Figure 11, it is illustrated that the rate of reaction decreases with increasing temperature. This decrease could be explained by a lower solubility of hydrogen in water at elevated temperatures, but solubility data of Young [9] show that the solubility of hydrogen in water slightly increases at temperatures above 350 K. The decrease in rate can be explained as follows. When a benzene hydrogenation is carried out at temperatures above the boiling points of the substrates and/or solvents, the saturation pressures of the liquids in the autoclave exceed
0.1 MPa. In this case the partial hydrogen pressure can be influenced considerably when the reaction is carried out at constant total pressure. The saturation pressures of pure benzene and pure water as a function of temperature are depicted in Figure 12.

Three regions can be distinguished for benzene/water mixtures. A two phase equilibrium between one liquid phase and the vapour phase can be expected at low molar fractions of water in benzene \( (x_w < 0.055) \), \( x_w \) = molar fraction of water in the autoclave, and at low molar fractions of benzene in water \( (x_w > 0.9978) \). Between these two regions a region with two coexisting liquid phases and a vapour phase is expected \( (0.055 < x_w < 0.9978) \). In the first two regions the vapour pressure for each of the vapour/liquid equilibria can be estimated by [10]:

\[
P_{vapour} = \gamma_B \cdot (1 - x_w) \cdot P_B^* + \gamma_W \cdot x_w \cdot P_W^*
\]

in which \( \gamma_i \) represents the activity coefficient of component \( i \) and \( P_i^* \) the saturation pressure. Unfortunately, the activity coefficients \( \gamma_B \) and \( \gamma_W \) are unknown at the applied reaction conditions. They are dependent on the temperature and on the molar fractions of the components. It was beyond the scope of the project to determine these coefficients.
In the region of two coexisting liquid phases the vapour pressure is approximately equal to the sum of the saturation pressures of benzene and water [10]:

$$P_{vapour} \approx P_B^* + P_W^*$$  \hspace{1cm} (2)

A detailed description of a system with two liquid phases, in which mutual miscibilities are poor, is given by Smith and Van Ness [10].

In Figure 13 the vapour pressures of several benzene/water mixtures, measured in the autoclave at 423 K, are depicted as a function of varying molar benzene fraction. The measurements have been carried out at two different stirring rates. The vapour pressure of the three phase system, $0.0022 < x < 0.945$, is estimated by using thermodynamic data of Reid et al. [11] and using equation (2). The results are depicted in Figure 13 by the solid line. The observation that the measured autogenic pressures are a function of the stirring rate, suggests that thermodynamical equilibrium is not completely reached. However, this phenomenon can be explained by the non-ideal temperature distribution of the reactor. At the top of the reactor the temperature is lower than at the bottom. Due to a higher stirring rate the temperature distribution is more uniform and, therefore, the experimental and theoretical value are close to each other at the highest stirring rates.

At higher temperatures the partial pressures of benzene and of water increase, and as a consequence, the partial pressure of hydrogen decreases when the total pressure is kept constant as is usually done. As will be shown in Chapter 4, the reaction rate of the benzene hydrogenation is limited by the diffusion of hydrogen and this is in accordance with the effect that the reaction rate is first order in the hydrogen pressure. When the temperature is increased, a higher rate might be expected, but the decreasing hydrogen pressure can have an opposite effect.

**EVALUATION**

The preparation and testing of non-supported ruthenium catalysts for the partial hydrogenation of benzene in a reproducible way appears to be very difficult. The manufacturing of catalysts includes many steps which are difficult to control. However, optimization is still possible. For instance, the formation of ruthenium hydroxide crystals, the reduction and the passivation of the ruthenium catalysts are steps in the catalyst preparation which are poorly controlled. The high pH-value during the formation and reduction of ruthenium hydroxide causes irregularities due
to corrosion of the reactor. By reduction at moderate conditions immediately after the formation of the ruthenium hydroxide crystals, it is possible to wash the ruthenium hydroxide suspension until neutrality. Afterwards the particles may be reduced further at high temperature in a non-basic solution. This procedure leads to less corrosion of the reactor and, thereby, reproducibility of the catalyst manufacturing could be obtained.

For the testing of the catalysts, external effects, like corrosion of the autoclave and dissolution of plasticizers from the gaskets, which influenced the involved reaction significantly, can be excluded. The precise effect of corrosion is not known, but corrosion prevention is in any case desirable. A TiN coating at the inner wall of the autoclave is adequate to prevent poisoning of the catalyst. After coating the reproducibility of the catalyst testing showed to be satisfactory.

All hydrogenation experiments have been performed in a batch reactor. This reactor is very convenient for screening different types of catalysts, and for testing the influence of temperature, hydrogen pressure, and of various amounts of salt, added to the aqueous solution. For measurement of the stability of the catalyst a continuous flow reactor is to be preferred. At elevated temperatures it has to be taken into account that the autogenic pressures of the substrate and/or the solvent raise and, as a consequence, the partial hydrogen pressure decreases when the total pressure is kept constant.

REFERENCES


_Trial and error in the preparation and testing of ruthenium catalysts_
Characterization of ruthenium catalysts used in the partial benzene hydrogenation

ABSTRACT

Characterization of ruthenium catalysts, which were used in the partial benzene hydrogenation, has been performed by using particle size and adsorption measurements, electron microscopy, XRD, TPR, TGA, and XPS. Ex-situ characterization has been performed; after synthesis and after use in the benzene hydrogenation. The catalyst consists of conglomerates of ruthenium crystallites with a mean crystallite diameter of 5 nm. The conglomerates have a mean diameter of 25 μm. The crystallites of fresh catalysts are partly oxidized on the outside and contain only small amounts of surface impurities. Used catalysts contain carbonaceous deposits and adsorbed zinc cations; zinc sulfate has been added to modify the catalyst for the partial benzene hydrogenation. Analysis by ICP-OES shows that the zinc coverage is high, varying from θ=0.2 to θ=0.5, which implies that a relative small fraction of the surface was available for catalyzing the hydrogenation reaction.

In the partial hydrogenation of benzene the addition of salt, e.g. zinc, iron, or cobalt sulfate, is essential to obtain high cyclohexene yields. Initial cyclohexene selectivities up to 50% are achieved. The activity of the catalyst and the selectivity to cyclohexene appears to be a function of the amount of salt added. By prereduction of the catalyst at a temperature of 723 K the initial selectivity to cyclohexene increases to 75%.
Chapter 3

INTRODUCTION

Cyclohexene is an intermediate, which can be used for the synthesis of many chemical products, for instance: epoxidation to cyclohexene oxide [1], hydration to cyclohexanol [2], or acetoxylation with acetic acid to cyclohexyl acetate [3]. Hence, the production of cyclohexene has been of interest to many researchers. At present, cyclohexene is produced by the dehydration of cyclohexanol, which is obtained by either hydrogenation of phenol or by oxidation of cyclohexane [4]. It is obvious that partial hydrogenation of benzene to cyclohexene could be a more elegant route.

Good results have been achieved in the catalytic hydrogenation of benzene at high pressure and high temperature in stirred autoclaves [5-7]. Several types of catalysts have been used: alloys, non-supported, and supported catalysts. The best results so far have been obtained by Nagahara and Konishi [5], who used a non-supported catalyst, consisting of ruthenium particles having an average crystallite size of 20 nm or less. The reaction comprises four phases; a gas phase (hydrogen), an organic phase (benzene, cyclohexene, and cyclohexane), an aqueous phase (water and salt), and a solid phase (catalyst). The reported catalyst is suspended in the aqueous phase. Therefore, the reactants and products transferred between four phases by dissolution and diffusion. Reaction temperatures of 373-453 K and reaction pressures of 3.0-10 MPa were the preferred conditions. Recently, Nagahara et al. reported a maximum cyclohexene yield close to 60% [8].

In Figure 1 the mechanism of the reaction as described by Nagahara and Konishi [5] and by Struijk et al. [6] is depicted. The benzene and hydrogen molecules have to diffuse through a stagnant water layer which is formed around the catalyst particles due to the adsorption of zinc sulfate. After chemisorption on the catalyst surface, they react sequentially to cyclohexadiene, cyclohexene, and cyclohexane. The produced cyclohexene and cyclohexane molecules desorb and diffuse to the bulk organic phase.

An extensive study of the partial benzene hydrogenation has been carried out by Struijk et al. [9,10]. According to Struijk, three aspects are important to achieve high cyclohexene selectivities. Firstly, the diffusionally retarded hydrogen transport through the water layer limits further hydrogenation of the intermediate cyclohexene to cyclohexane. Secondly, due to the low solubility of cyclohexene in water in comparison with benzene, the rate of diffusion of cyclohexene from the organic phase to the catalyst is slow, and consequently the hydrogenation rate of already formed cyclohexene is low. Thirdly, a high temperature favours the
desorption of cyclohexene over the consecutive hydrogenation step to cyclohexane.

In the partial hydrogenation of benzene the addition of modifiers to the reaction system appeared to be essential to obtain high cyclohexene selectivities. To have a good comprehension of the influence of the salt addition on the performance of the catalyst, a good description of the ruthenium catalyst is necessary. For this reason the ruthenium catalyst has been characterized with different techniques, like TPR, TPS, XRD, HREM/SEM, and adsorption techniques. The ruthenium catalyst will be tested in the benzene hydrogenation with varying amount of salt.

**EXPERIMENTAL**

**Chemicals**

Benzene was obtained from Fluka and Janssen Chimica; the benzene was thiophene free and reagent grade (purity >99.5%). Ruthenium trichloride, spec. pure, 42.0-42.3 wt% Ru, was supplied by Johnson Matthey. Ruthenium dioxide was obtained from Drijfhout B.V. (purity >99.5%). Sodium hydroxide and iron sulfate (FeSO₄·6H₂O), both pro analyse, were obtained from J.T. Baker. Zinc sulfate (ZnSO₄·7H₂O), pro analyse, was obtained from Merck. Hydrogen, purity >99.95%, was obtained from Air Products. For catalyst preparation and hydrogenation experiments distilled water was used.
Catalyst preparation

The method of preparation of the ruthenium catalyst was initially identical to the method of Struijk et al. [9] and will be classified with Ru-A-n, in which n indicates the batch number. Details of the preparation method are given in Chapter 2 of this thesis. To investigate the influence of the temperature on the reduction step, catalyst Ru-A-1 has been reduced in the gas phase in a micro-flow reactor set-up with a gas mixture of 10 vol% H₂ in nitrogen. Starting at room temperature the reduction temperature was elevated with 0.083 K/s to 573 K, and 723 K respectively, and kept at this temperature for 2 hours. After cooling down the catalyst was passivated with 1% air in nitrogen. Subsequently, the concentration of oxygen was raised step-wise until the gas stream contained only synthetic air. These catalysts are assigned with Ru-A-1/573 and Ru-A-1/723, respectively.

Some improvements have been made in the preparation. The preparation recipe of the catalyst, which has been used in nearly all experiments, described in this chapter, is the following one. An aqueous 0.04 M ruthenium trichloride solution (pH≈1.0) is heated to 353 K with vigorous stirring. Next, a 1 M sodium hydroxide solution is added drop-wise (ratio Ru³⁺ : OH⁻ ≈ 1 : 25), resulting in a black coloured suspension (pH>13). After one hour of stirring a gas mixture of nitrogen and hydrogen (H₂/N₂-ratio 1:3) is led through the ruthenium hydroxide solution. In this way the ruthenium hydroxide particles are partially reduced at low temperature and low pressure. When the stirring is stopped, the particles settle down quickly. Next, they are washed several times with distilled water until neutrality. Afterwards the particles, which are suspended in water, are transferred into the TiN-coated autoclave. After purging with nitrogen and hydrogen, the autoclave is pressurized with hydrogen to 2.0 MPa and the temperature is raised. At the point where the appropriate temperature, 423 K, is reached, the total pressure is adjusted with hydrogen to 5.0 MPa and the suspension is stirred for another 5 hours. After the additional reduction step the autoclave was cooled down to room temperature and the catalyst slurry is transferred in the open air to a glass vessel. The reduced ruthenium catalyst is further passivated overnight by slow reaction with air dissolving in the water with slow agitation. Finally, the passivated catalyst is filtered off, is washed again with distilled water until neutrality and dried, firstly at 303 K for 16 hours and subsequently during one night at 353 K. The catalysts prepared in this way will be classified Ru-B.

Characterization

Characterization of the catalyst under reaction conditions is unfeasible and, consequently, only ex-situ characterization has been performed. After synthesis and
after use in the benzene hydrogenation, the catalysts were passivated carefully by air as mentioned above. So, all characterizations of fresh and/or used catalysts are carried out on passivated samples.

Particle size

Particle-size measurements were performed using a Malvern 2600 particle sizer based on the principle of Fraunhofer Diffraction. Usually, the particles were suspended in water by a small stirrer and ultrasonic vibration and the suspension was led through a photoelectric cell. The measurements were carried out with and without ultrasonic vibration.

BET-surface area and pore-volume distribution

The BET-surface area, $S_{BET}$, and the pore-volume distribution of the catalysts were calculated from the N$_2$-adsorption isotherm at 78 K, taking for the cross-sectional area of a nitrogen molecule 0.162 nm$^2$. The samples, fresh and used, were predried in vacuum at a temperature of 373 K and the N$_2$-adsorption measurements were carried out on a Digisorb 2600 or an Autosorb 6B, both from Micromeretics.

Hydrogen chemisorption

Volumetric hydrogen adsorption measurements on the catalysts, Ru-A-1, Ru-A-1/573, and Ru-A-1/723, were carried out in a Chemisorb-2800 apparatus from Micromeretics. For calculation of the free metal surface area it is assumed that one hydrogen atom adsorbs at one ruthenium site and that 1 m$^2$ ruthenium corresponds with 1.63·10$^{19}$ ruthenium atoms. The samples were dried at 423 K for 30 minutes in a stream of pure helium, cooled to room temperature and finally pure hydrogen was introduced to reduce the sample. While the samples were under reducing atmosphere the temperature was raised with 0.033 K/s to 423 K; the samples were kept for 2 hours at this temperature. Next, the samples were degassed at 373 K down to a pressure of 0.133 Pa. After degassing hydrogen chemisorption measurements were carried out at 308 K.

Salt adsorption

To determine the salt coverage of the catalyst after reaction, catalyst Ru-A-4 was taken out of the reactor, washed with distilled water and dried at 353 K. Subsequently, 2.5 ml of concentrated sulfuric acid was added to 0.02 g of the dried catalyst, and the mixture was stored for two days. Next, the volume of the mixture was adjusted to 25 ml by addition of distilled water, after which the catalyst was filtered off and the metal content of the solution was measured by using inductive coupled plasma optical
emission spectrometry (ICP-OES). For these measurements a Perkin-Elmer spectrophotometer, type 2380, was used. The salt coverage was calculated from the BET-surface area of the catalyst and the zinc content of the solution, assuming the surface stoichiometry to be one (one zinc atom occupies one ruthenium site).

To investigate the rate of salt adsorption, the catalyst was first reduced in the autoclave at 423 K and 4.0 MPa total pressure. After cooling down to room temperature the catalyst was transferred into a glass vessel. A 3:1 vol% N₂/H₂ mixture was led through the solution and the temperature of the suspension was kept at 353 K. An aqueous solution of cadmium sulfate, which adsorbs strongly on the catalyst and which can also be used as a good modifier [10], was added to the suspension. After 2, 5, and 10 minutes samples were taken of the aqueous phase and the solution was analyzed by AAS. When zinc sulfate would have been used for this measurement, the amount of adsorbed zinc sulfate would have been only 5% of the total amount added. This difference is not measurable within the desired accuracy.

X-ray Diffraction (XRD)

For measuring XRD patterns of the catalysts a Philips PW-1830 diffractometer has been used. For the measurements the CuKα-line (λ=0.154 nm) has been used. Mean crystallite diameters were determined from X-ray diffraction line broadening (XRL), applying the Scherrer equation [11].

X-ray photoelectron spectroscopy (XPS)

XPS measurements of the Ru-A-3 catalyst were performed with a Philips PHI 5400 ESCA spectrophotometer with a hemispherical analyzer and an Omni-Focus lens 54. MgKα-radiation (1254.6 eV) has been used for sample excitation. The catalyst has been used in the benzene hydrogenation reaction for 15 hours in an aqueous zinc sulfate solution. Identification of the peaks was possible by using the Handbook of XPS [12]. For quantification of the atom percentages of the elements the PHI sensitivity factors, which have been determined by XPS analysis of standard compounds [13], have been used.

Temperature Programmed Reduction (TPR)

Temperature programmed reduction of the catalyst was performed according to the method of Arnoldy et al. [14]. The measurements were carried out with 10-20 mg of catalyst in a 2.1 vol% H₂/Ar mixture at a total flow rate of 0.42 ml/s. The samples were mixed with SiC, to promote the heat transfer and to prevent a high pressure drop over the reactor. The samples were heated from 200 K to 800 K. A starting temperature
of 200 K could be reached by using cold nitrogen vapour, originating from liquid nitrogen, flowing outside the quartz reactor tube. Water produced during reduction was removed by means of a membrane.

The hydrogen consumption during the temperature programmed reduction of pure RuO₂ was used for the calibration of the TCD. The calibration factor showed to be 0.505 µmol H₂/mV.s.

Temperature programmed reduction of catalyst Ru-A-3 (fresh) has been performed at a heating rate of 0.040, 0.082, and 0.167 K/s. The so-called Kissinger method was used to determine the apparent activation energy of the reduction steps [15].

**Thermogravimetical analysis coupled with mass spectrometry TGA-MS**

Thermogravimmetrical analysis (TGA) of the Ru-A-3 catalysts was performed on a STA 1500H thermobalance of Polymer Laboratories, which was coupled to a VG-Thermolab mass spectrometer (MS). A heating rate of 0.167 K/s and a flow of pure nitrogen or 21 vol% O₂ in pure nitrogen was used.

**Electron microscopy (EM)**

To investigate the morphology of the ruthenium catalyst, dried catalyst particles were analyzed on a JEOL (JSM-35) scanning electron microscope (SEM) to investigate the morphology. The samples have been sputtered with gold to suppress charging during SEM analysis. High resolution electron microscopy, HREM, has been performed on a Philips CM30-FEG.

**Catalyst testing**

Ruthenium catalyst, distilled water, benzene, and iron or zinc sulfate were introduced into the TiN-coated autoclave (type Zipperclave), equipped with baffle bars. Detailed information is given in Chapter 2. After purging with nitrogen and hydrogen, the pressure was elevated with hydrogen to 2.0 MPa. When the desired reaction temperature was reached, the total pressure was raised by further adding hydrogen. The hydrogenation reaction was started by switching on the stirrer (stirring speed 1500 rpm).

In a series of experiments the benzene was hydrogenated to cyclohexane at 423 K and a total pressure of 5.0 MPa. At the end of the hydrogenation run the organic phase was removed by pipetting and fresh benzene was added again. In order to increase the cyclohexene yield also an extra amount of iron sulfate was added. This procedure was repeated until the cyclohexene yield levelled off.
Chapter 3

The benzene conversion, the cyclohexene selectivity, and the cyclohexene yield are calculated according to the following equations:

Benzene conversion: \[ \xi = \frac{X_{C_6H_6,t=0} - X_{C_6H_6,t}}{X_{C_6H_6,t=0}} \] (1)

Cyclohexene selectivity: \[ S_{C_6H_{10}} = \frac{X_{C_6H_{10},t}}{X_{C_6H_6,t=0} - X_{C_6H_6,t}} \cdot 100\% \] (2)

Cyclohexene yield: \[ Y_{C_6H_{10}} = \frac{X_{C_6H_{10},t}}{X_{C_6H_6,t=0}} \cdot 100\% \] (3)

in which \( x_{i,t=0} \) is the molar fraction of component \( i \) in the organic phase at the start of the experiments and \( x_{i,t} \) is the molar fraction at time \( t \).

RESULTS

Particle size

In Figure 2 the mean particle size of the ruthenium catalyst as a function of the analysis time is depicted. The mean particle size is observed to be dependent on the procedure used. When the particles were suspended by stirring and ultrasonic vibration the mean size of the fresh and used catalyst was initially found to be 15 \( \mu \text{m} \) and decreased when the time of analysis was prolonged. Without ultrasonic vibration the mean particle size of the fresh catalyst was estimated to be approximately 40 \( \mu \text{m} \) and decreased also during the analysis. The mean size of the used catalyst was 27 \( \mu \text{m} \) and remained steady.

Adsorption measurements

Nitrogen adsorption

The BET surface area of the ruthenium catalysts varied between 30 and 100 \( \text{m}^2/\text{g} \). A typical nitrogen isotherm is shown in Figure 3. Based on IUPAC classification to all catalysts a type IV isotherm could be adjusted. In Table 1 the BET surface areas and micropore volumes of the catalysts are given. The micropore volume, as listed in Table 1, is equal to the cumulative pore volume of pores up to 2.0 nm.
Figure 2: The mean particle size of fresh and used ruthenium catalysts as a function of the analysis time. The measurements have been carried out with (solid lines) and without (dotted lines) ultrasonic vibration.

In Figure 4 the pore-volume distribution of the fresh catalyst is given. The distribution is typical for all unsupported ruthenium catalysts. The catalysts are macroporous and have a mean pore diameter of 60-70 nm. The used catalysts showed a lower total volume of micropores and sometimes a somewhat higher BET surface area. The pore volume distribution of the used catalyst differed not significantly from that of the fresh catalysts.

**Hydrogen adsorption**

For the catalysts Ru-A-1, Ru-A-1/573, and Ru-A-1/723, the free-metal surface areas were determined by hydrogen chemisorption; these surface areas were 30-50% lower than the BET areas.

**Zinc adsorption**

From the zinc content of the solution, obtained by adding concentrated sulfuric acid to a used catalyst and afterwards diluted with distilled water, the weight percentage of zinc on the ruthenium catalyst could be calculated. The zinc content varied between 30 mg and 68 mg Zn/g Ru. The coverage of the catalyst Ru-A-4 after reaction was calculated to be between 0=0.2 and 0.5. Only 4% of the added zinc sulfate was adsorbed, the remaining zinc sulfate was in the aqueous phase; equilibrium is reached. Efforts to follow the kinetics of the cation adsorption on the ruthenium catalyst surface, performed with cadmium sulfate instead of zinc sulfate, by following the concentration in the aqueous phase as a function of time, showed that the adsorption rate was high and that after two minutes equilibrium was reached.
Figure 3: The nitrogen adsorption (solid) and desorption (dotted) isotherm of Ru-B at 78 K.

Figure 4: The pore-volume distribution of the fresh catalyst Ru-B. $dV/dr$ is plotted as a function of the pore radius, $r$.

Table 1: BET-surface areas and micropore volumes of several ruthenium catalysts (n.m. = not measured).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$S_{\text{BET}}$</th>
<th>micropore volume (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru-A-1</td>
<td>45</td>
<td>n.m.</td>
</tr>
<tr>
<td>Ru-A-1/573</td>
<td>38</td>
<td>n.m.</td>
</tr>
<tr>
<td>Ru-A-1/723</td>
<td>25</td>
<td>n.m.</td>
</tr>
<tr>
<td>Ru-A-2 (fresh)</td>
<td>47</td>
<td>0.025</td>
</tr>
<tr>
<td>Ru-A-2 (used)</td>
<td>54</td>
<td>0.020</td>
</tr>
<tr>
<td>Ru-A-3 (fresh)</td>
<td>46</td>
<td>0.021</td>
</tr>
<tr>
<td>Ru-A-3 (used)</td>
<td>36</td>
<td>0.015</td>
</tr>
<tr>
<td>Ru-A-4 (fresh)</td>
<td>79</td>
<td>n.m.</td>
</tr>
<tr>
<td>Ru-A-4 (used)</td>
<td>77</td>
<td>n.m.</td>
</tr>
<tr>
<td>Ru-B (fresh)</td>
<td>84</td>
<td>0.018</td>
</tr>
<tr>
<td>Ru-B (used)</td>
<td>98</td>
<td>0.015</td>
</tr>
</tbody>
</table>

Table 2: BET, hydrogen chemisorption, and XRL surface areas of ruthenium catalysts ($S_{\text{BET}}$, $S_{\text{H}}$, and $S_{\text{XRL}}$, respectively), which were reduced at elevated temperatures. Also the ratios between $S_{\text{H}}/S_{\text{BET}}$ are listed.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$S_{\text{BET}}$</th>
<th>$S_{\text{H}}$</th>
<th>$S_{\text{XRL}}$</th>
<th>$S_{\text{H}}/S_{\text{BET}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru-A-1</td>
<td>45</td>
<td>24</td>
<td>123</td>
<td>0.54</td>
</tr>
<tr>
<td>Ru-A-1/573</td>
<td>38</td>
<td>25</td>
<td>99</td>
<td>0.67</td>
</tr>
<tr>
<td>Ru-A-1/723</td>
<td>25</td>
<td>17</td>
<td>67</td>
<td>0.70</td>
</tr>
</tbody>
</table>
Figure 5: XRD patterns of the fresh (solid line) and used (dashed line) Ru-A-2 catalyst. The reflection intensities, in arbitrary units, are plotted as a function of two times the glancing angle \( \theta \). The numbers in the figure indicate the hkl-values of the different ruthenium planes.

Figure 6: XRD patterns of the fresh catalysts Ru-A-1 (a), Ru-A-1/573 (b) and Ru-A-1/723 (c).

**XRD**

In Figure 5 the XRD patterns of a fresh and a used catalyst Ru-A-2 are shown; the patterns appear to be essentially identical. X-ray line broadening showed the mean crystallite diameter to be 4.3 nm for both the fresh and spent catalyst. The spent catalyst is a sample used for 8 hours in a benzene hydrogenation run at 423 K and a total pressure of 4.0 MPa.
Figure 6 shows that by reduction of the catalyst at 573 K and 723 K the X-ray line broadening becomes smaller. This means that at these temperatures the mean crystallite diameter has increased due to sintering during the additional reduction step. Using the Scherrer equation the mean crystallite diameter of the catalysts Ru-A-1, Ru-A-1/573, and Ru-A-1/723 is calculated to be 3.9, 4.8, and 7.2 nm, respectively. From these values a total crystallite surface area, based on spherical particles, could be calculated, which is given in Table 2 as $S_{XRL}$. Compared to $S_{BET}$ these values are about 2-3 times higher.

XPS

The overall XPS spectrum of the used catalyst Ru-A-3 is shown in Figure 7. When an XPS line showed several species the lines were deconvoluted. The various species have been assigned and an overview of the ‘reasonable’ possibilities is given in Table 3. For some lines different interpretations are possible. For instance, the O(1s) line at 530.4 could be assigned to ZnO or to RuO$_2$. However, RuO$_3$ is not expected to be formed, and, therefore, not listed in the table. In Figure 8 the deconvoluted peaks in the range of 278 and 290 eV are shown. A quantitative analysis was possible by using the areas of the (deconvoluted) peaks. The areas of other XPS lines, not listed in Table 3, have not been taken into account at determining the atom percentages.

Table 3: The results of a qualitative analysis of the XPS spectrum of the passivated ruthenium catalyst Ru-A-3 after use in the partial hydrogenation of benzene.

<table>
<thead>
<tr>
<th>XPS line</th>
<th>Binding energy (eV)</th>
<th>Compound</th>
<th>Atom %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(2p3)</td>
<td>1023.8</td>
<td>ZnSO$_4$</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>1021.2</td>
<td>ZnO</td>
<td></td>
</tr>
<tr>
<td>O(1s)</td>
<td>529.4</td>
<td>RuO$_2$</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>530.4</td>
<td>ZnO</td>
<td></td>
</tr>
<tr>
<td></td>
<td>532.4</td>
<td>ZnSO$_4$</td>
<td></td>
</tr>
<tr>
<td>Ru(3d5)</td>
<td>280.1</td>
<td>Ru</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>280.7/282.5</td>
<td>RuO$_2$</td>
<td></td>
</tr>
<tr>
<td>C(1s)</td>
<td>284.4-288.0</td>
<td>different species of C</td>
<td>27</td>
</tr>
<tr>
<td>Cl(2p)</td>
<td>198.4</td>
<td>RuCl$_3$</td>
<td>0.3</td>
</tr>
<tr>
<td>S(2p)</td>
<td>169.8</td>
<td>ZnSO$_4$</td>
<td>1.7</td>
</tr>
</tbody>
</table>
Figure 7: The XPS spectrum of the Ru-A-3 catalyst used in the partial benzene hydrogenation carried out with the addition of zinc sulfate.

Figure 8: Deconvolution of the XPS spectrum between 277-290 eV.

TPR

Temperature programmed reduction of fresh and used catalysts showed that the catalyst is reduced in two reduction steps. A characteristic TPR profile is shown in Figure 9. The first maximum was at 363 K, the second at 668 K. On the basis of the total hydrogen consumption the oxidation state of the catalyst was estimated to be

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Figure 9: TPR pattern of Ru-A-3 (fresh) as a function of the reduction temperature; heating rate 0.167 K/s.

1.6+ (RuO$_{0.8}$), for both fresh and used catalysts, presuming that zinc sulfate is not reduced in the TPR measurement. The stoichiometric value RuO$_x$ (0.7<x<0.9) has been found for all described ruthenium catalysts.

Using the Kissinger method the apparent activation energy of both reduction steps has been calculated [15]. The apparent activation energy of the first step was 163 kJ/mol, and of the second step 11 kJ/mol.

TGA-MS

When a used catalyst is oxidized in air the mass increases. In Figure 10 the mass of the catalyst Ru-A-3 is depicted as a function of the temperature. At first sight a smooth increase is observed suggesting a gradual change, but as can be seen from the DSC signal three heat effects can be noticed, with local maxima at 470 K, 580 K, and 740 K. With mass spectrometry mass 44, the molecular weight of CO$_2$, has been detected with maxima at approximately 460 K and 590 K. This suggests that also carbonaceous deposits and volatile organics were adsorbed at the surface of the catalysts, which are oxidized upon heating. TGA in pure nitrogen revealed a weight loss of 2%. On base of the increase in weight, and presuming that the ruthenium is finally oxidized to RuO$_2$, the oxidation state of fresh ruthenium catalysts at the start of the experiment showed to be approximately 1.4+ (RuO$_{0.7}$), which is in accordance with the results of the TPR analysis.
Figure 10: Mass of used Ru-A-3 catalyst during temperature programmed oxidation in a 21% oxygen in nitrogen gas stream. Also the DSC signal and the MS signal of mass 44 during the experiment are shown.

10 μm

1 μm

Figure 11: SEM micrographs of ruthenium catalyst Ru-A-2.

EM

SEM analysis of the ruthenium particles showed no structure changes due to their use in the benzene hydrogenation reaction. The SEM micrographs depicted in Figure 11 are characteristic of the structure of the particles. HREM micrographs, see Figure 12 and Figure 13, show that the particles are conglomerates of small ruthenium crystallites with different shapes and different planes. When an intensive electron beam was focused on the ruthenium crystallites, sintering was observed.
Indeed, electron diffraction lines were more intensive after analysis. Due to the sintering the crystallite size could not be determined from Dark Field micrographs. From the Bright Field micrographs an average crystallite size of 5 nm could be estimated, which is of the same order as the crystallite size determined from XRD-line broadening.

**Testing of the catalytic performance in the benzene hydrogenation**

Typical concentration profiles in the hydrogenation of benzene without the use of salt are depicted in Figure 14; hardly any cyclohexene is detected. In Figure 15 typical concentration profiles in a hydrogenation experiment with the use of iron sulfate are shown. The molar fraction of benzene decreased, whereas the cyclohexene fraction increased up to values of 0.2 and then gradually decreased. All benzene hydrogenation experiments show such patterns.

By addition of iron sulfate the reaction rate and the cyclohexene selectivity changes. As shown in Figure 16, when the added amount of iron sulfate was increased, the initial reaction rate, which is the hydrogen consumption at the start of the reaction, gradually declines. The initial selectivity to cyclohexene, that means the selectivity at the start of the batch operation, increases.

A very important phenomenon was observed, after the hydrogenation experiments, when the benzene/water suspension was transferred to a glass vessel. The catalyst particles were observed to be in the organic phase in the absence of salts, and in the water phase in the presence of salts.
Figure 14: Concentration profiles in the hydrogenation of benzene as a function of time over catalyst Ru-B without the use of salt. Conditions: 1.0 g Ru-B, 200 ml benzene; 150 ml water; $p_{total}=5.0\text{ MPa}; T=423\text{ K}$.

Figure 15: Concentration profiles in the hydrogenation of benzene as a function of time over catalyst Ru-B with the use of iron sulfate. Conditions: 1.0 g Ru-B, 200 ml benzene; 2.4 g FeSO$_4\cdot6\text{H}_2\text{O}$; 150 ml water; $p_{total}=5.0\text{ MPa}; T=423\text{ K}$.

Figure 16: Initial reaction rate (left y-axis), initial selectivity and maximum yield (right y-axis) in the partial hydrogenation of benzene as a function of the molar iron sulfate concentration. The lower concentration data points have a relatively large error. The experiments were carried out with the same catalyst, Ru-B. After each hydrogenation reaction the organic phase was removed and fresh substrate and an additional amount of iron sulfate was added. Experimental conditions: 1.0 g Ru-B, 200 ml substrate, 150 ml aqueous iron sulfate solution, temperature 423 K, total pressure 5.0 MPa. The lines are drawn to guide the eye.

Characterization of ruthenium catalysts used in the partial benzene hydrogenation
Table 4: Results of the partial hydrogenation of benzene carried out with preduced catalysts in the presence of zinc sulfate. Experimental conditions: 0.1 g catalyst, 150 ml substrate, 100 ml distilled water, 1.75 g ZnSO₄·7H₂O, Temperature 423 K, Pressure 4.0 MPa.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Initial hydrogen consumption rate (mmol/s)</th>
<th>Initial selectivity (%)</th>
<th>Maximum yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru-A-1</td>
<td>0.11</td>
<td>52</td>
<td>11</td>
</tr>
<tr>
<td>Ru-A-1/573</td>
<td>0.07</td>
<td>72</td>
<td>20</td>
</tr>
<tr>
<td>Ru-A-1/723</td>
<td>0.04</td>
<td>75</td>
<td>10</td>
</tr>
</tbody>
</table>

The catalysts, Ru-A-1, Ru-A-1/573, and Ru-A-1/723 have been used also in the hydrogenation reaction. The results are listed in Table 4. As can be seen the catalyst which has been reduced at the highest temperature, Ru-A-1/723, shows the lowest activity, but the highest cyclohexene selectivity. The catalyst providing the highest yield, appeared to be Ru-A-1/573.

DISCUSSION

Catalyst characterization

The SEM micrographs show that the ruthenium catalyst particles have a highly porous structure; this observation is supported by BET measurements (30 to 100 m²/g). Figure 4 shows that the pore radii ranged from 1 to 100 nm, and that the mean pore radius was between 60 and 70 nm. The conclusion can be drawn that the unsupported ruthenium catalysts can be classified as macroporous.

The Bright Field HREM micrograph, see Figure 12, shows that the macroporous catalyst particles are conglomerates of small crystallites. The Dark Field HREM micrograph in Figure 13 shows clearly that these crystallites have different orientations and different shapes. The crystallite size is approximately 5 nm. These observations are confirmed by XRD analysis. XRD line broadening showed that the mean crystallite size of the ruthenium particles was approximately 4 nm. As can be seen in Table 1 the surface areas calculated on the basis of the crystallite diameters, Sₓₓₓ, are higher than the BET-surface areas. In calculation of Sₓₓₓ also the interfaces
from the crystallites boundaries are included. These interfaces are of course not accessible for nitrogen, and that means that $S_{BET}$ will be much lower than $S_{XRL}$.

Several indications have been found that the texture can be influenced very easily. For instance, the conglomerates of ruthenium crystallites can be broken by stirring. During particle size measurements the mean particle diameter of a fresh catalyst declines and by ultrasonic vibration even smaller particle sizes are observed. The conglomerates are very fragile and this conclusion is also supported by the micrographs. Due to the fragile structure the particles can be crushed easily. However, during the particle size measurements the mean particle size after use in the hydrogenation reaction, showed to be steady during the particle-size measurements when no ultrasonic vibration is used. The conclusion can be drawn that the catalyst particles will be crushed easily in a hydrogenation experiment, but in course of time it will reach a steady-state value of ca. 25 $\mu$m.

The crystallite size can be influenced by the temperature. The Hüttig temperature, $0.3T_{melting}$ of pure ruthenium is 817 K [16]. Nevertheless, below this temperature the Ru-A-1 catalyst showed already sintering of the crystallites. The mean crystallite diameter of the catalyst increased, when the reduction temperature was raised from 453 K to 723 K. As a consequence, the BET surface area decreased. This sintering is also described by Don et al. [17]. They found that, when starting with pure RuO$_2$ and raising the reduction temperatures from 523 K to 800 K, the BET surface areas changed from 17 m$^2$/g to 5 m$^2$/g. The reason for the sintering below the Hüttig temperature might be the mobility of ruthenium atoms in small particles being higher than in bulk ruthenium. It is also observed that hydrogen can induce sintering [18]. As a consequence of the ease of sintering, the reduction of the ruthenium hydroxide particles during the preparation of the ruthenium catalyst has to be controlled very accurately. Also, when the intensive electron beam of the high resolution electron microscope was focused on the crystallites, the crystallites started sintering.

After reaction the BET-surfaces areas appeared to be altered. As can be seen in Table 1 the surface areas can decrease, but also increase. This effect can be explained from the fragile structure of the catalysts. The boundaries between the crystallites are broken, resulting in a change of the BET-surface area. As can be seen in the table, the micropore volume diminishes; this can be explained also by the breakage of the interfaces between the crystallites. Another explanation could be sintering of the catalyst. But, as can be calculated from the XRD pattern of the used catalyst, shown in Figure 5, the mean crystallite size remained constant and hence, no significant sintering took place under reaction conditions.

The surface areas determined from hydrogen chemisorption were significantly lower than the areas determined from nitrogen adsorption (BET measurements). The

Characterization of ruthenium catalysts used in the partial benzene hydrogenation
$S_H/S_{BET}$-ratio of the catalysts Ru-A-1, Ru-A-1/573, and Ru-A-1/723 are 0.54, 0.67, and 0.70, respectively. Don et al. [17] found similar ratios for non-supported ruthenium catalysts. They explained this low ratio by the presence of adsorbed chlorine, remaining from the synthesis step, and hardly removable impurities. Removal of these impurities could only be performed satisfactory by calcination at 1473 K and followed by reduction at 673 K. Before calcination and reduction the $S_H/S_{BET}$ ratio was found to be 0.21, after calcination and reduction the ratio was 0.76 [17]. It has to be noted that during calcination at 1473 K the volatile and very toxic ruthenium tetraoxide will be formed [19]. So, this purification method has to be avoided.

The XPS data in Table 3 showed that only minor amounts of chlorine were present. Nevertheless, from the raising $S_H/S_{BET}$ ratio, from 0.54 to 0.70, when the reduction temperature is increased in the pretreatment, the conclusion can be drawn that the surface of the catalyst is further cleaned by the additional reduction step. It should be noted that other explanations are possible for the observation that $S_H/S_{BET}<1$. When it is supposed that the amount of ruthenium sites is not equal to $1.63 \times 10^{19}$ Ru-atoms/m$^2$, but to $1.2 \times 10^{19}$ Ru-atoms/m$^2$ according to Dalla Betta [20], the ratio is more close to 1. Also the assumption that one hydrogen atom adsorbs at one ruthenium site could be wrong. For instance, Goodwin proposed that one hydrogen atom is adsorbed at 1.1 ruthenium sites [21]. It is concluded that $S_H$ and $S_{BET}$ are in somewhat better agreement and that some impurities are present at the surface.

The XRD pattern of the fresh catalyst Ru-A-2 as shown in Figure 5 showed no peaks which could be assigned to the presence of bulk ruthenium oxide crystallites. This does not mean that the catalyst does not contain oxygen. Only crystallites larger than 2 nm can be detected by XRD line broadening. It is clear that the passivated catalysts contain oxygen as shown by TPR and TGA, and so it can be presumed that the oxygen is only present at the outer side of the ruthenium crystallites. From the absence of a crystalline ruthenium oxide phase the conclusion can be drawn that the passivation of the catalyst has been carried out adequately. In Figure 6 XRD patterns are shown of catalysts for which the passivation step has not been carried out carefully enough. Small oxide peaks from RuO$_2$ can be observed, but also from some unknown impurities probably originating from the catalyst preparation.

The presence of oxygen in the passivated catalyst is demonstrated by the TPR experiments. Two reduction peaks were observed. Only minor amounts of chlorine have been observed with XPS; and hence, the reduction peaks cannot be assigned to the reduction of residual chlorine, originating from the starting material ruthenium trichloride. The different peaks might be due to different types of ruthenium oxide. But, on the base of the weight growth during the TGA experiment, see Figure 10, the
conclusion can be drawn that only RuO$_2$ can be formed at oxidation temperatures up to 800 K, which is confirmed by observations of Verdonck et al. [22]. RuO$_x$ oxides with $x<2$ are not reported in literature and, consequently, it is concluded that the two peak pattern is not due to stepwise reduction via an intermediate bulk ruthenium oxide. The occurrence of surface oxygen and sub-surface oxygen can also be a good explanation for the two-step reduction. Not only the outer surface is oxidized during the passivation step, but also parts of the inner crystallites are oxidized.

The latter explanation is supported by the calculated activation energies of both reduction steps. The activation energy of surface oxygen reduction is generally above 60 kJ/mol [23]. The first peak showed an apparent activation energy of about 160 kJ/mol; the apparent activation energy of the second peak is about 10 kJ/mol. This means that the second reduction step is a non-activated reaction, probably diffusion of sub-surface oxygen to the outer surface of the ruthenium crystallite. The second peak maximum is at 668 K, above the temperature of a benzene hydrogenation experiment, nevertheless it can be concluded that under reaction conditions the catalyst will be reduced totally, because this reduction step has an almost negligible activation energy. The amount of hydrogen needed for total reduction of the outer RuO$_2$ surface layer (mean crystallite diameter 4.0 nm) is also in accordance with the hydrogen consumption in the first TPR peak.

From the fresh passivated ruthenium catalyst is given a schematic representation in Figure 17. The figure is based on the observations which have been discussed above.

The XPS measurements confirm that different species of ruthenium are present. The positions of the Ru(3d5/2) lines of Ru and RuO$_2$ are at 280.0 and 280.7 eV,

![Ruthenium particle (d = 25 μm) and Ruthenium crystallite (d = 4 nm)](image)

*Figure 17: Schematic representation of a fresh ruthenium catalyst after passivation.*

*Characterization of ruthenium catalysts used in the partial benzene hydrogenation*
respectively. However, for RuO$_2$ also lines at 282.0 eV have been observed [24]. In Figure 8 the XPS signal between 277 and 290 eV is depicted. Deconvolution of the Ru(3d5/2) line showed that both Ru$^0$ and Ru$^{4+}$ are present in the measured spectrum, which is in accordance with our hypothesis that the ruthenium crystallites are only partly oxidized during the passivation step.

The electron binding energy of Ru(3d5/2) and of carbon overlap each other. Deconvolution of the Ru(3d5/2) line between 277 eV and 290 eV showed that some carbonaceous species are present. The carbonaceous deposits probably originate from adsorbed benzene, cyclohexene or cyclohexane. During oxidation (TGA) of a used ruthenium catalyst two CO$_2$-peaks have been observed with mass spectrometry, see Figure 10, and this figure also shows various DSC peaks. This confirms that different types of carbon are present at the surface of the used catalyst.

The O(1s) line is also interesting with respect to the analysis of the catalyst composition. The oxygen line at 530 eV can be split up into three lines; 529.4, 530.4, and 532.4 eV. The first line can be assigned to RuO$_2$, which is formed by the passivation step, and the third to ZnSO$_4$, which has been added to modify the catalyst. The second peak could be assigned to ZnO. XPS showed that indeed two types of zinc are present at the catalyst surface. XPS lines at 1023.8 eV and 1021.2 are observed. The line at 1023.8 eV can be assigned to ZnSO$_4$. The line at 1021.2 to Zn$^0$ or ZnO. The formation of Zn$^0$ is not likely, because TPR of a ruthenium catalyst impregnated with ZnSO$_4$ showed no reduction of Zn$^{2+}$ at temperatures up to 1200 K [25]. ZnO might be formed by reduction of ZnSO$_4$, but sulfates are normally not reduced at temperatures below 550 K [26]. It is more likely that the zinc cations, which are strongly adsorbed on the ruthenium surface, have also a strong interaction with the oxygen atoms of the passivated ruthenium surface. The zinc line can be observed due to a strong interaction of Zn$^{2+}$ with the oxygen of the passivated ruthenium surface as mentioned above. Another possibility could be a strong interaction of Zn$^{2+}$ with ruthenium, which results in a shift of the ZnSO$_4$ line.

Analysis by ICP-OES showed that the zinc coverage is high, varying from $\theta=0.2$ to $\theta=0.5$. These coverages are in reasonable accordance with the XPS results. The ratio of the atom percentages between zinc and ruthenium was 0.38, see Table 3, and is in the same order as calculated from the ICP-OES results. A zinc coverage of $\approx0.4$ means that only a small fraction of the ruthenium sites is available for catalyzing the reaction.
Influence of salt on the performance of the catalyst

All ruthenium catalysts showed activity in the hydrogenation of benzene. The selectivity to cyclohexene depends on the addition of zinc or iron sulfate and on type of catalyst. XPS analysis of a catalyst, used in a hydrogenation experiment in which zinc sulfate was used as a modifier, showed that the ruthenium surface is covered with zinc cations. Adsorption of cations at the surface of the catalyst, makes the catalyst hydrophilic, and hence the ruthenium particles are no longer in the benzene phase, but in the water phase. In Figure 18 a schematic representation of the hydrated catalyst surface is given.

The effect of increasing the amount of iron sulfate, see Figure 16, is a decrease of the hydrogen consumption rate and an increase of the selectivity to cyclohexene. It is remarkable that the hydrogen consumption rate reaches a constant value at a salt concentration of 20 mmol/l. Struijk et al. [10] reached this point at 100 mmol/l when using zinc sulfate as a modifier. The observation that more zinc sulfate has to be added to obtain the same performance, suggests that iron sulfate is adsorbed more strongly than zinc sulfate. It can be assumed that the hydrogen consumption rate declines due to the formation of a stagnant water layer by the change in hydrophilicity. The hydrophilicity reaches a steady state and, therefore, the hydrogen consumption rate will also become constant. Due to the formation of the stagnant water layer the cyclohexene selectivity increases, but the modification of the surface by salt adsorption plays a role in increasing the selectivity as well. The latter conclusion is based on the results of the gas-phase hydrogenation of benzene carried out by van der Steen and Scholten [27], who found that addition of ethanediol enlarged the cyclohexene selectivity from 0 to 40%. In their case no aqueous phase was present, and hence adsorbed ethanediol modifies the ruthenium surface. This interpretation is based on the fact that at the ruthenium surface a site distribution exists. When the most strongly bonding sites are blocked by ethanediol
or by adsorbed salts as is the case in the present work, the adsorption strength of cyclohexene is lowered and so the formed cyclohexene molecules will desorb more easily and diffuse to the organic phase. This effect will be discussed in more detail in Chapter 8.

If the catalyst is reduced additionally in a N\textsubscript{2}/H\textsubscript{2} gas stream at 573 K, it shows an increase in the initial selectivity to cyclohexene, see Table 4. This can be explained along the same lines as above. The catalyst surface now contains less strongly bonding sites due to the larger ruthenium crystallites. Commonly, the edges of catalyst surfaces adsorb substrates more strongly. Due to the additional reduction step at 573 K, the crystallites grow and less edges, corners and rough planes, will be present. At the same cation concentration in the water phase, the catalyst will then cause a higher cyclohexene selectivity and also a higher maximum cyclohexene yield.

If the catalyst is reduced at 723 K, the initial cyclohexene selectivity further increases, but the maximum cyclohexene yield is lower. As can be seen in Table 4, the hydrogen consumption rate decreases, when the catalyst is prereduced. The maximum cyclohexene yield, measured during benzene hydrogenation in a batch-wise operated system, is a function of both selectivity and activity of the catalyst, and hence lower rates will lead to lower maximum yields. It should be noted that these results can be a lead to further catalyst optimization.

The catalytic test results show that for each ruthenium catalyst an optimum in selectivity can be found. The cyclohexene selectivity appears to depend on the salt concentration, the catalyst pretreatment step, and reaction conditions.

**CONCLUSIONS**

From the results of the characterization of the fresh and used catalysts the conclusion can be drawn that the texture of the catalyst is very fragile. The catalysts consist of conglomerates of small ruthenium crystallites and indications have been found that the macroporous conglomerates are easily destructed by mechanical stress. The catalyst is made up of conglomerates of ruthenium crystallites with a mean diameter of about 5 nm and the conglomerates have a mean diameter of about 25 \( \mu \)m. During the partial hydrogenation of benzene the BET surface areas of the catalysts change due to attrition and breakage.

Characterization of the catalysts by XRD, TPR, TGA, and XPS shows that the passivated ruthenium catalysts are made up of a ruthenium nucleus covered with an
oxygen layer. Only small amounts of impurities are present at the surface of the catalyst. The used catalysts contained carbonaceous species and adsorbed zinc cations.

In the partial hydrogenation of benzene the addition of iron or zinc sulfate is essential to obtain high cyclohexene yields. The salts adsorb on the surface of the catalyst and due to the presence of the zinc and/or iron cations a stagnant water layer is present around the particles. The adsorption strength of formed cyclohexene is lowered by the presence of the salts, resulting in an increased cyclohexene desorption rate and higher selectivities to cyclohexene. The cyclohexene selectivity is a function of the amount of salt added; the higher the amount of salt, the higher the selectivity. Furthermore, the hydrogenation activity diminishes due to the increased salt coverage and therefore an optimum in the maximum cyclohexene yield can be established.

The preparation of non-supported ruthenium catalysts is difficult to reproduce and this means that different batches, will have a different performance in the partial hydrogenation of benzene. Reduction of the catalysts at elevated temperatures in a N₂/H₂ gas mixture, showed to be effective in improving the cyclohexene selectivity, and gives possibly opportunities to develop a more reproducible catalyst. For each batch an optimum in the salt concentration has to be found.

REFERENCES


Characterization of ruthenium catalysts used in the partial benzene hydrogenation
Chapter 3

25 See Chapter 6 of this thesis.
The hydrogenation of benzene and cyclohexene

**ABSTRACT**

The batch-wise hydrogenation of benzene and cyclohexene over ruthenium catalysts in the presence of an aqueous salt solution has been investigated. The hydrogenation reactions were performed at temperatures varying from 403 K to 443 K and total pressures of 3.0 MPa to 7.0 MPa. The benzene hydrogenation rate is governed by diffusion limitation of hydrogen. At constant hydrogen pressures the temperature hardly influenced the benzene conversion rate. The selectivity to cyclohexene increased by raising the temperature from 403 K to 443 K and maximum cyclohexene yields up to 28% have been achieved. When the hydrogen pressure was raised from 1.3 MPa to 5.3 MPa the cyclohexene yield increased from 11% to 28%.

The apparent activation energy of the hydrogenation of cyclohexene appeared to be -37 kJ/mol, which implies that the cyclohexene hydrogenation rate decreases when the temperature is raised. During hydrogenation of cyclohexene the formation of benzene was observed. The benzene formation was favoured by lowering the partial hydrogen pressure and raising the temperature. At a temperature of 423 K and a partial hydrogen pressure of 0.4 MPa a maximum benzene yield of 9% was observed at $\xi_{\text{che}} = 0.68$.

During benzene hydrogenation not only cyclohexene and cyclohexane but also by-products, like methylocyclopentane and n-pentane, were formed due to isomerization and hydrogenolysis.
INTRODUCTION

An industrial process for the partial hydrogenation of benzene to cyclohexene might mean a major improvement for the production of $\varepsilon$-caprolactam (the monomer of Nylon-6). A process running via the cyclohexene route entails a considerable hydrogen saving and can bypass the potential hazardous cyclohexane oxidation route. The route via partial hydrogenation, however, is thermodynamically very unfavourable (yields less than 0.1% under equilibrium conditions at temperatures between 303-500 K and pressures ranging from 0.1-5.0 MPa), and a kinetic solution has to be found.

Good results in the partial hydrogenation of benzene have been achieved at high pressure and high temperature in a multi-phase system, comprising two liquid phases; selectivities up to 80% and yields exceeding 50% have been achieved. An unsupported ruthenium catalyst, suspended in an aqueous zinc sulfate solution, shows a good catalytic performance [1-5]. The benzene and hydrogen molecules have to diffuse through a stagnant water layer which is present around the catalyst particles due to adsorption of zinc sulfate. After chemisorption on the catalyst surface, they react sequentially to cyclohexadiene, cyclohexene, and cyclohexane. The produced cyclohexene and cyclohexane molecules can desorb and diffuse to the organic phase. In Figure 1 the diffusion mechanism is depicted. Three aspects are important to achieve high cyclohexene selectivities [4]. Firstly, the diffusionally controlled hydrogen transport through the water layer limits further hydrogenation of the intermediate cyclohexene to cyclohexane. Secondly, due to the low solubility of cyclohexene in water in comparison with benzene the equilibrium occupancy of cyclohexene at the catalyst surface is low, and consequently the hydrogenation rate of already formed cyclohexene is low. Thirdly, a high temperature favours the

![Figure 1: Representation of the diffusion steps in the formation of cyclohexene in the partial hydrogenation of benzene over ruthenium catalysts.](image-url)
desorption of cyclohexene over the consecutive hydrogenation step to cyclohexane.

It is the aim of this chapter to present an overview of the performance of unsupported ruthenium catalysts in the partial hydrogenation of benzene and to investigate in more detail the mechanism of the reaction. For this reason the influence of pressure and temperature on both the overall hydrogenation rate and the cyclohexene selectivity have been studied, but also the (de-)hydrogenation of cyclohexene at reaction conditions analogously to the benzene hydrogenation will be investigated.

EXPERIMENTAL

Chemicals

Benzene was obtained from Fluka and Janssen Chimica; the benzene was thiophene free and reagent grade (purity >99.5%). Cyclohexene was obtained from Fluka (purity >99%), and was distilled before use. Ruthenium trichloride, spec. pure, 42.0-42.3 wt% Ru, was supplied by Johnson Matthey. Sodium hydroxide and iron sulfate (FeSO₄·6H₂O), both pro analyse, were obtained from J.T. Baker. Zinc sulfate (ZnSO₄·7H₂O), pro analyse, was obtained from Merck. Hydrogen, purity >99.95%, was obtained from Air Products. For catalyst preparation and activity measurements distilled water was used.

Catalyst preparation

The ruthenium catalyst was prepared by reduction of ruthenium hydroxide, prepared by adding a sodium hydroxide solution to a ruthenium trichloride solution. The reduction of ruthenium hydroxide was performed in an aqueous solution with a stirred autoclave at 423 K and a partial hydrogen pressure of 4.0 MPa. The method of preparation was initially identical to the method applied by Struijk et al. [4] and will be classified as Ru-A. The preparation method is described in more detail in Chapter 2. The ruthenium catalyst Ru-B was prepared following the preparation method as described in detail in Chapter 3.

Testing of the catalyst

In a TiN-coated autoclave equipped with baffle bars, ruthenium, distilled water, the substrate, benzene and/or cyclohexene, and iron or zinc sulfate were introduced. Detailed information about the equipment is given in Chapter 2. For the hydrogenation two slightly different autoclaves have been used: a 500 ml Zipperclave from Autoclave Engineers (reactor I) and a home-made 400 ml
autoclave (reactor II). After purging with nitrogen and hydrogen, the pressure was elevated with hydrogen to 2.0 MPa. When the desired reaction temperature was reached, the total pressure was elevated by adding hydrogen. The hydrogenation reaction was started by switching on the stirrer. The hydrogenation runs which were performed in reactor I were carried out at a stirring rate of 1500 rpm, in reactor II at a stirring rate of 1200 rpm. When the reactions were carried out at partial hydrogen pressures lower than 2.0 MPa, the total pressure was accomplished by supplying nitrogen for sampling reasons.

The progress of the reaction was monitored by taking small samples of the reaction mixture at periodic intervals, followed by gas-chromatographic analysis. For this purpose a sampling tube was positioned in the organic upper liquid layer, which is formed by breaking of the water-benzene emulsion as soon as stirring ceased.

RESULTS

To check the stability of the catalyst during a batch reaction two successive hydrogenation runs have been carried out. The first run started with a molar benzene fraction in cyclohexane of 0.95 and the second with 0.51. The hydrogen and benzene consumption rates as a function of the molar fraction of benzene are

![Graph](image)

**Figure 2**: The reaction rate of the hydrogenation experiments, carried out with initial two different benzene fractions, as a function of the molar benzene fraction in cyclohexane.

- □ experiment started with a molar benzene fraction of 0.95, Δ experiment started with a molar benzene fraction of 0.51.
- ········· benzene consumption rate, ········· hydrogen consumption rate. Experimental conditions: 0.5 g Ru-B, 200 ml substrate, 150 ml water, 2.4 g iron sulfate, temperature 443 K, $P_{tot}=5.0$ MPa.
depicted Figure 2. The rates follow nearly the same course, and hence, it can be concluded that the performance of the catalyst alters to a very minor extent during a hydrogenation experiment and no significant poisoning of the catalyst took place.

The influence of temperature and hydrogen pressure have been studied as well. The influence of the temperature was investigated at two different total pressures, as shown in Figure 3 and Figure 4. When the total pressure was kept constant at 3.0 MPa, both the benzene consumption rate and the cyclohexene yield decreased, when the temperature was increased from 423 to 443 K. When the total pressure was kept constant at 7.0 MPa, the benzene consumption rate was nearly constant, but the cyclohexene yield increased strongly from 14% to 28% with increasing temperature.

Figure 5 shows the results of hydrogenation experiments at three different partial hydrogen pressures carried out at 443 K. The benzene consumption rate increased when the hydrogen pressure is raised; the maximum cyclohexene yield increased significantly with the hydrogen pressure, from 11% to 28%.

The course of the catalytic hydrogenation of cyclohexene over catalyst Ru-B is depicted in Figure 6. Benzene was formed during the cyclohexene hydrogenation, even when the reaction was carried out at a partial hydrogen pressure as high

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**Figure 3:** Influence of the temperature on the course of the partial hydrogenation of benzene over a Ru-B catalyst carried out at a relatively low total pressure. For clarity the profiles of cyclohexane are left out. Experimental conditions: 0.5 g Ru-B, 2.4 g iron sulfate, 200 ml benzene, 150 ml water, total pressure 3.0 MPa, reactor I.

**Figure 4:** Influence of the temperature on the course of the partial hydrogenation of benzene over a Ru-B catalyst carried out at a relatively high total pressure. For clarity the profiles of cyclohexane are left out. Experimental conditions: 0.5 g Ru-B, 200 ml benzene, 150 ml water, 2.4 g iron sulfate, total pressure 7.0 MPa, reactor I.

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*The hydrogenation of benzene and cyclohexene*
as 3.7 MPa (total pressure 5.0 MPa).

The maximum molar benzene fraction during this experiment was 0.5 mol%. Cyclohexene hydrogenation carried out with catalyst Ru-A showed a lower hydrogenation activity, but also with this catalyst the formation of benzene was observed during the reaction. When the partial hydrogen pressure was lowered the overall benzene fraction increased in the course of time. In Table 1 the maximum benzene yields are listed, which have been observed during the cyclohexene hydrogenation at different partial hydrogen pressures. The results in the table demonstrate that benzene formation becomes more favourable at lower partial pressures.

**Figure 5:** Influence of the hydrogen pressure on the course of the partial benzene hydrogenation. For clarity the profiles of cyclohexane are left out. Experimental conditions: 0.5 g Ru-B, 200 ml benzene, 150 ml water, 2.4 g iron sulfate, temperature 443 K, reactor I.

**Figure 6:** The hydrogenation of cyclohexene. Conditions: 0.5 g Ru-B, 2.4 g iron sulfate, 200 ml cyclohexene, 150 ml water, T=443 K, P<sub>total</sub>=5.0 MPa, reactor I.

**Table 1:** The influence of the pressure on the maximum measured benzene yield in combination with the cyclohexene conversion during the hydrogenation of cyclohexene. Reaction conditions: 0.1 g Ru-A, 75 ml water, 160 ml distilled cyclohexene, 1.75 g zinc sulfate, T=423 K, reactor I.

<table>
<thead>
<tr>
<th>Partial hydrogen pressure (MPa)</th>
<th>Maximum yield (%)</th>
<th>ξ&lt;sub&gt;chem&lt;/sub&gt; (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.4</td>
<td>9.0</td>
<td>0.68</td>
</tr>
<tr>
<td>0.6</td>
<td>6.8</td>
<td>0.86</td>
</tr>
<tr>
<td>0.8</td>
<td>4.8</td>
<td>0.89</td>
</tr>
<tr>
<td>4.0</td>
<td>0.6</td>
<td>0.85</td>
</tr>
</tbody>
</table>
hydrogen pressures. The amount of benzene formed during cyclohexene hydrogenation not only depends on the partial hydrogen pressure, but also on the temperature. In Table 2 and Table 3 the observed benzene yields at 50% cyclohexene conversion are listed at different temperatures and different partial hydrogen pressures. In both cases the benzene yield increased when the temperature was raised. As to be expected the benzene yield is much higher at relatively low hydrogen pressure. An interesting observation is that, although the temperature raised, the cyclohexene conversion rate declined.

Assuming formal Arrhenius kinetics an apparent activation energy of -37 kJ/mol was found for the cyclohexene hydrogenation.

When the hydrogen supply was closed, just after the reaction started, only 10% of the cyclohexene was converted. No further conversion could be observed due to lack of hydrogen. The cyclohexene concentration was followed during more than three hours, while the mixture was stirred vigorously; it appeared that the product composition did not change. When afterwards hydrogen was supplied, the cyclohexene converted totally to cyclohexane. From this experiment the conclusion can be drawn that both the cyclohexene hydrogenation and dehydrogenation can proceed only in the presence of hydrogen.

During the benzene hydrogenation experiments besides cyclohexene and cyclohexane some by-products have been observed. The product distribution is given in Table 4. Cyclohexadiene was never detected. The product distribution shows that both isomerization and hydrogenolysis of C-C bonds at the surface of the catalyst took place.

Table 2: The influence of the temperature on the conversion rate of cyclohexene and the benzene yield at ξ_{che} =0.5 during the cyclohexene hydrogenation carried out at constant total pressure.

| Reaction conditions: 0.1 g Ru-A, 75 ml water, 160 ml distilled cyclohexene, 1.75 g zinc sulfate. P_{total} = P_{H2} + P_{H2O} + P_{organic} = 4.0 MPa, reactor II. |

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>r_{che} (mmol/s)</th>
<th>Yield benzene at ξ_{che} =0.5 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>403</td>
<td>0.10</td>
<td>0.20</td>
</tr>
<tr>
<td>423</td>
<td>0.06</td>
<td>0.25</td>
</tr>
<tr>
<td>443</td>
<td>0.04</td>
<td>0.85</td>
</tr>
</tbody>
</table>

Table 3: The influence of the temperature on the conversion rate of cyclohexene and the benzene yield at ξ_{che} =0.5 during the cyclohexene hydrogenation carried out at constant hydrogen pressure.

| Reaction conditions: 0.1 g Ru-A, 75 ml water, 160 ml distilled cyclohexene, 1.75 g zinc sulfate, P_{H2} = 0.4 MPa, P_{total} = P_{H2} + P_{H2O} + P_{organic} + P_{N2} = 4.0 MPa, reactor II. |

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>r_{che} (mmol/s)</th>
<th>Yield benzene at ξ_{che} =0.5 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>403</td>
<td>0.046</td>
<td>3.0</td>
</tr>
<tr>
<td>423</td>
<td>0.030</td>
<td>6.7</td>
</tr>
<tr>
<td>443</td>
<td>0.017</td>
<td>8.2</td>
</tr>
</tbody>
</table>

The hydrogenation of benzene and cyclohexene
Table 4: Product distribution in the partial hydrogenation of benzene at $\xi_{\text{benzene}} = 0.5$.
Experimental conditions: 1.0 g Ru-B, 200 ml benzene, 150 ml water, 57.5 mmol/l FeSO$_4$·6H$_2$O, temperature 423 K, total pressure 5.0 MPa, reactor I.

<table>
<thead>
<tr>
<th>Product</th>
<th>Amount (mol%)</th>
<th>Boiling point (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexene</td>
<td>11.5</td>
<td>356.2</td>
</tr>
<tr>
<td>1-Methylcyclopentene</td>
<td>0.15</td>
<td>348.6</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>87.6</td>
<td>353.9</td>
</tr>
<tr>
<td>Methylcyclopentane</td>
<td>0.30</td>
<td>345.0</td>
</tr>
<tr>
<td>Cyclopentane</td>
<td>0.07</td>
<td>322.4</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>0.29</td>
<td>342.2</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>0.31</td>
<td>309.3</td>
</tr>
</tbody>
</table>

**DISCUSSION**

From the results described above, it can be concluded that the hydrogen pressure, the temperature, but also the concentration of the substrate in the organic phase is a parameter, which influences the reaction rate. In Figure 2 the reaction rate of benzene is depicted as a function of its degree of conversion. It is shown that the reaction rate of benzene increases linearly at small concentrations of benzene and becomes constant at higher concentrations. The conclusion can be drawn that the benzene conversion is governed either by the mass-transfer processes or by the chemical reaction.

Calculation of the Carberry numbers of hydrogen and benzene shows indeed that during the hydrogenation reaction both benzene and hydrogen transport are governed by mass-transfer limitation. For details about the calculations see Chapter 8. The reaction rate up to $\xi_{\text{benzene}} = 0.5$ is dominantly limited by the diffusion rate of hydrogen, but is also limited, though to a minor extent, by the benzene diffusion rate. As the reaction proceeds the Carberry number for hydrogen decreases, whereas the Carberry number for benzene increases. This means that the decline in concentration of benzene results in a lower mass-transfer rate and that the reaction is then controlled mainly by the diffusion of benzene.

If the reaction rate is governed by diffusion limitation, one might expect that the benzene reaction rate is hardly influenced by the temperature. However, in Figure 3 the reaction rate decreases on raising the temperature. This effect can be explained at least partly from a decrease of the partial pressures of hydrogen. The vapour pressure of benzene and water together increases from 0.6 MPa to 1.7 MPa, when the temperature increases from 403 to 443 K. This means that the partial hydrogen pressure in the autoclave is influenced significantly by the temperature at low total
pressures [6]. Due to the hydrogen mass-transfer limitation the reaction rate can, therefore, decrease. When the hydrogenation reaction is carried out at a higher total pressure, the decrease in the partial hydrogen pressure will be relatively less. Indeed, the temperature hardly influenced the benzene consumption rate when the reaction is carried out at a total pressure of 7.0 MPa. This effect can be seen in Figure 4.

The reaction rate increases linearly with increasing hydrogen pressure, as shown in Figure 5, and this can be explained from the occurrence of mass-transfer limitation. If the reaction is controlled by diffusion, the reaction rate depends linearly on the concentration gradient. In Chapter 8 this phenomenon will be discussed in more detail. Remarkably, the selectivity and the maximum cyclohexene yield increased also with the hydrogen pressure. It is generally to be expected that in consecutive hydrogenation reactions, the selectivity towards the intermediate product decreases when the pressure is raised. Two explanations are at hand, namely i) the hydrogen coverage on the catalyst surface area and ii) the temperature of the catalyst. Firstly, at higher hydrogen pressures the hydrogen coverage on the catalyst surface will increase and due to this a lower adsorption coverage of cyclohexene is to be expected. At high hydrogen pressures high coverages of hydrogen on iron surface areas are observed in gas-phase hydrogenations [7] and analogously high coverages of hydrogen on the ruthenium catalyst surface area can be expected. In this investigation the ruthenium particles are, however, suspended in the water phase and the hydrogen concentration in water phase is low. This low hydrogen concentration in the water phase in combination with a reaction rate, which is governed by diffusion limitation of hydrogen, points to a very low hydrogen coverage on the catalyst surface area. Furthermore, Döbert found the cyclohexene selectivity decreased when the partial hydrogen pressure was increased during benzene hydrogenation in a three-phase system in which a gas flow consisting of benzene, nitrogen, and hydrogen was led through an aqueous zinc chloride solution, which contained a Ru/La₂O₃ catalyst [8]. Secondly, the temperature of the catalyst particles will raise in temperature due to the exothermicity of the reaction and the high rate of conversion in combination with heat-transfer limitation. In Chapter 8 of this thesis this phenomenon will be described in more detail. This will result in an increased desorption rate of the intermediates. The shift in adsorption/desorption equilibria for cyclohexene as a result of temperature of the catalyst particle is in agreement with the lower cyclohexene conversion rate with increasing reaction temperature, as shown in Table 2 and Table 3, and with the increase in cyclohexene yield when the temperature was raised at constant total pressure, as shown in Figure 4.

During cyclohexene hydrogenation the formation of benzene is observed as has been observed frequently [9-11]. For this formation of benzene several mechanisms have been proposed. Carra et al. [10] proposed an intramolecular rearrangement of

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The hydrogenation of benzene and cyclohexene

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hydrogen between two cyclohexene molecules, which were chemisorbed adjacently; cyclohexene disproportionates in one reaction step to benzene and cyclohexane. When this mechanism is followed a benzene/cyclohexane ratio of 1:2 should be found and no hydrogen would be observed in the product stream. This mechanism is possible in the absence of hydrogen. However, no change in the molar fractions was observed when no hydrogen was added, and for this reason the mechanism proposed by Carra et al. gives not a satisfactory explanation. Rebhaen and Haensel [11] observed that hydrogen was one of the products and so it is inevitable that benzene can be formed by dehydrogenation of cyclohexene. The observed benzene in cyclohexene hydrogenation experiment gives evidence that the mechanism of the hydrogenation reaction at the surface of the ruthenium catalyst is in accordance with the mechanism proposed by Horiuti and Polanyi [12,13]. In Figure 7 a schematic representation of the Horiuti and Polanyi mechanism is given for the catalytic hydrogenation of benzene. As can be seen from this figure all hydrogenation steps are reversible. Indeed, Richard et al. [14] showed in the hydrogenation of benzene-d₆ with H₂ a variety of H/D ratios which means that the desorption and adsorption steps are reversible.

The dehydrogenation will be promoted by low hydrogen pressures and high reaction temperatures. These effects have also been observed in the performed cyclohexene hydrogenation experiments and endorses the proposed mechanism.

The reaction rate during cyclohexene hydrogenation is governed to a lesser extent by the hydrogen mass-transfer rate. This can be noticed from Figure 6, because the cyclohexene curve shows a first order behaviour. The reaction rate decreased when the partial hydrogen pressure was kept constant and the temperature was raised, see Table 3. It can be concluded that, when the temperature is raised, the cyclohexene coverage on the catalyst surface area will be diminished, which will lead to an overall reduced hydrogenation rate of cyclohexene. This explains also why the cyclohexene yield increases during the benzene hydrogenation when the temperature is raised, as

\[
\begin{align*}
&\text{Catalyst} \\
&\text{Figure 7: Schematic representation of the Horiuti-Polanyi mechanism for the catalytic hydrogenation of benzene (a = adsorbed).}
\end{align*}
\]
illustrated in Figure 4. The consecutive hydrogenation of cyclohexene to cyclohexane will be partially suppressed. As can be seen in Table 2 and Table 3, higher amounts of benzene are found during the cyclohexene hydrogenation, which means that the dehydrogenation rate is diminished to a lesser extent than the hydrogenation rate.

During the cyclohexene hydrogenation benzene fractions up to 0.01 have been observed at hydrogen pressures around 4.0 MPa. The reaction rate is diffusionally controlled by the transport of hydrogen, though to a minor extent than during the benzene hydrogenations under identical conditions. This means that during the cyclohexene hydrogenation the hydrogen coverage on the catalyst surface is higher than during the benzene hydrogenation. At low partial hydrogen pressure the formation of benzene is more favoured as can be concluded from the results listed in Table 2 and Table 3. Therefore, the dehydrogenation of cyclohexene during the benzene hydrogenation has to be taken into account, when the diffusion of cyclohexene from the catalyst to the organic surface is rate limited, for instance by pore diffusion limitation. To prevent pore diffusion limitation an unsupported ruthenium catalyst with macropores is the best catalyst configuration.

In the benzene hydrogenation experiments besides cyclohexene and cyclohexane, also some by-products have been observed. When the reaction will be scaled up to a continuous process, cyclohexane can be dehydrogenated to benzene and, together with the non-converted benzene, recycled to the feed. However, nearly 1% of the benzene is converted to products like methylcyclopentane, cyclopentane, n-hexane, and n-pentane, which can only be recycled after reforming and that makes the development of such process more complex. The formation of cyclohexylbenzene, a by-product which might be expected during the gas-phase hydrogenation of benzene [15], was not detected during this investigation.

In Figure 8 the possible routes to the by-products are presented. Cyclohexene can isomerize to methylcyclopentene. The formation of 1-methylcyclopentene is more likely than the formation of 3- or 4-methylcyclopentene. Ring-opening by breakage of the double bond in cyclohexene and methylcyclopentene results in the formation of n-hexane. Hydrogenolysis of methylcyclopentene gives cyclopentene.

![Figure 8: Possible routes to the by-products in the hydrogenation of benzene.](image)
and methane. n-Pentane is formed by opening of the cyclopentene ring. Cyclopentane can be formed by hydrogenation of cyclopentene or hydrogenolysis of methylcyclopentane.

It is well-known that isomerization and hydrogenolysis can occur in the presence of group VIII metal catalysts in an acid environment. The pH of the aqueous salt solution is in between 5 and 6. To suppress the by-product formation, the reaction can be performed at a higher pH. However, the pH choice is restricted because the hydroxide of the used modifiers have either to remain in solution or can be deposit onto the catalyst only at such an extent that activity (and selectivity) remains.

CONCLUSIONS

The benzene hydrogenation rate is retarded by the hydrogen transport rate. At constant hydrogen pressures the reaction temperature will hardly influence the reaction rate. The reaction rate of cyclohexene hydrogenation is governed by hydrogen transport limitation to a minor extent. Increasing the temperature during the cyclohexene hydrogenation results in a lower rate, due to a lower cyclohexene coverage at the surface of the catalyst. The apparent activation energy of the cyclohexene hydrogenation showed to be -37 kJ/mol.

During benzene hydrogenation the cyclohexene yield increases by raising the temperature. The cyclohexene yield increased when the hydrogen pressure is raised. This effect is not to be expected in a consecutive hydrogenation reaction. Presumably, a reduced cyclohexene coverage is obtained by an increase of the surface temperature of the catalyst particles due to heat-transfer limitation.

Cyclohexene can be dehydrogenated to benzene under the applied conditions (T=403-443 K, p_{H_2}=3-7 MPa). This supports the hydrogenation mechanism postulated by Horiuti and Polanyi. The dehydrogenation is favoured by low hydrogen pressures and high temperatures. The dehydrogenation of formed cyclohexene has to be taken into account and can influence the overall selectivity to cyclohexene. To avoid the dehydrogenation reaction pore diffusion limitation has to be eliminated. A non-supported ruthenium catalyst with macropores is, therefore, the best catalyst configuration.

During the benzene hydrogenation not only cyclohexene and cyclohexane, but also minor amounts of by-products are formed by isomerization and hydrogenolysis due to the slightly acidic character of the reaction medium.
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The hydrogenation of benzene and cyclohexene
The partial hydrogenation of benzene, toluene, and p-xylene

ABSTRACT

The partial hydrogenation of aromatics has been investigated over ruthenium catalysts in the presence of an aqueous salt solution. The reaction has been performed at temperatures ranging from 403 K to 443 K and total pressures ranging from 3.0 MPa to 5.5 MPa. Upon zinc salt addition the selectivities towards the cycloalkenes increase, whereas the activity of the catalyst diminishes. The conversion rates of the aromatics decrease in the order benzene>toluene>p-xylene. The maximum yields of the partial hydrogenated products were 20%, 27%, and 46%, respectively.

During competitive hydrogenation experiments, in which benzene/toluene and benzene/p-xylene mixtures were hydrogenated, the conversion rates are not only determined by mass-transfer limitation of hydrogen, but also by the solubilities of the substrates. Benzene is hydrogenated preferentially, and when nearly all benzene is converted, toluene, or p-xylene will be hydrogenated.

In the hydrogenation of toluene 1-, 3-, and 4- methylcyclohexene were observed. On a thermodynamic point of view the ratio $S_1/S_{3+4}$, defined as the ratio between the selectivity to 1-methyl-1-cyclohexene and the selectivity to 3- and 4-methyl-1-cyclohexene, is approximately 30. The higher the amount of salt or the higher the temperature, the lower was the ratio $S_1/S_{3+4}$ and further away of thermodynamic equilibrium.
INTRODUCTION

Cyclohexene can be produced by partial hydrogenation of benzene over a ruthenium catalyst in the presence of an aqueous zinc sulfate solution at 423 K and at total pressures ranging from 5.0 to 7.0 MPa. From the patent literature [1,2,3] and publications by Odenbrand and Lundin [4], and by Struijk et al. [5,6] it follows that under the conditions quoted above, selectivities to cyclohexene up to 80% and cyclohexene yields of 40-55% may be achieved.

This method to produce cyclohexene can also be applied to other aromatic substrates. Nagahara et al. [1] hydrogenated benzene, toluene, and p-xylene and achieved yields of the partial hydrogenated products up to 54%, 43%, and 41%, respectively. The replacement of benzene by toluene or by p-xylene results in a decline in the reaction rate [1,7]; this is to be expected as a consequence of the solubilities of toluene and p-xylene in water deviating from the solubility of benzene in water [7].

The mechanism of Horiuti and Polanyi is generally accepted for the hydrogenation of aromatics [8]. An extensive description of the mechanism is given in Chapter 1. In the partial hydrogenation of toluene three hydrogenated isomers, 1-, 3-, and 4-methyl-1-cyclohexene, can be formed via intermediates, [C_7H_{12}^*] or [C_7H_{14}^*], which are adsorbed at the catalyst surface (see Scheme 1). Thermodynamically, the formation of 1-methyl-1-cyclohexene is favoured.

\[
\text{Scheme 1: Hydrogenation of toluene.}
\]

p-Xylene hydrogenation also results in the formation of three partially hydrogenated products, viz. 1,4-dimethyl-1-cyclohexene and cis- and trans-3,6-dimethyl-1-cyclohexene (see Scheme 2). Further hydrogenation of these cyclohexene derivatives yields cis- and trans-1,4-dimethylcyclohexane. On the basis of thermodynamics from the partially hydrogenated products, 1,4-dimethyl-1-cyclohexene will be formed preferentially.
Scheme 2: Hydrogenation of p-xylene.

A summary of the conditions and the results of the hydrogenation of substituted aromatics, which have been found in the literature, is given in Table 1. In the p-xylene hydrogenation Siegel et al. [9] observed a fraction of only 0.5% dimethylcyclohexene. The cis/trans-ratio of the dimethylcyclohexene changed when the partial hydrogen pressure was raised. A maximum selectivity of 8% to 1,2-dimethylcyclohexene has been achieved by Viniegra et al. [10] in the gas-phase hydrogenation of o-xylene over a Pd/SiO₂ catalyst. In the liquid-phase hydrogenation of substituted aromatics, Van Bekkum et al. [11] showed that the yields of cyclohexene intermediates are strongly increased when bulky substituents are used. Most toluene and xylene hydrogenation experiments have been carried out with platinum or palladium catalysts, notwithstanding the fact that on labscale rhodium and especially ruthenium catalysts have given the best results. Struijk and Scholten [12] showed that even under moderate conditions a methylcyclohexene yield of 8% can be achieved with an unsupported ruthenium catalyst in the liquid-phase toluene hydrogenation. Very good results are achieved by Nowack and Johnson [13] in the liquid-phase hydrogenation carried out at high pressures, 5.0-7.0 MPa, and high temperatures, 423-453 K. Yields up to 35% have been achieved with supported ruthenium catalysts. Al₂O₃ [13], BaSO₄ [14], mordenite [15], La₂O₃ [16], and SiO₂ [17] were used as support. The highest yields (up to 43%) during the partial hydrogenation of toluene and of p-xylene have been claimed by Nagahara and Konishi [1] using an unsupported ruthenium catalyst. Hardly any information is given about the mechanism of the reaction, as we are dealing mostly here with patent literature. In all high-pressure hydrogenations of aromatics the addition of an aqueous salt solution appears to be essential.

Useful information can be obtained from Cerveny and Ruzicka [18]. These authors compared the relative rate constants and adsorption coefficients in the catalytic
Table 1: Summary of the conditions and results of the hydrogenation of substituted aromatics. The yields of the partially hydrogenated products are presented. Experiments carried out in the liquid phase (L) have been performed batch-wise. Gas-phase (G) experiments were performed continuously. $\xi_{\text{benzene}}$ = benzene conversion.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Substrate</th>
<th>Additives/Modifiers</th>
<th>Conditions</th>
<th>Yield</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtO$_2$</td>
<td>p-Xylene</td>
<td>acetic acid</td>
<td>298 K 0.1 MPa L</td>
<td>not reported</td>
<td>0.5</td>
</tr>
<tr>
<td>Pd/SiO$_2$</td>
<td>o-Xylene</td>
<td>thiophene</td>
<td>413 K 0.11 MPa G</td>
<td>not reported</td>
<td>8</td>
</tr>
<tr>
<td>Ru</td>
<td>Toluene</td>
<td>methanol</td>
<td>313 K 0.11 MPa L</td>
<td>0.8-0.9</td>
<td>8</td>
</tr>
<tr>
<td>Ru/Al$_2$O$_3$</td>
<td>Toluene</td>
<td>Ni,Mo</td>
<td>467 K 6.9 MPa L</td>
<td>0.72</td>
<td>19</td>
</tr>
<tr>
<td>Ru/BaSO$_4$</td>
<td>Toluene</td>
<td>Fe,Cu CoSO$_4$</td>
<td>453 K 4.0 MPa L</td>
<td>0.65</td>
<td>26</td>
</tr>
<tr>
<td>Ru/mordenite</td>
<td>Toluene</td>
<td>Cu,Ag Co$_3$(PO$_4$)$_2$</td>
<td>443 K 4.0 MPa L</td>
<td>0.44</td>
<td>10</td>
</tr>
<tr>
<td>Ru/mordenite</td>
<td>p-Xylene</td>
<td>Co$_2$Ag Co$_3$(PO$_4$)$_2$</td>
<td>443 K 4.0 MPa L</td>
<td>0.49</td>
<td>12</td>
</tr>
<tr>
<td>Ru/La$_2$O$_3$</td>
<td>Toluene</td>
<td>ZnO, NaOH</td>
<td>423 K 5.0 MPa L</td>
<td>0.32</td>
<td>24</td>
</tr>
<tr>
<td>Ru/SiO$_2$</td>
<td>Toluene</td>
<td>Cu</td>
<td>463 K 7.0 MPa L</td>
<td>0.63</td>
<td>35</td>
</tr>
<tr>
<td>Ru</td>
<td>Toluene</td>
<td>ZnSO$_4$</td>
<td>423 K 5.0 MPa L</td>
<td>0.58</td>
<td>43</td>
</tr>
<tr>
<td>Ru</td>
<td>p-Xylene</td>
<td>ZnSO$_4$</td>
<td>423 K 5.0 MPa L</td>
<td>0.58</td>
<td>41</td>
</tr>
<tr>
<td>Rh/C</td>
<td>1,3,5-tri-tert-butyl benzene</td>
<td>-</td>
<td>298 K 0.1 MPa L</td>
<td>0.8</td>
<td>&gt;60</td>
</tr>
</tbody>
</table>
liquid-phase hydrogenation of substituted aromatics at moderate conditions. From their study the conclusion can be drawn that the adsorption behaviour of the aromatics varies with the type of catalyst. The higher substituted aromatics adsorb less strongly when Pt, Rh/Al₂O₃, or Ni catalysts are used, but adsorb more strongly when Ru or CoO-MoO₃/Al₂O₃ catalysts are used. When the aromatic is higher substituted the rate constant declines in all cases. Minot and Gallezot [19] state, that the methyl group is an electron donating group and that the electron donating effect makes the bonding between the ring and the metal surface, such as ruthenium, rhodium, and palladium, stronger. They base their theory on simple molecular-orbital arguments, supported by extended Hückel calculations. Their results are supported by competitive hydrogenation experiments over ruthenium catalysts from Yoshida [20]. Völter et al. [21] also found that over rhodium and cobalt catalysts the hydrogenation activity decreases with increasing number of methyl groups, but they report that the strength of adsorption decreases in the opposite sequence. From the literature so far, no unequivocal conclusion can be drawn on the adsorption strengths of aromatics on the group VIII metals.

As shown in Scheme 1 and Scheme 2 miscellaneous isomeric products can be expected when toluene or p-xylene are hydrogenated partially. On the base of statistics, in the toluene hydrogenation the ratio between the three isomeric products, 1-, 3-, and 4-methyl-1-cyclohexene is expected to be 1:1:1. From a thermodynamic point of view 1-methyl-1-cyclohexene will be formed preferentially. Also on this point different results have been attained; Mitsui [16] claims an excess of 3-methyl-1-cyclohexene (ratio 1 : 2.6 : 0), Nowack [13] and Hideyuki [15] an excess of 1-methyl-1-cyclohexene (ratio 4 : 1 : 1 and 6 : 1 : 1, respectively).

It is the aim of the present study to investigate the partial hydrogenation of substituted aromatics, viz. toluene and p-xylene, over a ruthenium catalyst in the presence of an aqueous salt solution. Several partially hydrogenated products can be expected and probably more information about the hydrogenation mechanism could be obtained. Therefore, the influence of temperature and the salt concentration on the methylcyclohexene selectivities have been examined. The kinetics of the partial hydrogenation of benzene depend on physical as well as on chemical parameters; using toluene or p-xylene, instead of benzene, will change these physical and chemical parameters, but the reaction mechanism probably remains the same. For this purpose the hydrogenation of benzene, toluene, and p-xylene have been compared with each other. The competitive hydrogenations of benzene/toluene and benzene/p-xylene mixtures have been studied as well.

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Chapter 5

EXPERIMENTAL

Chemicals
Benzene is obtained from Fluka and Janssen Chimica, toluene from Janssen Chimica and p-xylene from J.T. Baker. The aromatics were all thiophene free and reagent grade (purity >99.5%). Ruthenium trichloride, spec. pure, 42.0-42.3 wt% Ru, was supplied by Johnson Matthey. Sodium hydroxide and iron sulfate (FeSO₄·6H₂O), both pro analyse, were obtained from J.T. Baker. Zinc sulfate (ZnSO₄·7H₂O), pro analyse, is obtained from Merck. Hydrogen, purity >99.95%, was obtained from Air Products. For catalyst preparation and hydrogenation experiments distilled water was used.

Catalyst preparation
The method of catalyst preparation was nearly identical to the method described by Nagahara [1] and Struijk [5]. About 10 g of ruthenium trichloride, dissolved in 1 l distilled water, was heated to 353 K with vigorous stirring. Next, 45 g of sodium hydroxide dissolved in 150 ml water was added instantaneously to the ruthenium chloride solution and the resulting mixture was cooled to room temperature and transferred to a measuring cylinder where the black colloidal ruthenium hydroxide was left to precipitate. The supernatant was decanted and the black colloidal precipitate was transferred into an autoclave. After purging with nitrogen and hydrogen, the hydrogen pressure was elevated to 3.5 MPa. After raising the temperature to 423 K the total pressure was raised to 5.0 MPa with hydrogen, after which further reduction of the ruthenium hydroxide to metallic ruthenium was performed under stirring. Subsequently, the autoclave was cooled down and the reaction mixture was transferred in the open air into a glass vessel. The ruthenium catalyst was further passivated overnight by slow reaction with air dissolving in the water with slow agitation. Finally, the passivated catalyst was filtered off, washed with distilled water until neutrality, dried at room temperature and subsequently at 353 K. About 5 g of the passivated catalyst (type A) was obtained. A second batch of ruthenium catalyst (type B) was prepared in a slightly different way. The preparation method was changed at three points: the sodium hydroxide solution was added dropwise to the ruthenium trichloride solution and after one hour of mixing a gas mixture of nitrogen and hydrogen (1.66 ml/s, H₂/N₂-ratio 1:3) was led through the solution. The black particles settled down more quickly when the stirring stopped. Finally, before further reduction at elevated temperature and pressure the particles were washed several times with distilled water until the solution reached neutrality.

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Experimental procedure

An amount of ruthenium catalyst, aromatic compound, distilled water and zinc sulfate or iron sulfate were introduced into the stainless-steel autoclave, equipped with baffle bars. For details, see the legends to the various figures in the text. After purging with hydrogen, the pressure was elevated to 3.5 MPa. When the desired reaction temperature was reached, the total pressure was adjusted to 5.0 MPa with hydrogen. The hydrogenation reaction was started by switching on the stirrer (stirring speed 1500 rpm).

The hydrogenation reaction was monitored by taking small samples of the reaction mixture at selected time intervals, followed by gas-chromatographic analysis. A Packard 429 gas chromatograph equipped with a 50 m CB 52 Carbowax WCOT column from Chrompack (column temperature 353 K) and a FID-detector was used. Molar fractions smaller than $10^{-5}$ could not be detected.

Hydrogenation of toluene was studied at temperatures ranging from 403 to 443 K. The competitive hydrogenation of benzene and of toluene has been studied as well; in that case a mixture of benzene and of toluene was introduced into the reactor. Ruthenium catalyst A was used for nearly all toluene hydrogenation experiments and for some benzene hydrogenation experiments. Furthermore, in the toluene hydrogenation the hydrogen pressure and the amount of zinc sulfate were varied.

Ruthenium catalyst B was used successively for benzene, toluene, and p-xylene hydrogenation experiments. This means that after the benzene hydrogenation experiment the organic phase was removed by pipetting, and the remaining water phase and catalyst, which was suspended in the water phase, were used for a toluene and later on for a p-xylene hydrogenation experiment. To check the stability of the catalyst, after the p-xylene hydrogenation, benzene was used again as the substrate. Also, a competitive hydrogenation experiment with benzene and p-xylene was carried out. The hydrogenations carried out over ruthenium catalyst B have been performed in a TiN-coated autoclave.

The benzene conversion, the selectivity to cyclohexene and the cyclohexene yield have been calculated according to the following equations:

Benzene conversion:

$$\xi = \frac{X_{C_6H_6,t=0} - X_{C_6H_6,t}}{X_{C_6H_6,t=0}} \quad (1)$$

Cyclohexene selectivity:

$$S_{C_6H_{10}} = \frac{X_{C_6H_{10},t}}{X_{C_6H_6,t=0} - X_{C_6H_6,t}} \cdot 100\% \quad (2)$$

---

The partial hydrogenation of benzene, toluene, and p-xylene
Cyclohexene yield: \[ Y_{C_6H_{10}} = \frac{x_{C_6H_{10},t}}{x_{C_6H_6,t=0}} \cdot 100\% \] (3)

In these equations \( x_{i,t=0} \) is the concentration of component \( i \) at the start of the experiments and \( x_{i,t} \) is the concentration at time \( t \). These equations have been used also for the toluene and p-xylene hydrogenation.

The 'initial selectivity' is the selectivity defined according to equation (2) at the start of the batch operation. The 'maximum yield' means the maximum observed yield during the hydrogenation reaction. Except when explicitly stated otherwise, the selectivities and yields reported refer to the sum of the partially hydrogenated products. \( S_1 \) means the selectivity to 1-methyl-1-cyclohexene in the toluene hydrogenation and \( S_{3+4} \) means the selectivity to 3- and 4-methyl-1-cyclohexene together.

The selectivity ratio, \( S_1/S_{3+4} \), is the ratio between the selectivity to 1-methyl-1-cyclohexene and the selectivity to the sum of 3- and 4-methyl-1-cyclohexene:

\[
\frac{S_1}{S_{3+4}} = \frac{S_{1-\text{methyl-1-cyclohexene}}}{S_{3-\text{methyl-1-cyclohexene}} + S_{4-\text{methyl-1-cyclohexene}}} \] (4)

RESULTS

Performance of ruthenium catalyst A with addition of zinc sulfate

Characteristic concentration profiles in the hydrogenation of benzene and toluene without addition of salt are depicted in Figure 1. The molar hydrogen consumption rate was in both cases high, viz. 4.2 and 5.2 mmol/s, respectively. The toluene was converted slightly more quickly than benzene in this case, but in a duplicate experiment this behaviour was just opposite. Hardly any partially hydrogenated products were detected. The maximum yield to cyclohexene in the benzene hydrogenation was only 0.3% and for toluene the maximum yield to the methylcyclohexenes was 1.8%.
Concentration profiles in the partial hydrogenation of benzene and of toluene in the presence of salt are shown in Figure 2. The same conditions have been applied as in the experiments described in Figure 1. With the use of zinc sulfate the hydrogen consumption rates decreased strongly, to 1.9 and 0.81 mmol/s for benzene and toluene, respectively, but the maximum yields to the partially hydrogenated products of benzene and toluene increased considerably, to 21% and 22% respectively. In the toluene hydrogenation the maximum yield to

**Figure 1**: Characteristic concentration profiles in the hydrogenation of pure benzene and of pure toluene as a function of time over a ruthenium catalyst without the use of zinc sulfate. Conditions: 0.2 g ruthenium catalyst A; 200 ml aromatic; 75 ml water; $p_{\text{total}}=5.0 \text{ MPa}; T=423 \text{ K}$.

![Graph](image1)

**Figure 2**: A) Characteristic concentration profiles of benzene (a), cyclohexene (b), and cyclohexane (c) in the hydrogenation of benzene as a function of time over a ruthenium catalyst with zinc sulfate added. B) Characteristic concentration profiles of toluene (a), 1-methyl-1-cyclohexene (b), 3- and 4-methyl-1-cyclohexene (c), and methylcyclohexane (d) in the hydrogenation of toluene as a function of time over a ruthenium catalyst with zinc sulfate added. Conditions: 0.2 g ruthenium catalyst A; 200 ml aromatic; 75 ml water; 0.6 g zinc sulfate; $p_{\text{total}}=5.0 \text{ MPa}; T=423 \text{ K}$.

**The partial hydrogenation of benzene, toluene, and p-xylene**
1-methyl-1-cyclohexene was 17% and to 3- and 4-methyl-1-cyclohexene together 6.4%; these yields were achieved at different degrees of conversion.

The influence of the amount of zinc sulfate added on the hydrogen consumption rate and on the initial selectivity, that means the selectivity at the start of the batch operation, to the methylcyclohexenes in the hydrogenation of toluene is shown in Figure 3. By increasing the salt concentration from 0 to 160 mmol/l the reaction rate decreased gradually. The initial selectivity remained constant at concentrations higher than 40 mmol/l. The maximum yield was also strongly influenced by the salt addition and an optimum of 25% is found at a zinc sulfate concentration of approximately 20 mmol/l.

The amount of salt influenced also the ratio $S_1/S_{3+4}$. Increasing the zinc sulfate concentration from 0 to 80 mmol/l the selectivity ratio decreased from 10 to 1.2 at $\xi=0.5$ (see Figure 4). At $\xi=0.25$ this ratio decreased from 7.1 to 0.74.

![Graph showing rate, maximum yield, and selectivity vs. concentration](image1)

**Figure 3:** The influence of the zinc sulfate concentration on the hydrogen consumption rate in the partial hydrogenation of toluene, the maximum yield to 1-, 3-, and 4-methyl-1-cyclohexene together, and the initial selectivity to 1-, 3-, and 4-methyl-1-cyclohexene together. Conditions: 0.2 g ruthenium catalyst A; 200 ml toluene; 75 ml water; zinc sulfate; $p_{\text{total}}=5.0$ MPa; $T=423$ K.

![Graph showing S1/S3+4 ratio vs. concentration](image2)

**Figure 4:** The influence of the zinc sulfate concentration on the selectivity ratio $S_1/S_{3+4}$ at three different degrees of conversion during a batch experiment. Conditions: 0.2 g ruthenium catalyst A; 200 ml toluene; 75 ml water; zinc sulfate; $p_{\text{total}}=5.0$ MPa; $T=423$ K.
Because of the low reaction rate at a zinc sulfate concentration of 160 mmol/l, the experiment was cut off before $\xi=0.25$ was reached. At $\xi=0.10$ the ratio, $S_1/S_{3+4}$, decreased from 3.3 to 0.65 on increasing salt concentration from 12 to 160 mmol/l. When no salt was added the reaction rate was in the order of 5 mmol/s and only data at high degrees of conversion could be obtained.

When the temperature was increased the hydrogen consumption rate appeared to decrease slightly, see Figure 5. The initial selectivity and the maximum yield to the methylcyclohexenes increased. Increasing the temperature influenced also the ratio $S_1/S_{3+4}$. Figure 6 demonstrates that this ratio decreased at higher temperatures and increased at a higher degree of conversion at the same temperature level.

Increasing the total pressure from 3.0 to 5.5 MPa resulted in an increase of the reaction rate. The maximum yields to the methylcyclohexenes increased from 13% to 24%. The results are presented in Figure 8.

**Figure 5:** The influence of the temperature on the toluene reaction rate, the total yield to 1-, 3-, and 4-methyl-1-cyclohexene, and the total initial selectivity to 1-, 3-, and 4-methyl-1-cyclohexene. Conditions: 0.2 g ruthenium catalyst A; 200 ml toluene; 75 ml water; 0.45 g zinc sulfate; $P_{\text{total}}=5.0$ MPa.

**Figure 6:** The influence of the temperature on the selectivity ratio $S_1/S_{3+4}$ at three different degrees of conversion during a batch experiment. Conditions: 0.2 g ruthenium catalyst A; 200 ml toluene; 75 ml water; 0.45 g zinc sulfate; $P_{\text{total}}=5.0$ MPa.

*The partial hydrogenation of benzene, toluene, and p-xylene* 87
The results of the competitive hydrogenation experiment with benzene and toluene are depicted in Figure 7. In this figure all fractions are normalized to the initial fractions of the individual substrates. In this experiment benzene appears to be hydrogenated preferentially. When nearly all benzene was converted, the rate of reaction of toluene increased significantly. The ratio of the initial benzene consumption rate and the initial toluene consumption rate was 14. Correction for the molar concentrations of benzene and toluene at the start of the experiment yields a ratio of 12.

Figure 7: The competitive hydrogenation of benzene and toluene. The molar fraction of benzene and toluene were normalized to unity. For clarity the profiles of the fully hydrogenated products are left out and the fractions of 1-, 3-, and 4-methyl-1-cyclohexene were added up. Conditions: 0.2 g ruthenium catalyst A; 100 ml benzene and 100 ml toluene; 0.6 g zinc sulfate; 75 ml water; $T=423\,\text{K}$; $p_{\text{total}}=5.0\,\text{MPa}$.

Figure 8: Influence of the pressure on the hydrogen consumption rate, the selectivity measured at $\xi=0.1$, and the yield to the methylcyclohexenes. Conditions: 0.2 g ruthenium catalyst A; 200 ml toluene; 75 ml water; 0.45 g zinc sulfate; $T=423\,\text{K}$.
Performance of ruthenium catalyst B with addition of iron sulfate

In Figure 9 the sequential partial hydrogenation of benzene, toluene, and p-xylene with the use of catalyst B and addition of iron sulfate is shown. In all sequential runs the organic phase was replaced, while the aqueous layer which contains the catalyst was left in the reactor. The maximum yields of the partially hydrogenated products were, respectively, 20%, 27%, and 46%. In the hydrogenation of p-xylene only one isomer of the dimethylcyclohexenes has been observed, viz. 1,4-dimethyl-1-cyclohexene, and both fully hydrogenated products, cis- and trans-1,4-dimethylcyclohexane. To investigate the stability of the catalyst, after the p-xylene hydrogenation, benzene was used once again as a substrate. The performance was nearly identical to that of the original benzene hydrogenation run, both with respect to activity and selectivity.

![Figure 9: Course of the partial hydrogenation of benzene, toluene and p-xylene as a function of time over ruthenium catalyst type B. For clarity the lines of the totally hydrogenated products are left out and the fractions of isomers of the partially hydrogenated products have been added up. Conditions: 1.0 g catalyst B; 200 ml aromatic; 150 ml water; 2.4 g iron sulfate; P_total=5.0 MPa, T=433 K.](image1)

![Figure 10: The hydrogen consumption rate in benzene, toluene and p-xylene hydrogenation as a function of the molar fraction of the aromatic in the organic phase. Conditions: 1.0 g catalyst B; 200 ml aromatic; 150 ml water; 2.4 g iron sulfate; P_total=5.0 MPa, T=433 K.](image2)
Figure 11: Course of the competitive hydrogenation of benzene and p-xylene. The molar fractions of benzene and p-xylene at the start of the reaction are normalized to unity. For clarity the profiles of the fully hydrogenated products are left out. Conditions: 1.0 g ruthenium catalyst type B; 100 ml benzene and 100 ml p-xylene; 2.4 g iron sulfate; 150 ml water; T=423 K; $P_{\text{total}}=5.0$ MPa.

In Figure 10 the hydrogen consumption rates of the successive benzene, toluene, and p-xylene hydrogenations are plotted as a function of the molar fraction of the aromatics in the organic phase. The initial reaction rates were 5.1, 3.1, and 1.2 mmol/s/\(g_{\text{cat}}\) respectively. As can be seen from this figure the hydrogen consumption rate increases almost linearly at low aromatic fractions and is nearly constant at high aromatic fractions.

The results of the competitive hydrogenation experiments with benzene and p-xylene are depicted in Figure 11. In the figure all fractions are normalized to the initial fractions of the individual substrates. Similarly, to the competitive benzene/toluene hydrogenation, benzene is hydrogenated preferentially; when the larger part of benzene has disappeared, the conversion rate of xylene increases strongly. The initial ratio of the benzene consumption rate and the p-xylene consumption rate was approximately 60. Corrections for the molar concentrations of benzene and p-xylene at the start of the experiment yields a ratio of 42.
DISCUSSION

Because catalyst A and B are different, it is preferred to discuss the results obtained with these catalysts separately.

Performance of ruthenium catalyst type A with zinc sulfate

Experiments showed that the initial reaction rates in the hydrogenation of benzene and of toluene, without the addition of salt but in the presence of water, differ slightly. When the reaction proceeded the reaction rates differed to an even lesser degree. The differences in the reaction rates are not significant and are likely due to start-up phenomena.

When salt was added the rates were significantly lower. As soon as water in combination with zinc sulfate was added, the surface of the ruthenium catalyst is partially covered by cations due to the chemisorption of zinc sulfate. Owing to this, the hydrophobicity of the ruthenium surface changes into hydrophilicity and the catalyst particles become surrounded by a stagnant water layer. The substrates, both the aromatics and hydrogen, have now to dissolve in the water phase and to diffuse through the water layer to the catalyst particles, where the reaction is catalyzed. Of course, the reaction rate is strongly diminished by the adsorption of salt. The readsorption of partially hydrogenated products is strongly retarded by the water layer around the catalyst particles and this contributes to the build-up of a high yield of partially hydrogenated products in the organic phase. The solubilities of the partially hydrogenated products in water are smaller than the solubilities of the aromatic substrates [22]. Due to this lower solubility the aromatics will hydrogenate preferentially, before further hydrogenation of the reaction intermediates takes place, assuming that the substrates and the intermediates have the same adsorption strength.

Similar results for benzene have been published in the literature and are described in Chapter 3 of this thesis. As reported by Soede et al. calculations for both the hydrogenation of benzene and of toluene show that their chemisorption on ruthenium is externally diffusionally controlled and at the same time internal diffusion of hydrogen and of the substrates, viz. in the pores of the catalyst, occur [23].

By increasing the salt concentration the reaction rate decreased gradually. Two factors can be put forward to explain this effect. Firstly, on adding more salt, the hydrophilicity of the catalyst particles increases by which the stagnant water layer becomes more dominant and hence the rate of diffusion of the reactants declines. Secondly, an increasing salt coverage will gradually poison the catalyst surface more and more, and finally to such an extent that the catalytic reaction becomes the rate determining step instead of the diffusional transport [24].
It is clear that the partial hydrogenation of toluene in a four-phase system results in high yields of the methylcyclohexenes. For the higher selectivities in the hydrogenation of a substituted aromatic with respect to benzene, two explanations are at hand. Firstly, the adsorption strength of the partially hydrogenated products is less than that of cyclohexene and those products have also a lower solubility than cyclohexene. The methyl group has a repulsive character, which is expected to enlarge the desorption rate. Secondly, because the methyl group is an electron donating group, the double bond at the side of a methyl group is stabilized. Due to this stabilization the activation energy of the consecutive hydrogenation step will be higher and as a result the rate of further hydrogenation is lower. None of these interpretations can be preferred on the basis of the results obtained so far.

During the toluene hydrogenation 1-methyl-1-cyclohexene is formed preferentially, and 1,4-dimethyl-1-cyclohexene during the p-xylene hydrogenation. For an adsorbed methylcyclohexene intermediate formed during toluene hydrogenation four possibilities have to be taken into account: dehydrogenation to toluene, further hydrogenation to methylcyclohexane, isomerization to the other methylcyclohexene intermediates, and desorption to the organic phase. These steps are first order processes and depending on the rate constants of the (de-)hydrogenation, isomerization, and desorption, different ratios of $S_1/S_{3+4}$ can be observed. In the toluene hydrogenation the ratio $S_1/S_{3+4}$ is initially 30 when thermodynamic equilibrium is reached, the ratio is 0.5 when only statistical reflections are taken into account and all rate constants are supposed to have the same value. The ratios observed vary between 0.5 and 10. This means that the thermodynamic equilibrium is not reached.

It is observed that the ratio $S_1/S_{3+4}$ shifted in all cases to the thermodynamic value when the hydrogenation prolongs. Two explanations are at hand. Firstly, in a consecutive reaction 3- and 4-methylcyclohexene are isomerized to 1-methyl-1-cyclohexene. Richard et al. [25] showed that under reaction conditions nearly identical as used in this study, for the hydrogenation of D$_6$-benzene the adsorption is a dynamic process. Continuously D$_x$-cyclohexene molecules adsorb, isomerize, and desorb in the stagnant water layer before they are transferred into the organic phase. Their results are in accordance with the hydrogenation mechanism of Horiuti and Polanyi presented in Scheme 1. When the average residence time of the methylcyclohexenes on the catalyst surface increases, this can result in a shift towards the thermodynamic equilibrium. Secondly, the hydrogenation of 3- and 4-methyl-1-cyclohexene to methylcyclohexane can be faster than the hydrogenation of 1-methyl-1-cyclohexene. This will also result in a shift of the ratio to higher values.
when the reaction prolongs. On the basis of the presented results none of the explanations are to be preferred.

Interestingly the ratio $S_1/S_{3,4}$ shifted to lower values when the temperature was raised or the salt concentration increased. In both cases it could be suggested that isomerization or further hydrogenation of 3- and 4-methyl-1-cyclohexene at the surface of the catalyst is prohibited. However, it is well-known that the desorption rate of adsorbed molecules increase when the temperature is raised. The average residence time at the catalyst surface is reduced and 3- and 4-methyl-1-cyclohexene might be isomerized or hydrogenated to a lesser extent. For the influence of the salt concentration the same arguments can be used. Due to the salt adsorbed on the catalyst surface the adsorption equilibria are changed and, as a consequence, the rate of isomerization or of further hydrogenation is lowered.

As can be seen in Figure 8, the reaction rate increased almost linearly with the total pressure. This means that the diffusion rate is first order in the hydrogen pressure. Remarkably the maximum yield and the selectivity also increase. A straightforward explanation cannot be given. Normally, in partial hydrogenation reactions, the selectivity towards the intermediate product decreases when the pressure is raised. Two explanations can be presented. Firstly, at higher hydrogen pressures the hydrogen coverage at the catalyst surface will be higher and due to this higher coverage a lower adsorption coverage of the methylcyclohexenes can be expected. In the gas phase high coverages of hydrogen on iron are observed [26] and, therefore, also high coverages of hydrogen on ruthenium can be expected. In the current investigation the ruthenium particles are, however, suspended in the water phase and the hydrogen concentration in the water phase is low. Thereby, the reaction rate is governed by diffusion limitation of hydrogen and, therefore, it is expected that the hydrogen coverage is low. Secondly, due to the exothermicity of the reaction and the high rate of conversion in combination with heat-transfer limitation, the temperature of the catalyst particles will rise. This results in an increased desorption rate of the intermediates. Figure 5 shows that the yield increases when the reaction temperature rises, while the reaction rate changes only slightly. An extensive description of these observations will be given in Chapter 8 of this thesis.

The temperature influenced the reaction rate only slightly, as can be seen in Figure 5. The fact that the reaction rate tends to decrease with increasing temperature can be explained by the increase of the autogenic pressure of both toluene and water. When the total pressure is kept constant, the partial hydrogen pressure in the reactor will decrease. Correction for this pressure drop shows that the conversion rate is only slightly influenced by the temperature, which confirms that under the conditions of the investigation the chemical reaction on the catalyst surface is not rate-determining.

The partial hydrogenation of benzene, toluene, and p-xylene
Performance of ruthenium catalyst type B with iron sulfate

In comparison with benzene, both toluene and p-xylene showed a higher selectivity to the intermediates. Nagahara and Konishi [1] reported the opposite, but they used higher concentrations of zinc sulfate in the water phase. For p-xylene a yield of 46% to dimethylcyclohexene has been obtained in this work, and up to now no more selective reaction systems have been reported in the literature.

Figure 10 shows that the hydrogen consumption rate diminishes in the order benzene > toluene > p-xylene. In Chapter 8 of this thesis a description is given of the kinetics of the benzene hydrogenation, the adsorption phenomena, and the mass-transfer processes. The proposed model describes the benzene hydrogenation adequately and it is logical to apply this model to the toluene and p-xylene hydrogenation. The reaction rate for the first hydrogenation step from the aromatic to the partial hydrogenated (substituted) cyclohexene can be expressed by:

in which \( r_{H_2} \) is the hydrogen consumption rate (mmol/s), \( k_i \) the reaction rate constant of component \( i \) (mmol/s), \( \theta_i \) the coverage of the aromatic of the catalyst and \( \theta_H \) the hydrogen coverage.

\[
r_{H_2} = k_i \cdot \theta_i \cdot \theta_H^4
\]  

(5)

The values \( k_i \) have been determined for the benzene, toluene, and p-xylene hydrogenation. To estimate the reaction rate constants the adsorption coefficients, \( K_{ads,i} \), of the aromatics have to be known. On base of the literature no reliable estimation could be performed about the difference in adsorption of the substituted aromatics at the applied conditions. It is assumed that the adsorption coefficient of toluene and of p-xylene is equal to the adsorption coefficient of benzene. The results for \( k_i \) are listed in Table 2. The \( k_i \) values decline in the order benzene > toluene > p-xylene. If the adsorption strengths of benzene, toluene, and p-xylene are indeed equal to each other, this result is in accordance with some reported literature [18,19]. When the aromatic ring is more substituted the hydrogenation of the aromatic ring is more prohibited. The aromatic character of the toluene and p-xylene ring is stabilized by the methyl groups.

In the competitive hydrogenation of benzene and p-xylene the ratio of the conversion rates is much higher than the ratio of the individual rate constants, \( k_{benzene}/k_{p-xylene} \). This effect is also seen in the competitive hydrogenation of benzene and toluene, which was carried out with ruthenium catalyst A and in the presence of an aqueous zinc sulfate solution. These effects can be explained by the difference in solubility. The aromatics are present in the water phase and, therefore,
their solubilities have to be taken into account. The solubilities of the pure components, $K'_{\text{sol},i}$, in pure water have been calculated using the method of Tsonopoulos [27] and the solubility data of McAuliffe [28] and listed in Table 2. Using the values of $k_i$ in Table 2 and the solubilities the relative hydrogenation rates of the aromatics in a competitive hydrogenation experiment could be estimated. The calculated ratios of $k_i K'_{\text{sol},i} / k_j K'_{\text{sol},j}$ for benzene/toluene and benzene/p-xylene are listed in Table 3. The conclusion can be drawn that the estimated ratios approximate the experimental ratios very well. So, the assumption that the adsorption constants are of similar order does not lead to illogical results.

In the discussion no attention has been given to the effect of salt addition on the solubilities of the aromatics. The function of zinc or iron sulfate addition is changing the catalyst particles from hydrophobic to more hydrophilic. The consequence of salt addition might be, however, the introduction of a "salting-in" or "salting-out" effect as described by Xie et al. [29] and Bradley et al. [30]. The solubilities of the aromatics in water will be influenced by the addition of salt; the concentration of the aromatic can be higher ("salting-in effect") or lower ("salting-out effect"). From [29] it can be concluded that sulfates show a large salting-out effect as compared with the chlorides and nitrates.

Table 2: Calculated values for the parameters $k_i$ and solubility $K'_{\text{sol},i}$ of the components in water at 423 K.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$k_i$ (mol/s)</th>
<th>$K'_{\text{sol},i}$ (mol/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>$10 \cdot 10^9$</td>
<td>111</td>
</tr>
<tr>
<td>Toluene</td>
<td>$3.5 \cdot 10^7$</td>
<td>27</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>$2.4 \cdot 10^7$</td>
<td>8</td>
</tr>
</tbody>
</table>

Table 3: Calculated and experimental values for the relative hydrogenation rates in the competitive hydrogenation of benzene/toluene and benzene/xylene. The benzene/toluene experiment is carried out with ruthenium catalyst A and zinc sulfate; the benzene/p-xylene experiment with ruthenium catalyst B and iron sulfate.

<table>
<thead>
<tr>
<th>Mixture i/j</th>
<th>$k_i K'<em>{\text{sol},i} / k_j K'</em>{\text{sol},j}$ calculated</th>
<th>$r_{\text{H}<em>2,i} C_j / r</em>{\text{H}_2,i} C_i$ experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene/Toluene</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>Benzene/p-Xylene</td>
<td>58</td>
<td>42</td>
</tr>
</tbody>
</table>

The partial hydrogenation of benzene, toluene, and p-xylene 95
Chapter 5

Bradley showed that silver cations cause a salting-in effect. Perhaps, these cations bind to the π-face of the aromatic compound through a rather strong, non-covalent strength up to 160 kJ/mol, termed the cation-π interaction, as recently published by Dougherty [31] and as depicted in Figure 12. The cations will be strongly hydrated. Bradley [30] reports that for an aqueous silver nitrate solution that the change in benzene solubility corresponds to a change in the heat of complex formation of 34 kJ/mol at room temperature and a total pressure of 0.1 MPa; for toluene this change was 23 kJ/mol. This difference in complex formation enthalpy means that benzene compared to pure water will dissolve even more preferentially in the salt-containing water phase during the competitive hydrogenation of benzene and toluene and as a consequence benzene can be hydrogenated preferentially.

Also, the rate constants should be handled with care as those are strongly influenced by the temperature. When heat transfer limitation influences the catalyst temperature, the fitted constants will differ from the real ones. Furthermore, when external mass-transfer controls the reaction rate, also pore diffusion limitation will occur. Thereby, the effectiveness of the catalyst is unknown and the fitted rate constants are too low. It can be assumed that the effectivity will be changed when other aromatics are used.

CONCLUSIONS

The results of the toluene and p-xylene hydrogenation experiments are in qualitative accordance with those of the benzene hydrogenation. Hence it may be concluded that the reaction mechanism, which explains the high selectivities to cyclohexene in the case of benzene hydrogenation, is also applicable to the hydrogenation of other aromatics. The conversion rates of the aromatics decrease in the order benzene > toluene > p-xylene.
In the hydrogenation of substituted aromatics higher yields to the partially hydrogenated products are found. The adsorption strength of these products is less strong and the solubility is lower than of cyclohexene. The double bond at the side of a methyl group is stabilized and, therefore, the rate of further hydrogenation is lower than that of cyclohexene.

The hydrogenation reaction rate is determined by diffusion limitation and not by the kinetics of the chemical reaction. Competitive hydrogenation experiments showed that the solubility of the substrates can also influence the conversion rate. Further investigations on the influence of reaction parameters on the solubility and adsorption constants are required.

Upon zinc salt addition the selectivities towards cycloalkenes increase, whereas the activity of the catalyst is diminished. In the hydrogenation of toluene the selectivities towards the various methylcyclohexenes is influenced by the salt coverage. The higher the amount of salt, the higher is the selectivity to 3- and 4-methyl-1-cyclohexene. The same effect is noticed for an increase in the temperature. At higher hydrogen pressures the selectivity to the partial hydrogenated products increases.

**LIST OF SYMBOLS**

\[
\begin{align*}
    k_i & = \text{intrinsic rate constant of component } i & \text{(mol/s)} \\
    x_i & = \text{molar fraction of component } i \text{ in the water phase} & (-) \\
    r_i & = \text{reaction rate of component } i & \text{(mol/s)} \\
    p & = \text{pressure} & \text{(MPa)} \\
    C_i & = \text{molar fraction of component } i \text{ in the organic phase} & (-) \\
    K_{ads,i} & = \text{adsorption coefficient of component } i & (-) \\
    K_{sol,i} & = \text{solubility coefficient of component } i & (-) \\
    S_i & = \text{selectivity to product } i & (%) \\
    Y_i & = \text{yield to product } i & (%) \\
    \theta_i & = \text{coverage of component } i \text{ on the catalyst surface} & (-) \\
    \xi & = \text{conversion} & (-) \\
    i & = \text{component } i \\
    j & = \text{component } j \text{ not similar to } i
\end{align*}
\]
REFERENCES

The partial hydrogenation of benzene over supported ruthenium catalysts

ABSTRACT

Supported ruthenium catalysts have been used in the partial hydrogenation of benzene. The hydrogenation reaction was performed in a four-phase system at a temperature of 423 K and a total pressure of 5.0 MPa. The best results were obtained with macroporous supports, like α-Al₂O₃ and La₂O₃. The performance of the supported ruthenium catalysts was in some cases improved by adding zinc or cobalt sulfate as a modifier.

TPR showed that the zinc cations, which are adsorbed on the catalyst surface, were not reduced even at temperatures up to 1100 K and, therefore, the cations will not be reduced during the hydrogenation reaction at 423 K.

Alcohols and amines showed to be effective as a modifier in the partial hydrogenation of benzene. An initial cyclohexene selectivity of 65% and a maximum yield of 15% could be achieved with ethanolamine as a modifier; without a modifier the yield to cyclohexene was only 2%.
Chapter 6

INTRODUCTION

In the partial hydrogenation of benzene high initial cyclohexene selectivities (up to 80%) and yields (up to 60%) are achieved with non-supported ruthenium catalysts [1]. In order to obtain a high cyclohexene yield an aqueous salt solution has to be added. Not only the addition of water to the reaction system is essential for a high selectivity; also the addition and the kind of a salt. The high selectivities can be explained as follows. The cations of the salt adsorb on the surface of the ruthenium catalyst and make the catalyst hydrophilic (see Figure 1A). A water layer is formed around the catalyst particles by which the re-adsorption of the desorbed cyclohexene intermediate is suppressed; a higher selectivity to cyclohexene can be achieved. Not all active ruthenium sites are occupied by the cations; otherwise, the activity of the catalyst would be zero. There the cations are strongly hydrated, it is likely that the stagnant water layer is spread out over the total surface of the catalyst particles.

A major drawback of the use of an aqueous salt solution, especially when the process has to be scaled up to commercial production, are the technical complications arising during separation of reactants and products, and corrosion from the reactor. Corrosion from the reactor is a major problem and as a consequence the delicate salt adsorption/desorption equilibria on the catalyst will be disturbed resulting in a change in catalyst performances. Details of the corrosion has been described in Chapter 2. Therefore, the synthesis of a catalyst which is intrinsically hydrophilic would be of great interest. In principle, the application of a hydrophilic support might be attractive. A hydrophilic support is easily hydrated and the water shell formed will possibly also wet the supported ruthenium particles (see Figure 1B).

In recent literature it is claimed that applying ruthenium on a hydrophilic support will indeed lead to cyclohexene selectivity. Richard et al. [2] developed a Ru-Co/SiO$_2$/La$_2$O$_3$/LaONO$_3$ catalyst which showed a maximum cyclohexene yield of 40%. It is claimed also that after pre-adsorption of cobalt sulfate on the catalyst and washing with distilled water, the performance of the catalyst in a benzene/water emulsion without further additives is comparative with the performance of the

\[ \text{non-supported ruthenium} \]

\[ \text{Catalyst support} \]

\hspace{1cm}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Schematic representation of A) the formation of a water layer due to the addition of an aqueous salt solution, B) the formation of a water layer due to the use of a hydrophilic support. \textit{W = water, \textit{M}^{n+} = cation of salt, \textit{Ru} = ruthenium.} }
\end{figure}

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catalyst in a benzene/water emulsion with additives. Niwa et al. prepared a supported ruthenium catalyst in different alcohols by chemical mixing of two catalyst precursors, ruthenium trichloride and tetraetoxyisilane. After separation, drying, and reduction of the Ru-SiO$_2$ catalyst yields up to 30% were reported. The strong interaction between the ruthenium and the support increases the cyclohexene yield [3,4].

The use of supported ruthenium catalysts in the partial hydrogenation of benzene is very promising and, therefore, a study of this topic has been carried out. Different types of supports have been used for the preparation of supported ruthenium catalysts, viz.: silica, zeolite NaY, α-Al$_2$O$_3$ (21 and 30 m$^2$/g), La$_2$O$_3$, and zeolite ZSM-5. The supported ruthenium catalysts were prepared by ion exchange or dry impregnation and tested with and without the addition of zinc sulfate. On the basis of gas-phase hydrogenation studies of selective benzene hydrogenation, where organic modifiers showed to have a promoting effect on the cyclohexene yield, also organic modifiers have been examined [5].

**EXPERIMENTAL**

**Chemicals**

Benzene is obtained from Fluka and Janssen Chimica; the benzene was thiophene free and reagent grade (purity >99.5%). Ruthenium trichloride, spec. pure, 42 wt% Ru, and hexaammineruthenium trichloride, 32 wt% Ru, were supplied by Johnson Matthey. Ruthenium dioxide was obtained from Drijfhout B.V. (purity 99.5%). Sodium hydroxide and iron sulfate, both pro analyse, were obtained from J.T. Baker. Zinc sulfate, cobalt sulfate and nickel sulfate, all pro analyse, were obtained from Merck. Hydrogen (purity >99.95%) and nitrogen (purity >99.995%) were obtained from Air Products. For catalyst preparation and hydrogenation experiments distilled water is used.

SiO$_2$ was obtained from Aldrich Chemicals, zeolite NaY and γ-Al$_2$O$_3$ from Akzo-Nobel, La$_2$O$_3$ from Merck, α-Al$_2$O$_3$ from Norton and ZSM-5 was prepared in the laboratory of Organic Chemistry and Catalysis from Delft University of Technology.

Ethanol and 2-propanol were obtained from Baker. 2-Butanol, 1-amino propane, 1-aminobutane, and ethanolamine, all reagent grade, were obtained from Merck.

**Catalyst preparation**

For the preparation of a Ru/SiO$_2$ catalyst the method of Weiqing and Gonzales has been applied [6]. To remove traces of alkali metal ions, 10 g of silica was washed with
an aqueous 0.144 N HNO₃ solution. After washing with distilled water the silica particles were dried at 353 K. A silica slurry was prepared by adding 500 ml of distilled water to the powder of the acid-treated silica under continuous stirring. The pH of the solution, containing the silica, was increased to 9.0 by adding an aqueous solution of NH₄OH. Next, 1.5 g Ru(NH₃)₆Cl₃ was added instantaneously to the slurry. The pH was readjusted to 9.0 and the solution was stirred for 12 hours. The resulting slurry was filtered and washed with distilled water. After drying in air at 333 K the catalyst was coloured brownish, but turned slowly to black. The catalyst was activated by reduction at 673 K for 3 hours in a gas stream of hydrogen and nitrogen (molar ratio H₂/N₂ = 3:1).

Ruthenium supported on zeolite NaY was prepared following the method introduced by Blackmond [7]. A slurry of 10 g zeolite NaY and 500 ml distilled water was prepared. 1.5 g of Ru(NH₃)₆Cl₃ was added to the slurry and mixing was continued for 12 hours. After filtration and washing with distilled water, the catalyst was dried in a vacuum oven at 333 K. The catalyst was coloured purple. Next, the catalyst was activated similarly to the activation of the Ru/SiO₂ catalyst. Analogously to the preparation of Ru/NaY, a catalyst was prepared with ZSM-5 as a support.

Also ruthenium on lanthanum oxide has been prepared. After washing the lanthanum oxide support with distilled water and drying, the catalyst particles were impregnated to incipient wetness with an aqueous solution of RuCl₃, followed by drying in a vacuum oven at 333 K. Also the same activation method as described above for the Ru/SiO₂ catalyst has been used.

Ru on α-alumina has been prepared by dry impregnation. Two types of α-Al₂O₃ have been used. The first type had a BET-surface area of 21 m²/g, and the second a BET-surface area of 31 m²/g. The α-Al₂O₃ spheres were crushed and sieved and the fraction between 38 and 63 mm was used for catalyst preparation. After washing with distilled water and drying at 353 K for 16 hours ruthenium chloride was deposited by impregnation to incipient wetness. After drying in a vacuum oven the catalyst was activated as described above. Different metal loadings could be obtained by repeated impregnation.

Ru on γ-Al₂O₃ has been prepared by dry impregnation analogously to the Ru/α-Al₂O₃ catalyst.

**Catalyst characterization**

To determine the ruthenium loading of the catalysts prepared by NaY, ZSM-5, and silica, 10 mg of the catalyst was dissolved in a mixture of hydrofluoric acid and sulfuric acid. The concentration was determined by atomic adsorption spectrometry.
(AAS). The ruthenium loading of the catalysts supported by La$_2$O$_3$ and Al$_2$O$_3$, which have been prepared by dry impregnation, was calculated from the ruthenium chloride concentration of the impregnation solution and the volume added to the catalyst.

The BET-surface area, $S_{\text{BET}}$, and the pore-volume distribution of the catalysts were calculated from the N$_2$-adsorption isotherm at 78 K, taking for the cross-sectional area of a nitrogen molecule 0.162 nm$^2$. The samples were pre-dried in vacuum at a temperature of 373 K and the adsorption measurements were carried out on a Digisorb or an Autosorb 6B apparatus from Micromeretics.

Temperature Programmed Reduction (TPR) was performed according to the method of Arnoldy et al. [8]. The measurements were carried out with 60-80 mg sample in a 2:1 H$_2$/Ar mixture at a total flow rate of 0.42 ml/s. The samples were mixed with SiC, to promote the heat transfer and to prevent a pressure drop over the reactor. The samples were heated from 300 K to 1000 K at a heating rate 0.167 K/s. Water produced during reduction was removed by means of a membrane. TPR measurements have been carried out for Ru/γ-Al$_2$O$_3$, Ru/γ-Al$_2$O$_3$ impregnated with zinc sulfate, Ru/γ-Al$_2$O$_3$ impregnated with zinc chloride, and the bare γ-Al$_2$O$_3$ support impregnated with zinc sulfate.

**Catalyst testing**

A quantity of the catalyst, benzene, water and a certain amount of additive were introduced into a stainless-steel autoclave, equipped with baffle bars. After purging with hydrogen, the pressure was elevated to 3.5 MPa by the addition of hydrogen. When the desired reaction temperature (423 K) was reached, the total pressure was adjusted to 5.0 MPa by addition of hydrogen. The benzene hydrogenation started as soon as stirring commenced.

Also experiments have been carried out with addition of organic modifiers. The 5 w% Ru/α-Al$_2$O$_3$ ($S_{\text{BET}}$=21 m$^2$/g) catalyst has been used, and the experiments were carried out in a TiN-coated autoclave (see Chapter 2) at 423 K and 5.0 MPa total pressure.

**RESULTS AND DISCUSSION**

**Bare supported ruthenium catalysts**

The catalysts were used in the hydrogenation of benzene and the results are shown in Table 1. For Ru/γ-Al$_2$O$_3$ no reliable data could be obtained. The reason is that the catalyst was totally crushed to fine powder during the reaction by which the

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sampling tube was blocked. Apparently, the vigorous mixing conditions were too severe for the mechanically weak $\gamma$-Al$_2$O$_3$ carrier. Therefore, no further hydrogenation experiments have been carried out with this type of catalyst. Obviously, not only the hydrophilicity of the support is important, but also the strength of the particles.

For all other catalysts the degree of benzene conversion, $\xi$, after 1 hour of reaction and the cyclohexene selectivity at $\xi=0.1$ is given in Table 1. As can be seen from the table all catalysts show activity in the benzene hydrogenation. Due to the variation of the ruthenium content of the catalysts, the activities should be compared taking into account the concentration of the active phase. The conclusion can be drawn that, when the ruthenium content was raised, the activity of the catalyst increased.

The ZSM-5 supported ruthenium catalyst is hydrophobic and, as to be expected, a very low cyclohexene selectivity is observed. The silica- and NaY-supported catalysts are more hydrophilic. After reaction, it was observed that the catalysts were entirely in the water phase. Nevertheless, the selectivities of the silica and NaY supported ruthenium catalysts were very small and a maximum cyclohexene yield of only 2% has been reached. When La$_2$O$_3$ and $\alpha$-Al$_2$O$_3$ are used as a support, the selectivities are much higher; selectivities up to 45% are observed. Also these catalysts were hydrophilic; but they show a higher cyclohexene selectivity than Ru/silica and Ru/NaY. This can be explained from the pore structure of the supports. Silica and NaY are microporous materials, La$_2$O$_3$ and $\alpha$-Al$_2$O$_3$ are macroporous. When cyclohexene is formed in the micropores, diffusion of the cyclohexene molecules to the bulk fluid is strongly retarded and further hydrogenation to cyclohexane or dehydrogenation to benzene is favoured. This reasoning applies generally to sequential reaction schemes of the type $A \rightarrow B \rightarrow C$, where $B$ is the desired product. For this reason, hydrophilic macroporous catalyst supports are to be preferred in the partial hydrogenation of benzene.

**Supported catalysts with inorganic additives**

To enlarge the cyclohexene selectivities, zinc sulfate has been added as a modifier. In all cases the benzene conversion after one hour of reaction was lowered, as compared with the salt free runs; the ruthenium sites are now partly covered by zinc cations. For the microporous supports, silica, ZSM-5, and NaY, the cyclohexene selectivities were approximately the same after 10% conversion, but the maximum cyclohexene yield decreased.

In some experiments macroporous supports, like La$_2$O$_3$ and $\alpha$-Al$_2$O$_3$, showed higher selectivities and yields. When more zinc sulfate was added the reaction rate gradually decreased, whereas the selectivity tended to increase. An optimum in the
cyclohexene yield was found for the Ru/α-Al₂O₃ catalysts, whereby the alumina support with the lowest BET-surface area showed higher cyclohexene selectivities at lower zinc sulfate concentrations. The maximum yield showed to be depending on the activity and on the selectivity of the catalyst. The amount of salt, adsorbed on the active ruthenium sites, lowers the total surface area of active ruthenium, so that the activity of the catalyst decreases.

**Table 1: Results of the hydrogenation of benzene over different supported ruthenium catalysts.** Y<sub>che,max</sub> = maximum cyclohexene yield; ξ = benzene conversion, S<sub>che</sub> = cyclohexene selectivity. Conditions: temperature 423 K, total pressure 5.0 MPa, 1500 rpm, 0.5 g catalyst, 75 ml H₂O, 200 ml benzene and zinc sulfate.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Amount of zinc sulfate (g)</th>
<th>S&lt;sub&gt;che&lt;/sub&gt; at ξ=0.1 (%)</th>
<th>Y&lt;sub&gt;che,max&lt;/sub&gt; (%)</th>
<th>ξ t=60 min (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru/Silica (250 m²/g)</td>
<td>0</td>
<td>7.3</td>
<td>2.0</td>
<td>0.50</td>
</tr>
<tr>
<td>0.56 w% Ru)</td>
<td>0.1</td>
<td>7.4</td>
<td>1.0</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>6.0</td>
<td>0.8</td>
<td>0.12</td>
</tr>
<tr>
<td>Ru/NaY (4.4 w% Ru)</td>
<td>0</td>
<td>13</td>
<td>2.3</td>
<td>0.62</td>
</tr>
<tr>
<td>Ru/ZSM-5 (0.2 w% Ru)</td>
<td>0</td>
<td>6.8</td>
<td>1.7</td>
<td>0.14</td>
</tr>
<tr>
<td>12 m²/g)</td>
<td>0.2</td>
<td>6.0</td>
<td>0.5</td>
<td>0.083</td>
</tr>
<tr>
<td>1 w% Ru)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru/L₂O₃ (12 m²/g)</td>
<td>0</td>
<td>23</td>
<td>3.1</td>
<td>0.11</td>
</tr>
<tr>
<td>1 w% Ru)</td>
<td>0.2</td>
<td>31</td>
<td>7.8</td>
<td>0.027</td>
</tr>
<tr>
<td>Ru/α-Al₂O₃ (31 m²/g)</td>
<td>0</td>
<td>41</td>
<td>9.4</td>
<td>0.15</td>
</tr>
<tr>
<td>1 w% Ru)</td>
<td>0.5</td>
<td>40</td>
<td>12</td>
<td>0.032</td>
</tr>
<tr>
<td>Ru/α-Al₂O₃ (31 m²/g)</td>
<td>0</td>
<td>35</td>
<td>9.6</td>
<td>0.95</td>
</tr>
<tr>
<td>5 w% Ru)</td>
<td>0.5</td>
<td>37</td>
<td>11</td>
<td>0.54</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>39</td>
<td>14</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td>46</td>
<td>12</td>
<td>0.34</td>
</tr>
<tr>
<td>Ru/α-Al₂O₃ (31 m²/g)</td>
<td>0</td>
<td>43</td>
<td>16</td>
<td>0.95</td>
</tr>
<tr>
<td>5 w% Ru)</td>
<td>0.5</td>
<td>55</td>
<td>20</td>
<td>0.48</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>39</td>
<td>17</td>
<td>0.34</td>
</tr>
</tbody>
</table>

_The partial hydrogenation of benzene over supported ruthenium catalysts_
In Table 2 the results of the benzene hydrogenation experiments are listed for a Ru/α-Al₂O₃ catalyst (S BET=21 m²/g) in the presence of various salts, viz. cobalt, zinc, iron, and nickel sulfate. The reaction rate decreased in the same order. So, the conclusion can be drawn that the salts are adsorbed more strongly in the order cobalt<zinc<iron<nickel. Nickel sulfate adsorbs very strongly and for this reason a lower amount of nickel sulfate was added but, nevertheless, in this system the lowest reaction rate was observed. Larger amounts resulted in total poisoning of the catalyst. Iron sulfate adsorbs also strongly, and consequently a low yield was observed. The best results were obtained on adding zinc sulfate or cobalt sulfate; in both cases a maximum cyclohexene yield of 20% has been obtained.

The question remains whether the cations are reduced during the hydrogenation reaction and loose their hydrophilic character. For Zn²⁺ this was investigated by TPR. The TPR profiles of Ru/γ-Al₂O₃ without promoter, Ru/γ-Al₂O₃ impregnated with zinc sulfate, Ru/γ-Al₂O₃ impregnated with zinc chloride, and the bare support, γ-Al₂O₃, and the bare support impregnated with zinc sulfate are shown in Figure 1.

The TPR-profile of the bare support showed no peaks (Figure 1a). Ru/γ-Al₂O₃ showed one small peak at 465 K (Figure 1c), which is due to the reduction of ruthenium oxide formed by exposure to air after preparation of the catalyst [9]. The bare support impregnated with ZnSO₄ showed one peak with a maximum at 820 K (Figure 1b). It seems likely that ZnSO₄ is transformed to ZnO, but perhaps the cation Zn²⁺ is reduced. However, the catalyst which was impregnated with zinc chloride showed only one small peak at 510 K (Figure 1e), and the catalyst which was impregnated with zinc sulfate gave two peaks, at 470 K and 760 K (Figure 1d). The

Table 2: The use of various salts in the hydrogenation of benzene over a 5 w% Ru/α-Al₂O₃ (S BET = 21 m²/g). Conditions: temperature 423 K, total pressure 5.0 MPa, 1500 rpm, 0.5 g catalyst, 75 ml H₂O, 200 ml benzene.

<table>
<thead>
<tr>
<th>Salt</th>
<th>Amount added</th>
<th>S_{che} (z=0.1)</th>
<th>Y_{che,max}</th>
<th>ξ (t=1 h)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[g/mmol]</td>
<td>[%]</td>
<td>[%]</td>
<td>[-]</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>43</td>
<td>16</td>
<td>0.96</td>
</tr>
<tr>
<td>CoSO₄</td>
<td>0.5/1.9</td>
<td>43</td>
<td>21</td>
<td>0.81</td>
</tr>
<tr>
<td>ZnSO₄</td>
<td>0.5/1.7</td>
<td>55</td>
<td>20</td>
<td>0.48</td>
</tr>
<tr>
<td>FeSO₄</td>
<td>0.5/1.8</td>
<td>35</td>
<td>9.3</td>
<td>0.17</td>
</tr>
<tr>
<td>NiSO₄</td>
<td>0.2/0.7</td>
<td>18</td>
<td>8.7</td>
<td>0.095</td>
</tr>
</tbody>
</table>
small peaks, at 510 K and 470 K, can be assigned to the reduction of ruthenium oxide and the peak at 760 K to the reduction of sulfate. Therefore, the conclusion can be drawn that zinc is not reduced during the TPR measurements, even not at temperatures as high as 1200 K. The conclusion is that the reduction of sulfate is induced by the presence of ruthenium: the peak maximum shifted from 820 K to 760 K. It is clear that the zinc cations are not reduced to metallic zinc during the benzene hydrogenation carried out at 423 K. This means that the cations keep their hydrophilic character.

**Supported ruthenium catalysts with organic modifiers**

Also, when the hydrogenation reaction is carried out at high temperature and pressure, organic modifiers can be used. In Table 3 the results are listed of the hydrogenation experiments which are carried out over a 5 w% Ru/α-\( \text{Al}_2\text{O}_3 \) catalyst (S\(_{\text{BET}}\)=21 m\(^2\)/g) in the presence of organic modifiers. A selectivity increase is observed in nearly all cases.

When alcohols are used the reaction rate was not changed much; only a slight decrease is observed. Ethanol showed to be the best modifier of the alcohols. Probably, either ethanol adsorbs more strongly than 2-propanol and 2-butanol, or ethanol has a more hydrophilic character and in this way the production of cyclohexene will be favoured.
Table 3: The use of organic modifiers in the hydrogenation of benzene over a 5 w% Ru/α-Al₂O₃ catalyst ($S_{BET}$=21 m²/g). The reaction rate is taken at $\xi$=0.3. Conditions: temperature 423 K, total pressure 5.0 MPa, 1500 rpm, 1.0 g catalyst, 2 ml additive, 150 ml water, 200 ml benzene and an organic modifier. For comparison the results of the benzene hydrogenation without the use of an additive are listed as well.

<table>
<thead>
<tr>
<th>Organic additive</th>
<th>Amount added</th>
<th>Amount added</th>
<th>$S_{che}$ ($\xi$=0.1)</th>
<th>$Y_{che,max}$</th>
<th>$r_{H2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[ml]</td>
<td>[mmol]</td>
<td>[%]</td>
<td>[%]</td>
<td>[mmol/s]</td>
</tr>
<tr>
<td>ethanol</td>
<td>2</td>
<td>35</td>
<td>16</td>
<td>5.5</td>
<td>8.6</td>
</tr>
<tr>
<td>2-propanol</td>
<td>2</td>
<td>26</td>
<td>7.8</td>
<td>2.4</td>
<td>8.3</td>
</tr>
<tr>
<td>2-butanol</td>
<td>2</td>
<td>22</td>
<td>7.0</td>
<td>2.2</td>
<td>8.5</td>
</tr>
<tr>
<td>1-amino propane</td>
<td>2</td>
<td>24</td>
<td>27</td>
<td>6.2</td>
<td>5.1</td>
</tr>
<tr>
<td>1-amino butane</td>
<td>2</td>
<td>20</td>
<td>27</td>
<td>6.0</td>
<td>5.0</td>
</tr>
<tr>
<td>ethanolamine</td>
<td>2</td>
<td>33</td>
<td>-</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>no additive</td>
<td>-</td>
<td>-</td>
<td>6.0</td>
<td>2.0</td>
<td>9.0</td>
</tr>
</tbody>
</table>

Figure 2: Initial reaction rate (left y-axis), initial selectivity and maximum yield (right y-axis) in the partial hydrogenation of benzene as a function of the amount of ethanol amine added. The experiments are carried out with a 5 w% Ru/α-Al₂O₃ catalyst. Experimental conditions: 1.0 g catalyst, 150 ml water, 200 ml benzene, temperature 423 K, total pressure 5.0 MPa.
When amines are used higher selectivities and higher yields are obtained. The amines adsorb more strongly than the alcohols and the reaction rate decreased more in comparison with the corresponding alcohols. No reaction was observed, when 2 ml of ethanolamine was added; obviously, ethanolamine poisoned the catalyst totally. When a lower concentration of ethanolamine was used the catalyst showed to be active. The concentration of ethanolamine has been varied and the results are shown in Figure 2. The reaction rate is a function of the amount of ethanolamine. Selectivities up to 65% and maximum yields up to 14% were obtained. The course of the reaction rate, selectivity and yield in Figure 2 corresponds with the results obtained when iron or zinc sulfate is used [9].

It is remarkable that the selectivities and yields to cyclohexene obtained with the 5 w% Ru/α-Al₂O₃ catalyst (Table 3) are much lower than those reported in Tables 1 and 2. It is clear that the catalyst system is very sensitive and that the reproducibility is a point of concern. The high selectivities and yields reported in Table 1 were obtained in the stainless-steel autoclave and the other results in the TiN-coated autoclave. Probably, modification of the catalyst took place by impurities originating from the stainless steel reactor wall during the start-up of the reaction. This effect has already been discussed in Chapter 2.

The results confirm that hydrophilicity is very important to obtain high selectivities to cyclohexene. Even ruthenium on hydrophilic supports can be used for the partial hydrogenation of benzene. In practical application a supported catalyst without salts is very attractive, but the cyclohexene yields obtained so far are less than in the case of unsupported ruthenium catalysts [1]. Two major groups of supported catalysts can be distinguished: microporous and macroporous ones. Microporous ruthenium catalysts were active in the benzene hydrogenation, but did not show any selectivity to cyclohexene. This observation supports the general accepted hypothesis, that for the microporous supports further hydrogenation to cyclohexane and/or dehydrogenation to benzene is favoured due to slow diffusion of cyclohexene to the bulk organic phase. In agreement with this reasoning, macroporous catalysts showed selectivity to cyclohexene. The selectivities and yields could be increased by the addition of various modifiers. This supports the hypothesis that the function of the additive is not only to make the catalyst hydrophilic, but also to modify the ruthenium sites; the additives are preferentially adsorbed on the sites which will adsorb the cyclohexene molecules most strongly and which will favour further hydrogenation [9].

When this reasoning is correct, a modifier-free, highly selective ruthenium catalyst is not feasible. Nevertheless, further optimization of the supported catalysts has not yet been performed and maybe better results can be obtained. Finally, an interesting
aspect of supported catalysts, not discussed in this chapter, is the easiness of preparation.

CONCLUSIONS

The aim to prepare a catalyst with a hydrophilic support, so that no salt has to be used, and giving rise to high cyclohexene selectivities and yields, led to promising results. The selectivity to cyclohexene is enlarged by using a hydrophilic support even without adding any modifier. Selectivities up to 43% at a benzene conversion of 10% with a maximum yield of 16% are achieved when α-Al₂O₃ with a low surface area is used as a support. However, when an amount of salt was added to the reaction mixture as well, a selectivity of 55% and a maximum yield of 20% was observed. Therefore, it can be concluded that the modifiers not only make the catalyst hydrophilic, but also change the catalytic behaviour of the ruthenium sites. Macroporous supported catalysts showed better selectivities than microporous ones.

Applying TPR it has been shown that the adsorbed zinc cations are not reduced during the partial hydrogenation of benzene and, hence, will keep their hydrophilic character under the applied reaction conditions.

To increase the selectivity to cyclohexene also organic modifiers, like alcohols and amines, can be used. The best results so far have been obtained by using ethanolamine as a modifier.

REFERENCES

9 See Chapter 3 of this thesis.

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The partial hydrogenation of benzene over SiC-based ruthenium catalysts

ABSTRACT

Chemical Vapour Deposition is a powerful method to develop a high surface area SiC support with a tuneable hydrophilic character. This new type of high surface area SiC support has been used in the liquid-phase benzene hydrogenation. The cyclohexene selectivity appeared to depend on the preparation method of the SiC-support.
INTRODUCTION

Gas-phase methods, e.g. Chemical Vapour Deposition (CVD) have been reported in the literature as a promising technique for catalyst design [1-3]. Firstly, CVD can be used to deposit metals on catalyst supports, which opens the area of loading structured catalytic packings with metals. Secondly, CVD is a powerful technique for the synthesis of completely new supports. And thirdly, surface modification of catalysts (supports) can easily be carried out, which means that the adsorption strengths of reactants and solvents on the catalyst surface can be influenced.

An example of the last two techniques is the use of CVD for the preparation of a new catalyst support and comprises the catalytic conversion of activated carbon into high surface area SiC and thereby having the opportunity to change the hydrophobic/hydrophilic character of the support. The starting point is a porous preformed solid, activated carbon, which has been loaded with a suitable nickel precursor. Subsequently, a mixture of hydrogen and silicon tetrachloride is admitted. Hydrogen gasifies the carbon to methane (1) and simultaneously the formed methane reacts with silicon tetrachloride to the desired porous SiC (2) with the same starting morphology [4]. From thermodynamic data it can be concluded that at the applied reaction conditions silicon dichloride is the active species in the conversion process [5]. The carbon has two functions, it is a reactant and it acts as a template for the deposition of the material.

\[
C (s) + 2 H_2 (g) \rightarrow CH_4 (g) \quad (1)
\]

\[
SiCl_4 (g) + CH_4 (g) \rightarrow SiC (s) + 4 HCl (g) \quad (2)
\]

The application of this high surface area SiC, BET-surface areas varying between 25 and 70 m²/g, is limited to high temperature methane reforming in the presence of carbon dioxide [6]. In this chapter the high surface area silicon carbide has been tested in the selective hydrogenation of benzene to cyclohexene in order to investigate if this new material has specific surface properties, which can strongly influence the selectivity to the desired cyclohexene intermediate.
EXPERIMENTAL

Materials

Nickel nitrate and benzene were obtained from Janssen Chimica; the benzene was thiophene free and reagent grade (purity >99.5%). Ruthenium trichloride, spec. pure, 42.0-42.3 wt% Ru was supplied by Johnson Matthey. Zinc sulfate, pro analyse, was obtained from Merck. Hydrogen, purity >99.95%, was obtained from Air Products. For catalyst preparation active carbon from Norit (granulated Elorit, BET-surface area 655 m²/g) was used. In the preparation and hydrogenation experiments distilled water was used.

Preparation of the catalyst

Three types of catalysts have been prepared with different surface properties.
Ruthenium on active carbon, Ru/C: After sieving (mesh 300-425 mm) the activated carbon (granulated Elorit) was washed with distilled water, hydrochloric acid solution, distilled water, sodium hydroxide solution and again with distilled water. Subsequently, the particles were impregnated with an aqueous ruthenium trichloride solution to arrive at 5 w% ruthenium loading. After drying at 353 K in air the particles were reduced in a 20 vol% H₂ in N₂ gas stream at 523 K for 1 hour.
Ruthenium on silicon carbide, Ru/SiC-C: A high surface area silicon carbide support is prepared in the way developed by Moene et al. [4]. The activated carbon granulates were impregnated with nickel nitrate. After drying at 353 K the particles have been introduced in a fluidized bed reactor in an argon flow at 1380 K. A schematic picture of the CVD equipment is shown in Figure 1. Subsequently, the argon flow rate was lowered and hydrogen and silicon tetrachloride were admitted. After synthesis, around 30% of the carbon has been converted into silicon carbide, deposited on the surface of the activated carbon granulates. The obtained granulates, which still contains nickel showed no benzene hydrogenation activity under the conditions applied. The SiC/C was loaded with ruthenium and pretreated in the same way as the Ru/C-catalyst.

Figure 1: Scheme of the CVD apparatus.

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Ruthenium on calcined silicon carbide, Ru/SiC: The SiC support was prepared in the same way as the SiC-C support, but the residual carbon was removed by oxidation in dry air for 16 h at 1023 K. The calcined SiC was loaded with ruthenium and pretreated as described above.

Testing of the catalyst

Into a TiN-coated autoclave equipped with baffle bars, 0.5 g of the catalyst, 200 ml benzene, and 150 ml of distilled water were introduced. After purging with nitrogen and hydrogen, the benzene hydrogenation reaction was carried out at a temperature of 423 K and a total pressure of 5.0 MPa. The hydrogenation reaction was monitored by taking small samples of the reaction mixture at periodic intervals followed by chromatographic analysis.

RESULTS AND DISCUSSION

After hydrogenation the particles of the Ru/C and the Ru/SiC-C catalysts were found in the organic layer, whereas the Ru/SiC catalyst was situated in the aqueous layer. For the Ru/SiC particles some attrition was observed.

Table 1: Results of the hydrogenation of benzene with 5 w% Ru/C, 5 w% Ru/SiC-C, and 5 w% Ru/SiC. Listed are the amount of zinc sulfate used, the benzene conversion after a reaction time of 1 hour, the cyclohexene selectivity at ξ_{benzene} = 0.1 and the observed maximum cyclohexene yield during the experiment. Conditions: 423 K, 5.0 MPa total pressure, 1500 rpm, 0.5 g catalyst, 150 ml H₂O, 200 ml benzene, and hydrogen.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Zinc sulfate</th>
<th>ξ_{benzene t=1 h}</th>
<th>S_{C\text{CHE}}</th>
<th>Y_{C\text{HE,max}}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[g]</td>
<td>[-]</td>
<td>[%]</td>
<td>[%]</td>
</tr>
<tr>
<td>Ru/C</td>
<td>0.0</td>
<td>0.98</td>
<td>2</td>
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<td></td>
<td>3.5</td>
<td>0.76</td>
<td>1</td>
<td>0.1</td>
</tr>
<tr>
<td>Ru/SiC-C</td>
<td>0.0</td>
<td>0.49</td>
<td>2.4</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>0.42</td>
<td>1.8</td>
<td>0.2</td>
</tr>
<tr>
<td>Ru/SiC</td>
<td>0.0</td>
<td>0.7</td>
<td>29</td>
<td>5.9</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>0.4</td>
<td>33</td>
<td>5.3</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>0.3</td>
<td>26</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td>0.003</td>
<td>24</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

n.d.=not detected

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The hydrogenation results for the three different ruthenium catalyst are listed in Table 1. The activity of the Ru/C catalyst (1.2 mmol/g\text{cat}/s) is high and the initial selectivity to cyclohexene is poor, only 2%, resulting in a maximum cyclohexene yield of 0.2%. The Ru/SiC-C catalyst behaves similar. The Ru/SiC catalyst showed a relatively low activity of 0.089 mmol/g\text{cat}/s, but a remarkably high cyclohexene selectivity was observed, up to 33%, and a maximum cyclohexene yield of 6%. After reaction, the SiC support was found to be in the aqueous phase. The high selectivity to cyclohexene in this case can be explained as follows. Due to the poor solubility in water the diffusion rate of cyclohexene to the catalyst is low and consecutive hydrogenation to cyclohexane is diminished. The formed cyclohexene will therefore accumulate in the organic phase and will not hydrogenate further immediately. This explanation is in agreement with the postulated mechanism for the selective hydrogenation of benzene as described by Struijk et al. [7]. The Ru/C and Ru/SiC-C catalysts are hydrophobic. Apparently, no retardation of the substrates towards the catalyst is introduced and the desorption rate of adsorbed cyclohexene is not altered significantly. For Ru/SiC-C the hydrophobic character of the remaining carbon overrules the hydrophilic character of the SiC. The affinity of benzene towards these graphitic basal planes is so large that the SiC/C support mimics the activated carbon adsorption behaviour. By calcination at temperatures above 1000 K the part of the activated carbon which was not converted during the Chemical Vapour Deposition, is oxidized. At the same time SiC, with probably some silanol groups at its surface, will give the catalyst support a more hydrophilic character.

The change of the hydrophilic character of the catalyst has been reported for non-supported ruthenium catalysts [7,8] and for supported catalysts [9] by the addition of among others zinc sulfate. Therefore, also zinc sulfate was added in some hydrogenation experiments. Addition of zinc sulfate to the Ru/SiC catalyst system only results in a decrease of the activity with no further enhancement in the cyclohexene selectivity. In the cases of Ru/C and Ru/SiC-C the effect of the zinc sulfate on the cyclohexene selectivity was also negligible.

CONCLUSIONS

The described results show that CVD offers new opportunities in the manufacture of high surface area SiC supports. Preparation procedures can result in a tailor-made support with an hydrophilic or hydrophobic character, which can result in a better selectivity to the desired product without addition of modifiers.

The partial hydrogenation of benzene over SiC-based ruthenium catalysts
Chapter 7

Application of the new type of high surface area SiC supports in liquid-phase reactions is feasible and allows utilization in liquid-phase operations at demanding pH conditions.

REFERENCES

Modelling of the partial hydrogenation of aromatics

ABSTRACT

A model for the partial hydrogenation of aromatics is presented. Experiments are described, which were carried out in a four-phase system at temperatures ranging from 403 K to 443 K and at total pressures up to 7.0 MPa. Calculations and integrated modelling have been carried out. With the proposed model the results of the partial hydrogenation could be described successfully.

The influence of several aspects on the performance of the hydrogenation reaction are discussed; the water layer which is formed around the catalyst particles, the temperature, the hydrogen pressure and the adsorption behaviour of the substrates on the modified catalyst. The reactions are controlled by diffusion of hydrogen. Not the gas/liquid mass-transfer was rate limiting, but the liquid/solid mass-transfer. The cyclohexene selectivity showed to be very sensitive to small changes in temperature of the reaction system and its adsorption strength. The benzene hydrogenation is a very exothermic reaction and, therefore, temperature gradients between the catalyst particles and the fluids may take place, which will influence the cyclohexene selectivity.
GENERAL INTRODUCTION

Over the past decades a considerable amount of research has been carried out on the hydrogenation of benzene to cyclohexene. Horiuti and Polanyi [1] proposed a mechanism in which adsorbed hydrogen atoms are step-wise added to the adsorbed benzene ring. The partial hydrogenated products, cyclohexadiene and cyclohexene, although postulated to exist on the surface, were not detected by Horiuti and Polanyi. Later on, direct evidence for the correctness the proposed mechanism was given by Anderson [2], who also observed a minor amount of cyclohexene in the gas phase.

The main objective of many research programmes dealing with the selective hydrogenation of benzene is to enlarge the selectivity to cyclohexene. When the hydrogenation reaction is carried out in a multi-phase system containing, besides the organic phase, an aqueous salt solution, see Figure 1a, a high activity and selectivity are claimed. The most important examples are the following ones. Nagahara and Konishi [3] observed a cyclohexene yield of 55% by using a ruthenium catalyst in a finely dispersed benzene/water emulsion at a total pressure up to 9 MPa and a temperature of 423 K. Struijk et al. [4] reported a high yield to cyclohexene in a benzene/water system containing zinc sulfate. These authors concluded that the surface of the catalyst is partly covered by chemisorbed zinc sulfate, which causes the catalyst particles, which are initially hydrophobic, to become more hydrophilic and, hence, they are surrounded by water, as illustrated in Figure 1b. Through the formation of a stagnant water layer around the catalyst a diffusion barrier is initiated [5]. The benzene and hydrogen molecules have to diffuse through the stagnant water layer, see Figure 1c, and after chemisorption on the catalyst surface they can react sequentially to cyclohexadiene, cyclohexene, and cyclohexane, see Figure 1d. The reaction rates of all elementary hydrogenation steps are strongly declined. According to Struijk et al., the very low solubility of cyclohexene in water is the most important factor determining the yield of cyclohexene. Due to the poor solubility in the stagnant water layer the diffusion rate of cyclohexene to the catalyst is low and consecutive hydrogenation to cyclohexane is diminished.

In the description of the kinetics of the benzene hydrogenation, therefore, not only the kinetics of the chemical reaction, but also the mass-transfer processes, should be involved; in other words, diffusional transport of the substrates, benzene and hydrogen, and of the products, cyclohexadiene, cyclohexene, and cyclohexane, have to be taken into account.
Figure 1: Description of the four-phase hydrogenation of benzene at different stages.

Modelling of the partial hydrogenation of aromatics
Struijk et al. give a qualitative description of the chemical reaction and the mass-transfer phenomena, which can play a role in the partial hydrogenation of benzene [5]. Recently, Döbert and Gaube presented a kinetic model for the partial hydrogenation of benzene in a three-phase system [6,7]. They performed a kinetic study carried out in a continuously operated slurry reactor in the absence of an organic liquid phase. The vapour pressure of the organics was kept below the saturation vapour pressure.

It is the objective of the present work to give a quantitative description of the four-phase reaction system, which has been used in this study. In the following section a model will be presented and an attempt is made to quantify the kinetics of each step by using the results of several hydrogenation experiments and literature data. When each step is modelled, calculations and integrated modelling will be carried out based on experiments by varying several parameters, like hydrogen pressure and temperature, to obtain more insight in the optimum conditions for the partial hydrogenation of aromatics.

**MASS TRANSFER AND REACTION RATE EQUATIONS**

Except for the work by Döbert and Gaube [6,7], in processes, in which high cyclohexene yields are claimed, a four-phase system (GLLS) is used: hydrogen as the gas phase, two immiscible liquid phases, an organic and an aqueous phase, and a catalyst as a solid phase. Three-phase catalytic systems have received considerable attention [8,9]. Roberts [9] gives a convenient overview of the relevant steps in a gas/liquid/solid-system (GLS). In this study Roberts' description will be extended to a four-phase system. The four-phase system will be modelled as two three-phase systems, a gas/liquid/solid-system (GLS), in which the hydrogen diffuses through the water phase to the catalyst surface, and a liquid/liquid/solid phase (LLS), in which organic molecules dissolve in the water phase and diffuse to the solid catalyst surface.

In the GLS-system, the hydrogen molecules from the gas phase dissolve into the bulk water phase, and then diffuse to the external surface of the catalyst. In Figure 2 a qualitative representation of the concentration profiles in the GLS-system is given. The concentration of hydrogen in the bulk water phase is constant and drops in the stagnant water layer. When the reaction rate is controlled by diffusion, especially pore diffusion limitation, and so a hydrogen concentration profile in the catalyst particle, are also quite conceivable.
The concentration of hydrogen in the different phases is determined by the transport rates of hydrogen through the gas/liquid interface and the liquid/solid interface. The rate of hydrogen transport from the gas to the bulk water phase, $-J_{H_2}$, is given by:

$$-J_{H_2} = k_{gl} \cdot A_{gl} \cdot (C_{H_2eq,w} - C_{H_2,w})$$  \hspace{1cm} (1)

$J_{H_2}$ = hydrogen transport rate \hspace{1cm} (mol/s)

$k_{gl}$ = mass-transfer coefficient from the gas phase to the water phase \hspace{1cm} (m/s)

$A_{gl}$ = interfacial area between the gas phase and the water phase \hspace{1cm} (m$^2$)

$C_{H_2eq,w}$ = equilibrium concentration of hydrogen in the aqueous solution \hspace{1cm} (mol/m$^3$)

$C_{H_2,w}$ = concentration of hydrogen in the aqueous solution \hspace{1cm} (mol/m$^3$)

The equilibrium hydrogen concentration in water, $C_{H_2,w}$, can be estimated by means of Henry's Law:

$$x_{H_2,w} = \frac{M_w}{\rho_w} \cdot C_{H_2eq,w} = \frac{P_{H_2}}{H_{H_2}}$$  \hspace{1cm} (2)

$x_{H_2,w}$ = molar fraction of hydrogen in the aqueous solution \hspace{1cm} (mol/mol)

$M_w$ = molecular weight of water \hspace{1cm} (g/mol)

$\rho_w$ = density of water \hspace{1cm} (g/m$^3$)

$P_{H_2}$ = partial hydrogen pressure \hspace{1cm} (Pa)

$H_{H_2}$ = Henry's law constant \hspace{1cm} (Pa-mol/mol)

Modelling of the partial hydrogenation of aromatics
Chapter 8

Hydrogen diffuses through a stagnant water layer around the catalyst particles and the diffusion rate through this layer is given by:

$$-\dot{J}_{\text{H}_2} = k_{\text{ls, H}_2} \cdot A_{\text{ls}} \cdot (C_{\text{H}_2,w} - C_{\text{H}_2,s})$$

(3)

- $k_{\text{ls, H}_2}$ = mass-transfer coefficient from the water phase to the catalyst \( \text{(m/s)} \)
- $A_{\text{ls}}$ = interfacial area between water phase and catalyst \( \text{(m}^2) \)
- $C_{\text{H}_2,s}$ = concentration of hydrogen at the surface of the catalyst \( \text{(mol/m}^3) \)

In the steady-state $\dot{J}_{\text{H}_2} = \dot{J}'_{\text{H}_2}$.

For the case of benzene, in the LLS system, diffusional transport of benzene will run analogously to the hydrogen transport mechanism and thus similar equations can be used. The rate of transport of benzene to the water phase is given by:

$$-\dot{J}_{\text{C}_6\text{H}_6} = k_{\text{II}} \cdot A_{\text{II}} \cdot (C_{\text{C}_6\text{H}_6,eq,w} - C_{\text{C}_6\text{H}_6,w})$$

(4)

- $k_{\text{II}}$ = mass-transfer coefficient from the benzene to the water phase \( \text{(m/s)} \)
- $A_{\text{II}}$ = interfacial area between benzene phase and water phase \( \text{(m}^2) \)
- $C_{\text{C}_6\text{H}_6,w}$ = concentration of benzene in an aqueous solution \( \text{(mol/m}^3) \)
- $C_{\text{C}_6\text{H}_6,s}$ = concentration of benzene at the surface of the catalyst \( \text{(mol/m}^3) \)

and from the stagnant water layer to the surface of the catalyst by:

$$-\dot{J}'_{\text{C}_6\text{H}_6} = k_{\text{ls, C}_6\text{H}_6} \cdot A_{\text{ls}} \cdot (C_{\text{C}_6\text{H}_6,w} - C_{\text{C}_6\text{H}_6,s})$$

(5)

In steady state $\dot{J}_{\text{C}_6\text{H}_6} = \dot{J}'_{\text{C}_6\text{H}_6}$.

It was observed that the water phase is the continuous phase, while the benzene phase is the dispersed phase. The hydrogen and benzene molecules will diffuse to the outer surface of the catalyst and are chemisorbed on the ruthenium sites. The chemisorbed benzene and hydrogen will react sequentially to cyclohexadiene, cyclohexene, and cyclohexane.

The postulated reaction model, here formulated according to the Langmuir-Hinshelwood-Hougen-Watson (LHHW) formalism, is based on the mechanism described by Horiuti and Polanyi; the carbon ring takes up every hydrogen atom separately [2]. To simplify the kinetics it is assumed that benzene is hydrogenated in three separate steps to cyclohexane.
Firstly, benzene is hydrogenated to cyclohexadiene and the reaction rate can be given by:

\[ r_1 = k_1 \cdot \theta_{C_6H_6}^\alpha \cdot \theta_H^\beta \]  

(6)

- \( k_1 \) = reaction rate constant per unit surface area (mol/s)
- \( \theta_{C_6H_6} \) = coverage of benzene on the catalyst surface (-)
- \( \theta_H \) = coverage of hydrogen on the catalyst surface (-)
- \( \alpha, \beta \) = order

where it is assumed that the reaction of a benzene molecule with two different hydrogen atoms is an elementary step: \( \alpha = 1 \) and \( \beta = 2 \). Strictly speaking, internal mass-transfer limitation can play a major role. It was outside the scope of the study to assess the quantitative influence of internal diffusion limitations and it was chosen to neglect it. As a consequence, the rate constant \( k_1 \) is an apparent rate constant.

The coverages of benzene and hydrogen can be estimated when Langmuir adsorption is presumed. Langmuir adsorption was initially only applied in gas/solid reactions [10]. The assumptions of the Langmuir model imply an ideal surface, and only few systems in practice will follow this closely. Experimental determinations of the heat of adsorption, \(-\Delta H^0_{ads}\) as a function of coverages show that usually the heat of adsorption decreases with increasing coverage [11,12]. This indicates that catalyst surfaces are non-uniform and/or the adsorbed molecules exhibit intramolecular repulsion forces. Other adsorption models which take this coverage dependency into account are, among others, the Freundlich and the Temkin isotherms. In practice of kinetic modelling, however, these isotherms are hardly used since the analytical solution of rate expressions is cumbersome [4] and multicomponent adsorption can nearly always be described adequately by the Langmuir model. One of the assumptions for the use of the Langmuir model in gas/solid reactions is that the partial pressures of the adsorbed gases are low. Within the Langmuir approach the general expression for the net adsorption rate of component, \( r_{a,i} \), is:

\[ r_{a,i} = r_{ads,i} - r_{des,i} = k_{ads,i} \cdot p_i \cdot \theta_* - k_{des,i} \cdot \theta_i \]  

(7)

- \( k_{ads,i} \) = adsorption rate constant of component \( i \) (mol/s)
- \( k_{des,i} \) = desorption rate constant of component \( i \) (mol/s)
- \( p_i \) = relative pressure of component \( i \) (Pa/Pa)
- \( \theta_* \) = vacant site coverage (-)
- \( \theta_i \) = coverage of component \( i \) (-)

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At equilibrium \( r_{ad} = 0 \) and the general expression for the fractional coverage of multicomponent adsorption for gas/solid systems can then be given by the Langmuir-Hinshelwood-Hougen-Watson (LHHW) equation:

\[
\theta_i = \frac{K_{ads,i} \cdot P_i}{1 + K_{ads,i} \cdot P_i + \sum_{j \neq i} K_{ads,j} \cdot P_j}
\]  

(8)

\( K_{ads,i,j} \) = adsorption constant of component \( i \) or \( j \)

In our case we deal with a liquid/solid reaction. The reactants are dissolved in the water phase and according to Bonné [13] and Atkins [14] the partial pressures in the equations should be translated to molar fractions. The molar fractions above the surface of the catalyst are small, as shown later, and therefore the occupancy can be given by:

\[
\theta_i = \frac{K_{ads,i} \cdot x_{i,s}}{1 + K_{ads,i} \cdot x_{i,s} + \sum_{j \neq i} K_{ads,j} \cdot x_{j,s}}
\]  

(9)

\( x_{i,j} \) = molar fraction of component \( j \) (mol/mol)

Hydrogen will be chemisorbed dissociatively and each molecule will need two vacant sites. In that case, the Langmuir-Hinshelwood isotherm for hydrogen is described by

\[
\theta_H = \frac{\sqrt{K_{ads,H_2} \cdot x_{H_2}}}{1 + \sqrt{K_{ads,H_2} \cdot x_{H_2}} + \sum_j K_{ads,j} \cdot x_{j,s}}
\]  

(10)

This equation can be applied to reversibly adsorbed atoms at all degrees of surface coverage or to irreversibly adsorbed atoms at small values of \( \theta_H \) [15].

If hydrogen and benzene adsorb dependently on the same sites, the equations (6), (9) and (10) will be combined to:

\[
r_1 = k_1 \frac{K_{ads,H_2} \cdot x_{H_2} \cdot K_{ads,B} \cdot x_B}{(1 + \sqrt{K_{ads,H_2} \cdot x_{H_2}} + K_{ads,B} \cdot x_B + \sum K_{ads,i} \cdot x_{i,s})^3}
\]  

(11)

Equation (11) shows that even if hydrogen molecules dissociate, a first-order process with respect to hydrogen will be observed if it is not strongly adsorbed relative to benzene (\( K_H < K_B \)). It can be anticipated that hydrogen atoms may add to benzene one
at the time; one of the additions being at equilibrium and the addition of the other being the rate-limiting step on the surface of the catalyst [15].

In the case that benzene and hydrogen are assumed to adsorb independently on different sites, equations (6), (9) and (10) can be combined to:

\[
    r_1 = k_1 \frac{K_{ads,H_2} \cdot x_{H_2} \cdot K_{ads,B} \cdot x_B}{(1 + \sqrt{K_{ads,H_2} \cdot x_{H_2}})^2 \left(1 + K_{ads,B} \cdot x_B + \sum K_{ads,i} \cdot x_{i,s}\right)} \tag{12}
\]

Adsorption on different sites is conceivable. Because hydrogen is a small molecule it is possible that hydrogen molecules adsorb at sites which are not accessible for benzene molecules. Even the formation of a benzene layer on top of a hydrogen layer is well conceivable [16]. These considerations also point to a reaction rate in which hydrogen and benzene adsorb independently and so equation (12) will be used in further calculations. A practical advantage of equation (12) compared to equation (11) is its higher simplicity.

In the second reaction step cyclohexadiene is hydrogenated to cyclohexene, and subsequently cyclohexene is hydrogenated to cyclohexane. The reaction rates are given by:

\[
    r_2 = k_2 \cdot \theta_{C_6H_8}^\gamma \cdot \theta_H^\delta \tag{13}
\]

\[
    r_3 = k_3 \cdot \theta_{C_6H_{10}}^\epsilon \cdot \theta_H^\zeta \tag{14}
\]

\[
    \gamma,\delta,\epsilon,\zeta = \text{order in the coverage coefficients} \tag{1-}
\]

Analogously to the orders in equation (6) the value of \( \gamma \) and \( \epsilon \) are assumed to be equal to 1, \( \delta \) and \( \zeta \) are equal to 2, respectively. The produced cyclohexene and cyclohexane can also desorb from the surface of the catalyst and diffuse through the stagnant water layer to the organic phase. For the description of the diffusion rates, equations analogous to the equations (4) and (5) can be used. The concentration gradient is now in the reverse direction.

To complete the set of reaction rate equations, also the dehydrogenation has to be taken into account. The dehydrogenation rates of cyclohexene to benzene can be described with the following equations:

\[
    r_{-1} = k_{-1} \cdot \theta_{C_6H_8}^\lambda \tag{15}
\]

\[
    r_{-2} = k_{-2} \cdot \theta_{C_6H_{10}}^\mu \tag{16}
\]

Modelling of the partial hydrogenation of aromatics
\[ r_{-3} = k_{-3} \cdot \theta_{C_6H_{12}}^\lambda \]  
\[ \lambda, \mu, \nu = \text{order in the coverage coefficient} \]  
\[ r_{12} = k_{12} \cdot \theta_{C_6H_6} \cdot \theta_H^4 \]  
\[ \Delta G^0 = RT \ln K_{12} = RT \ln \frac{k_{12}}{k_{-12}} \]  

It is presumed that the order \( \lambda, \mu \) and \( \nu \) are equal to unity. The (de-)hydrogenation rates are dependent on the hydrogen pressure and as a consequence it is expected that the selectivity to cyclohexene can be changed by variation in the hydrogen pressure.

The reaction rate constants in the equations (6), (13), (14), (15), (16) and (17) are unknown and have to be determined from experiments. Because, in all our experiments no cyclohexadiene has been observed, equations (6) and (13) can be combined to:

\[ r_{12} = k_{12} \cdot \theta_{C_6H_6} \]  
and the equations (16) and (17) to:

\[ r_{-12} = k_{-12} \cdot \theta_{C_6H_{10}} \]  
The ratio between \( k_{12} \) and \( k_{-12} \) is determined by the Gibbs energy of the reaction:

\[ \Delta G^0 = RT \ln K_{12} = RT \ln \frac{k_{12}}{k_{-12}} \]  
in which \( K_{12} \) is the equilibrium constant of the hydrogenation reaction from benzene to cyclohexene at the surface of the catalyst.

However, only the Gibbs energy of the overall reaction of benzene to cyclohexene is known and not the Gibbs energy of the reaction at the surface of the catalyst. The equilibrium constant of the overall reaction from benzene to cyclohexene, \( K_{\text{overall,12}} \), can be written as a product of all equilibrium constants:

\[ K_{\text{overall,12}} = \frac{K_{\text{sol,C}_6\text{H}_6} \cdot K_{\text{ads,C}_6\text{H}_6} \cdot K_{\text{sol,H}_2}^2 \cdot K_{\text{ads,H}_2}^2 \cdot K_{12}}{K_{\text{sol,C}_6\text{H}_{10}} \cdot K_{\text{ads,C}_6\text{H}_{10}}} \]  
in which the solubility constant \( K_{\text{sol,i}} \) is defined by:

\[ K_{\text{sol,i}} = \frac{x_i}{x_{\text{org},i}} \]
$$x_{org,i} = \text{molar fraction of component } i \text{ in the organic phase } i$$

$$K_{sol,i} = \text{solubility constant of } i$$

The solubility coefficients and the adsorption constants can be estimated. When $K_{12,overall}$ is known, $K_{12}$ can be calculated.

For the hydrogenation of cyclohexene to cyclohexane the Gibbs energy of the reaction at the surface of the catalyst is:

$$\Delta G^\circ = RT \ln K_3 = RT \ln \frac{k_3}{k_{-3}}$$

and the equilibrium constant of the overall reaction:

$$K_{overall,3} = \frac{K_{sol,C_6H_{10}} \cdot K_{ads,C_6H_{10}} \cdot K_{sol,H_2} \cdot K_{ads,H_2} \cdot K_3}{K_{sol,C_6H_{12}} \cdot K_{ads,C_6H_{12}}}$$

The kinetics of the benzene hydrogenation is described now in a set of general equations. Aim is to check the kinetic model and to quantify the parameters in the equations. Partly, the parameters can be obtained from literature, partly they have to be determined experimentally by fitting the data of different experiments. Before the parameters are evaluated, a few assumptions can be taken into account. A high yield in cyclohexene is only possible when accumulation of cyclohexene in the organic phase is realized. There are two possibilities for this accumulation. Firstly, the hydrogenation of cyclohexene at the surface of the catalyst might be slower than the desorption rate of cyclohexene ($r_{des,C6H_{10}} > r_3$). Secondly, the desorption rate of cyclohexene can be much higher than the cyclohexene adsorption rate ($K_{ads,C6H_{10}} << 1$).

Another goal of the kinetic model is to predict the influence of process conditions, like temperature and hydrogen pressure, on the cyclohexene selectivity. For this purpose the relative cyclohexene selectivity, $S_{rel}$, is defined; this selectivity is the ratio of the net cyclohexene production and the net cyclohexene production rate. Only the fractions of cyclohexene and cyclohexane in the organic phase are of interest, because only the organic fraction is analyzed during an experiment. The relative selectivity is given by:

$$S_{rel} = \frac{\frac{dC_{C6H_{10},org}}{dt}}{\frac{dC_{C6H_{12},org}}{dt}}$$

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Using the equations (4), (5), (7), (14) and (17), and assuming that the concentration of cyclohexene and of cyclohexane at the start of the benzene hydrogenation experiment is equal to zero, equation (25) can be written as:

\[
S_{rel} = \frac{k_{des,C_6H_{10}} \cdot \frac{C_6H_{10}}{\theta^*}}{k_{ads,C_6H_{10}} + \frac{1}{k_{ll}A_{ll}A_{ll}A_{ll}}} + \frac{1}{k_{ls,C_6H_{10}}A_{ls}A_{ls}A_{ls}A_{ls}} + \frac{1}{k_{ads,C_6H_{10}}A_{ll}A_{ll}A_{ll}A_{ll}}}
\]

From equation (26) it can be concluded that many parameters will influence this selectivity. There is a possibility to simplify this equation. The dehydrogenation rate of cyclohexane at the temperature at which the reaction is carried out is negligible. Equation (17) shows that the rate of dehydrogenation then vanishes for \(k_3 \to 0\) and or \(\theta_{C6H12} \to 0\). It is assumed that both are very low, which results in:

\[
\frac{k_{-3} + k_{des,C_6H_{12}}}{k_{-3} \cdot k_{ads,C_6H_{12}}A_{ll}A_{ll}A_{ll}A_{ll}} > \frac{1}{k_{ls,C_6H_{12}}A_{ls}A_{ls}A_{ls}A_{ls}} \cdot \frac{1}{k_{ll} \cdot A_{ll}A_{ll}A_{ll}A_{ll}}
\]

It can also be expected that the adsorption rate constant of cyclohexene is small, which will lead to:

\[
\frac{1}{k_{ads,C_6H_{10}}} \theta^* > \frac{1}{k_{ls,C_6H_{10}}A_{ls}A_{ls}A_{ls}A_{ll}} \cdot \frac{1}{k_{ll}A_{ll}A_{ll}A_{ll}}
\]
It can be presumed that the cyclohexane coverage is low due to a large desorption rate and therefore it can be assumed that $k_3 \ll k_{des,C6H12}$ and as a consequence equation (26) can be simplified to

$$S_{rel} = \frac{k_{des,C6H10}}{k_3} \cdot \frac{1}{\theta_H^2}$$

(27)

Assuming Arrhenius kinetics, equation (27) can be written as follows:

$$S_{rel} = \frac{k_{0,des,C6H10}}{k_{0,3} \cdot \theta_H^2} \cdot e^{\left(-\frac{E_a,des,C6H10}{R \cdot T} + \frac{E_a,hydr,C6H10}{R \cdot T}\right)} = \frac{k_0}{\theta_H^2} \cdot e^{\left(-\frac{E_{a,rel}}{R \cdot T}\right)}$$

(28)

in which $k_0$ is the total pre-exponential factor of the rate constants in equation (27) and $E_{a,rel}$ the apparent activation energy of the selectivity ratio. The apparent activation energy of the relative selectivity could easily be determined, when the hydrogen coverage is kept constant. The sign of $E_{a,rel}$ determines whether the relative selectivity increases or decreases when the temperature is raised. Equation (28) predicts that the relative selectivity decreases when the hydrogen coverage is increased. The influence of temperature and hydrogen pressure on the relative selectivity will be investigated.

EXPERIMENTAL

The hydrogenation experiments have been carried out with an unsupported ruthenium catalyst (mean particle diameter 25 $\mu$m, $S_{BET} = 80$ m$^2$/g), which was obtained by adding a sodium hydroxide solution to a ruthenium trichloride solution and subsequently reduced with hydrogen. Details are described in Chapter 2. Into a stainless-steel autoclave coated with TiN to prevent corrosion and equipped with baffle bars, catalyst, 200 ml of substrate, 150 ml of distilled water and 9.3 mmol (=2.4 g) FeSO$_4$$\cdot$6H$_2$O were introduced. After purging with nitrogen and hydrogen, the pressure was elevated to 2.0 MPa with hydrogen, after which the temperature was raised at a rate of 0.166 K/s. When the desired reaction temperature, was reached, the desired total pressure was adjusted by increasing the hydrogen partial pressure.
Figure 3: Course of the partial hydrogenation of benzene over a ruthenium catalyst as a function of the time. Conditions: 0.5 g catalyst, 150 ml water, 200 ml benzene, 2.4 g iron sulfate, $T=423 \, K$, $p=5.0 \, MPa$.

Figure 4: Influence of the hydrogen pressure on the course of the partial benzene hydrogenation. Conditions: 0.5 g catalyst, 150 ml water, 200 ml benzene, 2.4 g iron sulfate, $T=443 \, K$.

Figure 5: Influence of the temperature on the partial hydrogenation of benzene over a ruthenium catalyst carried out at relatively low total pressure. Conditions: 0.5 g catalyst, 150 ml water, 200 ml benzene, 2.4 g iron sulfate, $p_{total}=3.0 \, MPa$.

Figure 6: Influence of the temperature on the partial hydrogenation of benzene over a ruthenium catalyst carried out at relatively high total pressure. Conditions: 0.5 g catalyst, 150 ml water, 200 ml benzene, 2.4 g iron sulfate, $p_{total}=7.0 \, MPa$.
The hydrogenation started as soon as stirring commenced (stirring speed 25 s⁻¹). The hydrogenation reaction was carried out at different pressures and temperatures and besides benzene, also cyclohexene, toluene, and p-xylene have been used as a substrate.

The hydrogenation reaction was monitored by taking samples of the reaction mixture at selected intervals, followed by gas-chromatographic analysis. Molar fractions larger than 10⁻⁵ could be detected.

RESULTS OF THE HYDROGENATION EXPERIMENTS

Figure 3 shows the course of the product composition during the hydrogenation of benzene as a function of time; benzene was converted, and cyclohexene and cyclohexane were the main products. The molar fraction of cyclohexene increased as a function of time up to a value of 0.20 and then gradually decreased. Cyclohexadiene was never detected. All benzene hydrogenation experiments show a similar pattern.

Figure 4 shows the results of the hydrogenation reaction at three different partial hydrogen pressures. The benzene consumption rate increased with increasing
pressure. Also the maximum cyclohexene yield increased significantly. When the total
pressure was kept constant at 3.0 MPa, and the temperature was raised, both the
benzene consumption rate and the cyclohexene yield decreased, see Figure 5. When
this is performed at a higher total pressure, 7.0 MPa, the benzene consumption rate is
nearly constant, but the yield increases, see Figure 6.

According to the kinetic network cyclohexene is a reversible intermediate.
Cyclohexene has been used as reactant to check this. During the hydrogenation of
cyclohexene, performed at a temperature of 443 K and a partial hydrogen pressure of
4.0 MPa, not only cyclohexane is detected, but also some benzene, see Figure 7. The
maximum benzene fraction observed was 0.005 %. The results of these experiments
will be used to support the kinetic mechanism.

In Figure 8 the results are shown of the benzene, toluene and p-xylene
hydrogenation. The higher substituted aromatics react more slowly, but the yield in
partial hydrogenated products is higher. In the case of p-xylene a yield of 46% to the
cyclohexene derivatives is obtained.

ESTIMATION OF COEFFICIENTS AND PARAMETERS

To perform calculations and modelling it is necessary to determine the mass
transfer coefficients, adsorption and solubility coefficients of the substrates and
products. Also the interfacial areas have to be determined. In most cases a useful
estimation can be given by using data or empirical relations from literature.

Mass transfer coefficient \( k_{gl} \)

The mass transfer coefficient \( k_{gl} \) in equation (1) is affected by the stirrer speed, \( N \),
and the transport properties of the solution. Relations between \( k_{gl} \), the stirrer speed,
and the transport properties can be described by the film model, in which the
penetration model and the random surface renewal model are often used [17]. If \( \tau_{gl} \) is
the residence time of the liquid at the gas-liquid interface, the penetration theory
predicts that the average value of \( k_{gl} \) in the time interval \( 0 < \tau < \tau_{gl} \) derives as:

\[
k_{gl} = 2 \sqrt{\frac{D_{AB}}{\pi \cdot \tau}} \tag{29}
\]

\( D_{AB} = \) diffusion coefficient of component A in fluid B \( (m^2/s) \)
\( \tau = \) time constant \( (s) \)
If the replacement frequency of the liquid is assumed to be equal to that of the stirrer speed N, then $1/\tau_{gl}$ equals $25 \text{ s}^{-1}$. With a diffusion coefficient of hydrogen of $D_{AB}=2.0 \times 10^{-8} \text{ m}^2/\text{s}$, equation (29) leads to $k_{gl}=8.0 \times 10^{-4} \text{ m/s}$. The estimation of the diffusion coefficient is discussed below.

**Interfacial area $A_{gl}$**

The interfacial area between the gas phase and the liquid water phase, $A_{gl}$, in equation (1) can be estimated by:

$$A_{gl} = \frac{6}{d} \cdot V$$  \hspace{1cm} (30)

$d$ = diameter of gas bubble  \hspace{1cm} (m)

$V$ = volume of gas phase in contact with the water phase  \hspace{1cm} (m$^3$)

The hold-up of the hydrogen gas in the water phase is determined at normal pressure and room temperature by measuring the liquid level with and without stirring and reaches $0.15 \text{ m}^3_{\text{gas}}/\text{m}^3_{\text{liquid}}$ at a stirring speed of $25 \text{ s}^{-1}$. Odenbrand [18] found that the gas bubble size in the liquid phase varied from $0.1$ to $0.9 \times 10^{-3} \text{ m}$. So, during a hydrogenation experiment the interfacial area varies between $0.3$ and $3 \text{ m}^2$. For the fitting of experimental data the value of $1.8 \text{ m}^2$ has been chosen.

**Hydrogen concentration in the water phase**

According to Henry's law, the concentration of hydrogen is proportional to the hydrogen pressure, see equation (2). The Henry's law constant in the equation is estimated at $7.5 \times 10^9 \text{ Pa}$ at a temperature of $423 \text{ K}$ [19]. During an experiment the partial pressures of water and benzene have to be taken into account. The higher the temperature the higher the partial pressures of benzene and water in the vapour phase will be. In Figure 9 the partial pressures of the aromatics and

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water are depicted separately as a function of the temperature. The data are taken from Reid et al. [24]. When a three-phase system is formed, that means two liquid phases and one vapour phase, the total pressure of the system is equal to:

\[ P_{\text{total}} = P_B^* + P_W^* + P_{H_2} \]  \hspace{1cm} (31)

\[ P_B^* = \text{saturation vapour pressure of benzene} \]  \hspace{1cm} (MPa)

\[ P_W^* = \text{saturation vapour pressure of water} \]  \hspace{1cm} (MPa)

\[ P_{H_2} = \text{partial hydrogen pressure} \]  \hspace{1cm} (MPa)

The partial pressures of hydrogen in either a benzene/water, toluene/water, or p-xylene/water system can be estimated by using equation (31) and are represented as a function of the temperature by the decreasing lines in Figure 9 for a total pressure of 5.0 MPa. When the hydrogenation is carried out at a total pressure of 5.0 MPa and 423 K, the partial pressure of hydrogen in the autoclave is 3.9 MPa. The concentration of hydrogen in pure water is estimated to be 27 mol/m\(^3\)\text{liquid} at a total pressure of 5.0 MPa and at a temperature of 423 K.

The solubility of hydrogen in water is influenced by the addition of electrolytes. Intrapolation of solubility data in reference [20] and assuming that the ratio of the solubility of hydrogen in pure water and of the solubility of hydrogen in aqueous salt solutions is independent on the temperature [21], show that the solubility of hydrogen in aqueous salt solutions (concentration <0.06 M) deviates only 5% of the solubility of hydrogen in pure water. Therefore, in this study the solubility of hydrogen in pure water is used for calculations.

**Liquid/liquid mass-transfer coefficients**

Equation (29) has also been used for estimation of the mass-transfer coefficient of benzene to the water phase. The \(k_{\text{II}}\) for benzene is equal to 2.93\times10^{-4} \text{ m/s} at a temperature of 423 K and a time constant of 1/25 s.

**Interfacial area \(A_{\text{II}}\)**

The interfacial area \(A_{\text{II}}\) in equation (4) is estimated with equation (30). Odenbrand [18] found that the organic phase, a mixture of benzene, cyclohexene, and cyclohexane, is dispersed as small droplets with a diameter of 0.05-0.14 \times 10^{-3} \text{ m}. The total volume of the organic phase in a typical hydrogenation reaction is 200 \times 10^{-6} \text{ m}^3. As a consequence, the interfacial area between the organic phase and the water phase varies between 24 and 8.6 m\(^2\). For parameter estimation a value of 12 m\(^2\) has been used.
Liquid/solid mass-transfer coefficients

The liquid/solid mass transfer coefficient, $k_{ls}$, for a sphere at rest in a large volume of stagnant liquid is given by [22]:

$$k_{ls} = \frac{2 \cdot D_{AB}}{d_p}$$  \hspace{1cm} (32)

\[ d_p = \text{particle diameter} \hspace{1cm} (m) \]

Any motion of the particle relative to the fluid will tend to make $k_{ls}$ larger than the value obtained by equation (32). Several relations have been derived to estimate the mass-transfer coefficients, in which the particles move relatively to the fluid.

One of the most reliable relations suitable for the estimation of mass transfer coefficients of solid catalyst spheres suspended in an agitated liquid, is that of Brian and Hales [23]:

$$k_{ls} \frac{d_p}{D_{AB}} = \left(4 + 1.21 \cdot \left(\frac{d_p \cdot v}{D_{AB}}\right)^{\frac{2}{3}}\right)^{\frac{1}{2}}$$  \hspace{1cm} (33)

\[ v = \text{velocity of solid particle relative to the surrounding liquid} \hspace{1cm} (m/s) \]

The mass-transfer rate can be enlarged by increasing the value of $v$ in equation (33). However, the catalyst particles are quite small (25 µm), and tend to move with the liquid. Since the catalyst has a higher density than the surrounding liquid, the particles tend to settle down through the fluid. Of course gravity leads to a net velocity. The terminal velocity of a particle settling through a fluid is given by Stokes’ Law. Further, in actuality, mechanical agitation and the gas bubbles rising through the liquid tend to make the value of the mass transfer coefficient somewhat higher than predicted by the above equation. To adjust for this effect, a value of $k_{ls}$ twice the predicted value has been assumed [9]. Inserting this factor of two and the Stokes’ law for the particle velocity in equation (33) gives:
\[ k_{ls} = \frac{2 \cdot D_{AB}}{d_p} \left( 4 + 1.21 \left( \frac{g \cdot d_p^3 \cdot (\rho_a - \rho_l)}{18 \cdot \mu_B \cdot D_{AB}} \right)^{\frac{2}{3}} \right)^{\frac{1}{2}} \]  

(34)

\[ g = \text{acceleration due to gravity} \quad (\text{m/s}^2) \]
\[ \rho_a = \text{apparent density of the catalyst particle in the liquid} \quad (\text{g/m}^3) \]
\[ \rho_l = \text{density of the liquid} \quad (\text{g/m}^3) \]
\[ \mu_B = \text{viscosity of the liquid} \quad (\text{g/m/s}) \]

The diffusion coefficient of solute A in solvent B, \( D_{AB} \), can be obtained from the Tyn and Calus relation [24]:

\[ D_{AB} = 8.93 \cdot 10^{-12} \cdot \frac{V_B^{0.267}}{V_A^{0.433}} \cdot \frac{T}{\mu_B} \left( \frac{\sigma_B}{\sigma_A} \right)^{0.15} \]  

(35)

\[ V_i = \text{molar volume of solute } i \text{ at the normal boiling temperature} \quad (\text{m}^3/\text{mol}) \]
\[ T = \text{temperature} \quad (\text{K}) \]
\[ \sigma_i = \text{surface tension of } i \text{ at the normal boiling temperature} \quad (\text{g/s}^2) \]

An approximation of the \( \sigma_i \) is given by

\[ \sigma_i = P_c^{\frac{2}{3}} \cdot T_c^{\frac{1}{3}} \left( 0.132 \cdot \alpha_c - 0.278 \right) \left( 1 - T_{br} \right)^{11/9} \]  

(36)

\[ P_c = \text{critical pressure} \quad (\text{bar}) \]
\[ T_c = \text{critical temperature} \quad (\text{K}) \]
\[ T_{br} = T_b/T_c \quad (-) \]
\[ \alpha_c = \text{correction factor} \quad (-) \]

and \( \alpha_c \) is given by

\[ \alpha_c = 0.9076 \left( 1 + \frac{T_{br} \cdot \ln(P_c / 1.013)}{1 - T_{br}} \right) \]  

(37)

The results of mass-transfer coefficient calculations are listed in Table 1. The calculated values are based on equation (34). When the equations (32) and (33) would have been used, the calculated values would have been a factor 4 or 2 lower, respectively.
<table>
<thead>
<tr>
<th>Component</th>
<th>$k_{ls}$ (m/s)</th>
<th>Solubilities (mol/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>$2.12 \times 10^{-3}$</td>
<td>111</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>$2.06 \times 10^{-3}$</td>
<td>19</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>$2.04 \times 10^{-3}$</td>
<td>5.8</td>
</tr>
<tr>
<td>Toluene</td>
<td>$2.01 \times 10^{-3}$</td>
<td>27</td>
</tr>
<tr>
<td>Methylcyclohexenes</td>
<td>$1.96 \times 10^{-3}$</td>
<td>4.7</td>
</tr>
<tr>
<td>Methylcyclohexane</td>
<td>$1.94 \times 10^{-3}$</td>
<td>1.5</td>
</tr>
<tr>
<td>Xylene</td>
<td>$1.91 \times 10^{-3}$</td>
<td>8</td>
</tr>
<tr>
<td>Dimethylcyclohexenes</td>
<td>$1.85 \times 10^{-3}$</td>
<td>2</td>
</tr>
<tr>
<td>Dimethylcyclohexane</td>
<td>$1.84 \times 10^{-3}$</td>
<td>1</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>$4.67 \times 10^{-3}$</td>
<td>27</td>
</tr>
</tbody>
</table>

The diffusion coefficient in aqueous salt solutions can differ from the diffusion coefficients in pure water. Because of the low concentration of the sulfates (<0.05 mol/l), the diffusion coefficients in pure water have been used.

**Interfacial area $A_{ls}$**

The area between the water phase and the catalyst surface is equal to 0.034 (m$^2$), when equation (30) is used. This area comprises only the outer surface of the catalyst particles. The interfacial area could be larger when also the surface area of the macropores of the catalyst is taken into account. BET measurements showed that the total surface of the catalyst is up to 80 m$^2$/g. However, it is assumed that the pores of the catalyst particles can only be reached by intraparticle diffusion and do not contribute to the interfacial area $A_{ls}$.

**Solubilities of the organics in the water phase**

The equilibrium concentrations, which can also be called solubilities of the organic substrates and (partially) hydrogenated products in water are obtained from Tsonopoulous and Wilson [25]. They determined the solubility of benzene and cyclohexane in a temperature range of 273 K to the critical temperature. The solubility of cyclohexene and that of other aromatic compounds are taken from McAuliffe [26].
and extrapolated by using the data from Tsonopolous and Wilson [25]. All these data were measured in binary systems: mixtures of the organic compound and water. During the reaction a quaternary system arises: water, benzene, cyclohexene and cyclohexane. Arich [27] showed that the fractions of the organics in the water phase should not always behave linear to the fractions in the organic phase. The fractions in the water phase of the more polar organics are relatively larger. The solubilities of the aromatics and the hydrogenation products at a temperature of 423 K are listed in Table 1. According to Tsonopolous and Wilson [25] the solubility is hardly influenced by the pressure when a three-phase system has been established. From the solubilities the solubility constants, $K_{sol,i}$, can be calculated.

**Adsorption coefficients**

The adsorption coefficient $K_{ads,i}$ can be estimated by:

$$K_{ads,i} = \exp \left(-\frac{\Delta G^0_{ads,i}}{R \cdot T}\right) = \exp \left(\frac{\Delta S^0_{ads,i}}{R} - \frac{\Delta H^0_{ads,i}}{R \cdot T}\right)$$ (38)

$\Delta G^0_{ads,i} =$ Gibbs energy of adsorption of component $i$ (J/mol)

$\Delta S^0_{ads,i} =$ adsorption entropy of component $i$ (J/mol/K)

$\Delta H^0_{ads,i} =$ adsorption enthalpy of component $i$ (J/mol)

$R =$ gas constant (J/mol/K)

$T =$ temperature (K)

To estimate the adsorption coefficients of the organic components and hydrogen the results of Schoenmaker-Stolk et al. [28] are used. They investigated the benzene

Table 2: Overview of the estimated adsorption enthalpies and entropies in the hydrogenation of benzene over a ruthenium catalyst [28]. The adsorption coefficients $K_{ads}$ are calculated values at a temperature of 423 K.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta H^0_{ads}$ (kJ/mol)</th>
<th>$\Delta S^0_{ads}$ (J/mol/K)</th>
<th>$K_{ads}$ (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hydrogen</td>
<td>-40</td>
<td>-120</td>
<td>0.047</td>
</tr>
<tr>
<td>benzene</td>
<td>-59</td>
<td>-140</td>
<td>0.94</td>
</tr>
<tr>
<td>1,3-cyclohexadiene</td>
<td>-122</td>
<td>-285</td>
<td>109</td>
</tr>
<tr>
<td>cyclohexene</td>
<td>-44</td>
<td>-100</td>
<td>1.62</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>-34</td>
<td>-100</td>
<td>0.094</td>
</tr>
</tbody>
</table>

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hydrogenation over ruthenium-on-silica catalysts in the temperature range from 300 to 425 K and at a total pressure of 0.13 MPa. In Table 2 the entropy and enthalpy values are given.

According to Konvalinka et al. different species of chemisorbed hydrogen are present on surface areas of group-VIII metals [11]: strongly bounded hydrogen and weakly bounded hydrogen. It must be noted that the adsorption enthalpy for hydrogen, mentioned in Table 2, is only valid for weakly bounded hydrogen.

**Activation energies**

It is assumed that the activation energy of the benzene hydrogenation is equal to 44 kJ/mol and the activation energy of the cyclohexene hydrogenation reaction is estimated to be equal to 5.5 kJ/mol, see reference [4]. The activation energy of the adsorption processes are presumed to be zero and of the desorption rates equal to the adsorption enthalpies as listed in Table 2.

**Adsorption and desorption rate constants**

The adsorption and desorption rate constants are unknown. In the computational modelling it was presumed that the adsorption/desorption equilibria were established very quickly and are not rate limiting.

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**Figure 10:** Course of the benzene hydrogenation, the lines are based on the model. □ = benzene, ◇ = cyclohexene, and Δ = cyclohexane are actual GC-data points, (for experimental details see Figure 3).

**Figure 11:** Course of the cyclohexene hydrogenation, the lines are based on the model. □ = benzene, ◇ = cyclohexene, and Δ = cyclohexane are actual GC-data points (for experimental details see Figure 7).

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*Modelling of the partial hydrogenation of aromatics*
Chapter 8

ANALYSIS OF THE EXPERIMENTAL RESULTS

Benzene hydrogenation

The benzene hydrogenation experiment in Figure 3 is used as the standard hydrogenation experiment. With the simulation programme Scientist® the data have been fitted. In equation (1) to (24) a number of coefficients and constants are defined. When these coefficient would be varied during the fitting procedure, a perfect fit is possible. It is obvious that this is not useful. It was chosen to vary only the interfacial areas \((A_{gl}, A_{ls}, A_{ll})\) and the rate constants \(k_{12}\) and \(k_{3}\), in equation (18) and (14), respectively. Normally, mass-transfer rates are estimated by using volumetric rate constants \((k_{gl}, k_{is}, k_{il})\): the product of the mass-transfer rate constants and the interfacial areas. In this investigation these parameters have been determined separately. The estimations of \(A_{gl}, A_{ls}, A_{ll}\) which were calculated in the previous section are used as starting values. Other parameters are estimated as described in the section above or taken from literature.

In Figure 10 the data points of Figure 3 and the fitted lines are depicted. The figure shows that it is possible to fit the data well and the conclusion can be drawn that the described model seems to be in accordance with the experimental results.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(W_{cat})</td>
<td>0.5 g</td>
</tr>
<tr>
<td>(d_p)</td>
<td>25 (\mu)m</td>
</tr>
<tr>
<td>(S_{BET})</td>
<td>80 (m^2/g)</td>
</tr>
<tr>
<td>(T)</td>
<td>423 K</td>
</tr>
<tr>
<td>(P_{tot})</td>
<td>5.0 MPa</td>
</tr>
<tr>
<td>(P_{water})</td>
<td>0.47 MPa</td>
</tr>
<tr>
<td>(P_{C6H6})</td>
<td>0.58 MPa</td>
</tr>
<tr>
<td>(P_{H2})</td>
<td>3.95 MPa</td>
</tr>
<tr>
<td>(m_{water})</td>
<td>0.192 (g/m^3)</td>
</tr>
<tr>
<td>(\rho_{water})</td>
<td>912 (kg/m^3)</td>
</tr>
<tr>
<td>(\rho_{app})</td>
<td>4332 (kg/m^3)</td>
</tr>
<tr>
<td>(k_{gl, H2})</td>
<td>2.08 (10^{-3} m/s)</td>
</tr>
<tr>
<td>(k_{ls, C6H6})</td>
<td>2.14 (10^{-3} m/s)</td>
</tr>
<tr>
<td>(k_{ls, C6H10})</td>
<td>2.05 (10^{-3} m/s)</td>
</tr>
<tr>
<td>(k_{ls, H2})</td>
<td>4.72 (10^{-3} m/s)</td>
</tr>
<tr>
<td>(k_{ll, C6H6})</td>
<td>2.9 (10^{-4} m/s)</td>
</tr>
<tr>
<td>(K_{overall, 12})</td>
<td>572.12</td>
</tr>
<tr>
<td>(K_{12})</td>
<td>3.3 (10^{11})</td>
</tr>
<tr>
<td>(K_{overall, 3})</td>
<td>4.6 (10^6)</td>
</tr>
<tr>
<td>(K_{3})</td>
<td>1.4 (10^{11})</td>
</tr>
<tr>
<td>(P_{water})</td>
<td>0.58 MPa</td>
</tr>
<tr>
<td>(K_{sol, C6H6})</td>
<td>2.2 (10^{-3})</td>
</tr>
<tr>
<td>(K_{sol, C6H10})</td>
<td>0.37 (10^{-3})</td>
</tr>
<tr>
<td>(k_{12})</td>
<td>(9.2 (\pm) 8.2) (10^{11}) mol/s</td>
</tr>
<tr>
<td>(k_{3})</td>
<td>(1.5 (\pm) 0.2) (10^6) mol/s</td>
</tr>
<tr>
<td>(A_{ls})</td>
<td>0.035 (\pm) 0.002 (m^2)</td>
</tr>
<tr>
<td>(A_{ll})</td>
<td>2.5 (\pm) 2.2 (m^2)</td>
</tr>
<tr>
<td>(A_{gl})</td>
<td>&gt;1 (m^2)</td>
</tr>
</tbody>
</table>

Table 3: Reaction constants, apparent activation energies and other parameters used in the curve fitting of the benzene hydrogenation in Figure 3 and which have been used as standard conditions in the model calculations. The values of \(A_{gl}, A_{ls}, A_{ll}\), \(k_{12}\) and \(k_{3}\) are obtained from the curve fitting.
In Table 3 a summary is given of the estimated and fitted parameters. The accuracy of $k_3$ is relatively high. From the fitted parameters $A_{1b}$ has the highest accuracy. The optimum value of $A_{1b}$ is estimated to be 0.035 m$^2$, which agrees well with the value calculated from the mean catalyst particle diameter by using equation (19), 0.034 m$^2$. The accuracy of $A_{gl}$ was very low; a reliable value could not be calculated but the value had to be above 1 m$^2$.

**Mass-transfer limitation during the benzene hydrogenation**

Using the model equations several aspects of the benzene hydrogenation can be studied more extensively. In Figure 12 the benzene and cyclohexene conversion rates are depicted as a function of time. The conversion rate of benzene decreases slowly until the conversion rate of cyclohexene exceeds the benzene conversion rate. Thereafter the rate decreases more quickly until the rate becomes zero. The dashed line in Figure 12 represents the net cyclohexene production rate, which is the difference between the benzene conversion rate and the cyclohexene conversion rate. When the net cyclohexene production rate is zero, the maximum cyclohexene concentration is reached. In Figure 13 the conversion rate of benzene is depicted as a function of the conversion. It is shown that the reaction rate of benzene increases linearly at small benzene concentrations of benzene and becomes more or less constant at higher

**Figure 12:** The calculated conversion rates of benzene (□) and cyclohexene (○) during the hydrogenation of benzene via cyclohexene to cyclohexane as a function of time. The dashed line is the net production rate of cyclohexene.

**Figure 13:** The calculated conversion rates of benzene during the hydrogenation of benzene via cyclohexene to cyclohexane as a function of the molar concentration of the components.
concentrations. The conclusion can be drawn that the benzene conversion rate is
governed either by mass-transfer processes or by Langmuir kinetics. From the fitting
results it is already concluded that the mass transfer is rate limiting.

The extent of external mass transfer can be determined according to the method
introduced by Carberry [29]. The method is based on the calculation of the quotient of
the observed reaction rate and the maximum mass-transfer rate:

\[ Ca = \frac{r_{\text{obs}}}{k_{ls} A_{ls} C_{H_2,w}} \]  

(39)
in which \( r_{\text{obs}} \) (mol/s) is the observed reaction rate. The Carberry number can vary
from zero to unity, corresponding to insignificant and total external mass-transport
limitation. A Carberry number smaller than 0.05 means that diffusion retardation by
external mass transport may be neglected. When the mass transfer rate of the
hydrogen to the water phase is fast, relative to the mass transfer rate of hydrogen to
the surface of the catalyst, it can be presumed, that \( C_w \) is equal to the equilibrium
concentration of hydrogen in water. For benzene the same assumption can be made.
Calculation of the Carberry numbers of hydrogen and of benzene, as illustrated in
Figure 14, show indeed that during the hydrogenation reaction both benzene
and hydrogen mass transfer are
governed by external diffusion
limitation. The reaction rate is
dominantly limited by the diffusion of
hydrogen, but is also limited to a minor
extent by benzene diffusion. As the
reaction proceeds the Carberry number of hydrogen decreases, whereas the
Carberry number of benzene increases.
This means that the declining
concentration of benzene results in a
smaller mass-transfer rate and that the
reaction will be controlled more and
more by the diffusion of benzene. This
effect is also seen in Figure 13, in which
the reaction rate is strongly dependent of
the molar concentration of benzene at
lower concentrations.

\[ \text{Figure 14: Carberry numbers of hydrogen and benzene during the hydrogenation of benzene via cyclohexene to cyclohexane as a function of time.} \]
The Carberry number doesn’t answer the question whether the mass transfer of hydrogen from the gas phase to the water phase is rate limiting or the mass transfer of hydrogen in the water phase to the surface of the catalyst. Combining the equations (1), (3), and (6), and eliminating $C_{\text{H}_2,s}$ and $C_{\text{H}_2,w}$ the following overall reaction rate expression can be obtained:

$$-J_{\text{H}_2} = \frac{C_{\text{H}_2eq,w}}{\frac{1}{k_{\text{gl}} \cdot A_{\text{gl}}} + \frac{1}{k_{\text{ls}} \cdot A_{\text{ls}}} + \frac{1}{k_{12}}}$$

(40)

This equation shows that the lowest product of $k_{\text{gl}}A_{\text{gl}}$, $k_{\text{ls}}A_{\text{ls}}$ or $k_{12}$ is determining the hydrogen consumption rate. From the values for the mass transfer coefficients and interfacial areas listed in Table 3 it could be estimated that $k_{\text{ls}}A_{\text{ls}}<k_{\text{gl}}A_{\text{gl}}<k_{12}$. That means that the mass transfer of hydrogen from the water phase to the catalyst surface is the paramount rate determining step.

On the basis of the model equations it is possible to estimate the hydrogen coverage $\theta_{\text{H}}$ during the hydrogenation experiment. As can be seen in Figure 15 the hydrogen coverage is initially low and reaches a maximum value at the end of the experiment. The lower values are due to the high rates and, as a consequence, are determined by mass-transfer limitation. When nearly all benzene is converted the hydrogen coverage will reach the equilibrium coverage.

![Figure 15: Hydrogen and benzene coverage during the hydrogenation reaction.](image1)

![Figure 16: Hydrogen coverage during the benzene hydrogenation as a function of the temperature.](image2)
Variation of the temperature

When the benzene hydrogenation is carried out at considerably low total pressures, both the reaction rate and the selectivity changed when the temperature is varied (see Figure 5), whereas at higher pressures only the selectivity is influenced by the temperature (see Figure 6). Qualitatively, the sensitivity of the reaction rate with respect to the temperature can be explained as follows. At higher temperatures the partial pressures of the organics and of water increase, and as a consequence, the partial pressure of hydrogen decreases. The reaction rate is diffusionally controlled by hydrogen. When the temperature is raised from 423 K to 443 K at a total pressure of 3.0 MPa the partial hydrogen pressure decreases from 2.0 to 1.3 MPa: a difference of 33%. It is clear that the reaction rate will be lower. When the reaction rate is carried out at a total pressure of 7.0 MPa the partial hydrogen pressure decreases from 6.4 to 5.3 MPa, when the temperature moves from 403 K to 443 K: a difference of 17%. The effect on the reaction rate will be then less significant as can be seen in Figure 6.

The relative selectivities have been calculated for the experiments described in Figure 6 and are depicted in Figure 17. From equation (28) it is clear that $E_{a,Srel}$ is equal to the activation energy of the cyclohexene desorption minus the activation energy of the cyclohexene hydrogenation. Assuming that (i) the activation energies of the desorption processes are equal to the adsorption enthalpies as listed in Table 2, and (ii) the activation energy of the cyclohexene hydrogenation is 5.5 kJ/mol, $E_{a,Srel}$ is predicted to be 39 kJ/mol. This value and the relative selectivity measured at 403 K has been used to calculate the relative selectivities at temperatures varying from 400 K to 445 K and these are depicted by the dotted line in Figure 17. The calculated values predict the relative selectivity quite well. This has been also checked for other series of experiments. The apparent activation energy of the relative selectivity, $E_{a,Srel}$, could also be estimated from the measured values. Assuming that the hydrogen coverage is constant, the apparent activation energy showed to be 40 kJ/mol. This value is in accordance with the value of the calculated value of 39 kJ/mol.

![Diagram](image)

Figure 17: The relative selectivity as a function of the temperature. The points are based on the experiments described in Figure 6 and the line is based on equation 28 and on the measured selectivity at 403 K.
Variation of the hydrogen pressure

It is remarkable that the maximum yield in the partial hydrogenation of benzene increased when the partial hydrogen pressure was raised, see Figure 4. Equation (28) shows that the relative selectivity should decrease when the hydrogen coverage raises. Possibly some of the assumptions made in the description of the model are not valid. For instance, it might not be correct to assume that hydrogen and cyclohexene adsorb independently. The molar fractions of both hydrogen and cyclohexene in the water phase are, however, small and the reaction is limited by diffusion and the temperature is that high that it can be presumed that the coverages are nearly equal to zero.

According to equation (28) the relative selectivity will decrease when the hydrogen coverage is increased. The hydrogen coverages increase, when the pressure is raised, and equilibrium can be reached. Using model calculations the hydrogen coverage can be estimated as a function of the hydrogen pressure at different stages of the hydrogenation reaction, see Figure 16. Initially, the hydrogen coverages at the start of the reaction are equal to the equilibrium hydrogen coverages. After the start of the reaction the hydrogen present at the surface of the catalyst is consumed in only a few seconds and, when diffusion limitation of hydrogen governs the reaction rate, the hydrogen coverage will become low. At the end of the reaction equilibrium

Figure 18: Hydrogen coverage as a function of the partial hydrogen pressure. Solid line: when all benzene is converted. Dotted line: at the start of the hydrogenation reaction.

Figure 19: The temperature of the fluids during the partial hydrogenation of benzene. Starting conditions: 0.5 g catalyst, 150 ml water, 200 ml benzene, 2.4 g iron sulfate, $P_{total}=5.0$ MPa.
will be reached again. In Figure 18 the hydrogen coverages are shown after the start and at the end of a hydrogenation reaction at hydrogen pressures up to 7 MPa. The hydrogen coverage after the start of the reaction is nearly constant above 2 MPa and, therefore, it can be assumed that the relative selectivity, see equation (28), is nearly constant. The influence of hydrogen on the selectivity is rather small, but based on the model no increase is expected.

**Consequences of the heat production**

Until now no attention has been paid to the heat production and the heat transfer. The heat, produced during the hydrogenation of benzene, can result in a temperature increase of the catalyst, the fluids and the reactor. In Figure 19 the temperature of the fluids is given during the hydrogenation reaction. It can be seen that in only 4 minutes a temperature rise of 25 K is established. The heat is produced at the external surface of the catalyst and, therefore, the temperature of the catalyst surface, $T_{\text{catalyst}}$, has to increase. Due to this temperature raise the cyclohexene selectivity and yield could be increased.

The heat production, $\Phi_{w,\text{prod}}$, is equal to:

$$\Phi_{w,\text{prod}} = r_{\text{obs}} \cdot -\Delta H_r$$  \hspace{1cm} (41)

$r_{\text{obs}}$ = observed reaction rate \hspace{3.5cm} (mol/s)

$-\Delta H_r$ = reaction enthalpy \hspace{3.5cm} (kJ/mol)

The heat dissipation, $\Phi_{w,\text{dis}}$, from the catalyst to the bulk fluid is equal to:

$$\Phi_{w,\text{dis}} = \alpha \cdot A_{ls} \cdot (T_{\text{catalyst}} - T_{\text{bulk}})$$  \hspace{1cm} (42)

$\alpha$ = heat transfer coefficient \hspace{3.5cm} (W/m$^2$/K)

$T_{\text{catalyst}}$ = surface temperature of the catalyst \hspace{3.5cm} (K)

$T_{\text{bulk}}$ = temperature of the bulk fluid \hspace{3.5cm} (K)

When $\Phi_{w,\text{prod}} = \Phi_{w,\text{dis}}$, combination of equation (40) and (41) gives:

$$(T_{\text{catalyst}} - T_{\text{bulk}}) = -\frac{r_{\text{obs}} \cdot \Delta H_r}{\alpha \cdot A_{ls}}$$  \hspace{1cm} (43)
The reaction enthalpy is around 200 kJ/mol, the observed reaction rate for the hydrogenation reaction carried out at 7 MPa and 443K is 2.2 mmol/s, the $A_{ke}$ equals 0.035 m². Data of heat-transfer coefficient $\alpha$ is limited. Values varying from $10^2$ to $10^4$ W/m²/K can be derived from literature [30, 31]. The value is dependent on operating conditions and type of catalyst; a value of $10^3$ W/m²/K seems to be a reasonable choice, but one has to keep in mind that higher values are also reasonable. This means that the temperature difference between the catalyst and the fluid can be up to 10-15 K. In Table 4 the temperature differences for the experiments carried out at different hydrogen pressures and at constant bulk fluid temperature are listed. Because of the high hydrogenation rate the temperature of the catalyst will be higher than in the bulk fluid. The temperature influences both the adsorption equilibrium and reaction constants remarkably. And, therefore, a change in selectivity cannot be ruled out. Tentatively, the conclusion can be drawn that the selectivity increase is mainly determined by the temperature increase of the catalyst particles, when the reaction is carried out at higher pressures. This observation is also confirmed by the cyclohexene hydrogenation experiments described in Chapter 4. When the temperature was raised during the reaction, the cyclohexene conversion rate declined.

<table>
<thead>
<tr>
<th>hydrogen pressure (MPa)</th>
<th>benzene consumption rate (mmol/s)</th>
<th>Maximum yield (%)</th>
<th>$T_{catalyst} - T_{bulk}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3</td>
<td>0.5</td>
<td>12</td>
<td>2.7</td>
</tr>
<tr>
<td>3.3</td>
<td>1.1</td>
<td>16</td>
<td>6.1</td>
</tr>
<tr>
<td>5.3</td>
<td>2.2</td>
<td>27</td>
<td>12</td>
</tr>
</tbody>
</table>

**Toluene and p-xylene hydrogenation**

As can be seen in Figure 20, the model fits also reasonably for the toluene and p-xylene hydrogenation. In the fitting procedure it was assumed that the adsorption coefficients of toluene and p-xylene are equal to the adsorption coefficient of benzene. For the

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$k_{12}$ (mol/s)</th>
<th>$k_3$ (mol/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>$10 \cdot 10^{10}$</td>
<td>$13 \cdot 10^5$</td>
</tr>
<tr>
<td>Toluene</td>
<td>$3.5 \cdot 10^{10}$</td>
<td>$4.5 \cdot 10^5$</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>$2.4 \cdot 10^{10}$</td>
<td>$0.95 \cdot 10^5$</td>
</tr>
</tbody>
</table>
(partial) hydrogenated products the same assumption have been made. The results for $k_{12}$ in equation (18) and $k_3$ in equation (14) are listed in Table 5.

The value $k_{12}$ declines in the order benzene $>$ toluene $>$ p-xylene. The decline in the rate constants supports the idea that the hydrogenation of the aromatic ring is more prohibited when the ring is substituted: the aromatic ring is stabilized by the methyl groups. The value $k_3$ declines also in the order benzene $>$ toluene $>$ p-xylene, which could also be expected due to the higher yields obtained in the toluene and especially in p-xylene hydrogenation.

The $k_{12}$-value of benzene in Table 5 is much lower than the fitted value in Table 3. The experimental data originate from different experiments. Other amounts of catalyst are used and this can lead to a different response of the reaction system.

### POSSIBLE IMPROVEMENTS FOR HIGHER CYCLOHEXENE YIELDS

It is clear that the model describes the partial hydrogenation quite satisfactory and so the influence of operating conditions on the selectivity and the maximum cyclohexene yield can be estimated. Conditions which can be varied are the physical quantities, like the interfacial areas by influencing the stirring speed or using different amounts of catalyst, and the reaction conditions, like temperature and pressure. The calculations are carried out with the kinetic parameters and reaction conditions listed in Table 3. These parameters fit the data of Figure 3 adequately. In all modelling experiments the reaction is presumed to be isothermal.

#### Variation of the interfacial areas

The hydrogenation reaction is controlled by the diffusion rate of the substrates. The mass-transfer rate can be increased by increasing the interfacial areas between gas and liquid phase, between both liquid phases, or between water phase and catalyst.

The first possibility is to vary the gas/liquid interfacial area, $A_{gl}$, in equation (1).
Variation from 0.0001 to 1000 m² results in an increase of the cyclohexene yield from 0.5% to 23%. The maximum yield obtained in the standard experiment with $A_{gl}=1.8$ m² is 23%. This means that no real improvement can be obtained by increasing the $A_{gl}$. Every value above 1 m² seems to be a proper choice.

When the interfacial area between the organic phase and the water phase, $A_{ll}$ in equation (4), is varied from 0.001 to 1000 the maximum yield of cyclohexene increases from zero to 23%, and the selectivity is 41% at $\xi_{benzene}=0.1$, see Figure 21. In the standard experiment also a maximum cyclohexene yield of 23% is reached with $A_{ll}=2.5$ m². The mass transfer of the organic phase to the water phase is satisfactory in this system.

Increasing the liquid/solid interfacial area, $A_{ls}$ in equation (3) and (5), results in a growth of the maximum yield from 0% to 44% and a maximum selectivity of 90 % is obtained at $\xi_{benzene}=0.1$, see Figure 22. This means that in our reaction system the reaction rate is limited by the liquid/solid mass-transfer and that good results can be obtained when the transfer of the liquid to the catalyst surface will be improved. In Figure 23 both interfacial areas, $A_{ll}$ and $A_{ls}$ are varied. When both areas are sufficiently high, a yield of 46% can be obtained.
Figure 23: The maximum cyclohexene yield as a function of the liquid/solid interfacial area and the area between the water and the organic phase. The spot points to the results of the standard experiment ($T=423 \, K$, $P_{\text{tot}}=5.0 \, MPa$).

Influence of the solubilities

Important parameters in the mass-transfer processes during the benzene hydrogenation are the solubilities of benzene and the hydrogenated products cyclohexene, benzene will preferentially dissolve in the water phase and will be cyclohexene and cyclohexane. Due to the higher solubility of benzene compared to hydrogenated more quickly than cyclohexene. This effect is illustrated in Figure 24, in which the maximum yield as a function of the cyclohexene solubility is depicted. Figure 24 shows that the maximum yield decreases when the solubilities of benzene and cyclohexene become equal to each other. This effect is also important, when diffusion limitations no longer have to be taken into account.

Figure 24: The maximum cyclohexene yield as a function of the solubility factor.
Influence of the hydrogen pressure

The dependency of the maximum yield to cyclohexene on the hydrogen pressure is already discussed above. Nevertheless, when it is possible to keep the catalyst and fluid phases isothermal, it is expected that the selectivity will decrease during the partial benzene hydrogenation. This is confirmed by experimental data of Göbert [7]. In agreement herewith calculations showed a decrease in the selectivity upon increasing the hydrogen pressure.

It should be noted that the time to reach the maximum yield drops significantly at higher pressures. This means that the heat production will be very high and that the temperature of the catalyst and the fluid phases can rise significantly. The selectivity will be strongly influenced. The heat produced during the reaction has to be removed in a very short time to keep an isothermal reaction. When the reaction is carried out adiabatically a temperature rise of more than 450 K is not inconceivable.

Influence of the temperature

In Figure 25 the influence of the temperature at constant hydrogen partial pressures is shown. The calculations have been performed for temperatures up to 550 K. The critical temperature of benzene is 562 K and as a consequence the mechanism can be totally different when this temperature is approached and calculations become irrelevant. The raise in the maximum yield is also shown by the experiments which are described in Figure 6 and Figure 17. The yield levels of at higher temperatures, because at higher temperatures the dehydrogenation is favoured strongly.

It can be stated that, when the reaction is performed at constant hydrogen pressure, the yield increases remarkably when the temperature is raised. This is due to a lower adsorption strength of cyclohexene. It is difficult to describe all effects of the temperature. The temperature influences not only the adsorption coefficients and reaction rate constants, but also the partial hydrogen pressure, the solubilities of hydrogen and aromatics in the water phase, the diffusion coefficients, the interfacial area between gas phase and liquid phase and between both liquid phases, other viscosities, and the equilibrium constants, $K_{12}$ and $K_3$, and last but

Figure 25: The maximum cyclohexene yield as a function of the temperature with a constant hydrogen pressure of 5.0 MPa.
not least the salt adsorption coverage on the catalyst. The salt adsorption is left out in the modelling, due to practical reasons. No data are known about the kinetics and the adsorption/desorption equilibria of the salt adsorption.

Influence of the catalyst performance

Until now the influence of the catalyst has not been discussed in this chapter. At least four aspects will be important, the amount of catalyst, the particle diameter, the adsorption behaviour of the catalyst and the chemical reaction rate constants.

Amount of catalyst and internal diffusion

When the amount of catalyst is enlarged in the hydrogenation reaction simulations, an increase in the reaction rates is expected, but hardly any change in selectivity and yield. The reason for this result is that by a change in catalyst amount, both the transfer rate of the substrates to the catalysts, by an increase of $A_{kg}$, and the chemical reaction rate are changed to the same extent. The adsorption equilibria are not influenced. When the benzene conversion is controlled by external diffusion, a rule of thumb is that also pore diffusion limitation within the catalyst occurs [32]. This effect is not included in the model. The hydrogen reaction rate is in that case equal to:

$$
\eta_2 = \eta_1 \cdot \eta_2 \tag{44}
$$

$$
\eta \quad = \text{effectiveness factor} \quad (-)
$$

The effectiveness factor is defined as the actual reaction rate divided by the rate that would have existed in the absence of pore-diffusion effects. It is presumed that the effectiveness factor of the catalyst is small, $\eta < 1$. In this study it was not considered to be possible to incorporate internal diffusion rates in the modelling. Probably, the conclusions would not be different when this had been done. Of course, in upscaling this has to be taken into account.

Particle diameter

Smaller particle diameters, see Figure 26, will result in a higher cyclohexene yield. By changing the particle diameter the interfacial area $A_{ia}$ is changed. This aspect has already been discussed.
Adsorption strength

When mass-transfer processes do not control the reaction rate, the yield to cyclohexene is only influenced by the adsorption equilibria and chemical reactions on the surface of the catalyst. The affinity to adsorption of the substrates and the (partial) hydrogenated products is strongly influenced by the addition of iron sulfate to the reaction system. The iron cations will probably adsorb on the most strongly bonding ruthenium sites and due to this only the ruthenium sites, which can bond the benzene and cyclohexene molecules weakly, are vacant for the hydrogenation reactions. The influence of the cations is determined mainly by the type of salt, the amount of salt used, and the reaction temperature.

In Figure 27 the maximum yield of cyclohexene is depicted as a function of the change in the adsorption enthalpy. The dashed line shows the change in the cyclohexene yield, when only the cyclohexene adsorption enthalpy is altered. When only the cyclohexene adsorption enthalpy is changed, it should be possible to get 100% yield; the catalyst adsorbs hardly any cyclohexene molecule at all. It seems rather impossible to modify the sites in such a way that only benzene molecules are adsorbed and no cyclohexene molecules. As illustration, when the adsorption energy of cyclohexene is changed with 2 kJ/mol in respect to the one of benzene, the yield changes remarkably from 20% to 30%. As a consequence, precise modification of the
catalyst is very cumbersome. Also when both the adsorption enthalpies of benzene and cyclohexene are changed a beneficial effect can be noticed, solid line in Figure 27.

**Apparent reaction rate coefficients**

Changing the apparent chemical reaction rate constants is possible, but changing the ratio between the $k_{12}$ and $k_3$ is not. As already mentioned in the introduction benzene is step-wise hydrogenated to cyclohexane and the mechanism of each step is presumed to be the same. Blocking sites for the cyclohexene hydrogenation will result in blocking sites for the benzene hydrogenation.

**EVALUATION AND CONCLUSIONS**

With the proposed model the partial hydrogenation of benzene can be described adequately. The selectivity is not only dependent on the adsorption equilibria and hydrogenation rates of individual reaction steps; in this four-phase system the mass-transfer processes influence the yields of cyclohexene. In principle, the adsorption/desorption equilibria on the surface of the catalyst are the most important parameters. When cyclohexene would be strongly adsorbed, all cyclohexene molecules would hydrogenate further to cyclohexane, before they can desorb. The affinity to adsorption of the substrates and the (partial) hydrogenated products is strongly influenced by the addition of salt to the reaction system. The addition of a salt, like zinc or iron sulfate, is inevitable to obtain high yields in cyclohexene [3]. In this study iron sulfate has been used. Due to the iron cations the surrounding of the catalyst is totally altered. The catalyst will become more hydrophilic. It is believed that the adsorption coverage of the organics are a function of the iron coverage, and the iron coverage on the catalyst is determined mainly by the amount of iron available in the aqueous solution and the temperature. The cations of the salts will adsorb probably on the most strongly bonding ruthenium sites and due to this adsorption only the ruthenium sites which can bond the benzene and cyclohexene molecules weakly, are vacant for the hydrogenation reactions [5]. As shown in Figure 23, a small change in the adsorption enthalpies influences the selectivity remarkably. It could be possible that the iron ions form a complex with the cyclohexene molecules. The enthalpy of the bonding between ethanol and cyclohexene varies between -3 to -5 kJ/mol at a temperature of 298 K [33] and the bonding enthalpy of iron and cyclohexene could be in the same order. But, there is no evidence in the literature that a complex will be formed at temperatures at 423 K.
Another parameter which can influence the adsorption equilibria is the temperature. From experiments carried out by Schoenmaker-Stolk [34], it is known that the hydrogenation rate of cyclohexene over ruthenium, even at very low temperatures, is high and hence the apparent activation energy is very low. The activation energy of the desorption step is higher, and an increase in temperature should increase the selectivity to cyclohexene considerably. This aspect is also supported by the results described in Chapter 4. Nevertheless, a further increase in the temperature will also have a negative effect. The dehydrogenation reaction is endothermic and will be propagated by an increase of the temperature. It can be concluded that an optimum in the temperature has to be found.

The most important effect of the water layer is not the diffusion limitation of hydrogen, but the selective 'permeability' for the organics. Because of the higher solubility of benzene in water, benzene will diffuse more quickly to the catalyst, than the produced cyclohexene and in this way benzene will be hydrogenated preferentially in comparison with cyclohexene. Due to the water barrier accumulation of cyclohexene in the organic phase is possible. It can be concluded from Figure 20, that the yield would be a factor 2.5 lower, when benzene and cyclohexene would have the same solubility in water. The difference in solubility of benzene and cyclohexene favours the cyclohexene yield. Solubility data have been extrapolated to the used standard conditions. Measurements of the solubilities of the components in water at the standard conditions should be performed. It is also known that the solubility of a component is changed by the addition of salts [21] and also this phenomena has to be investigated.

From the modelling results it can be concluded, that the yield would be higher, when the rate of reaction is not controlled by diffusion limitation. As can be seen from Figure 18, not the transfer of the gas or organic phase to the water phase, but the mass transfer of benzene and hydrogen in the water phase to the solid catalyst has to be enlarged. There are two possibilities to realize this, either the liquid/solid interface $A_{ls}$ or the mass-transfer coefficient $k_{ls}$ can be increased. The mass-transfer coefficient is determined by the reaction system and cannot be changed. To increase the liquid/solid interface, only the amount of catalyst can be changed or the particle diameter. The influence on the yield is expected to be small when the amount of catalyst is changed, but in the model the effect of pore diffusion limitation has not been taken into account. Internal diffusion limitation will always lead to reduced selectivities. Therefore, a microporous texture is unfavourable and meso/macroporous catalysts are optimal. Altering the particle diameter can be effective, when the catalyst become more macroporous.
One of the basic improvements in a reaction system, which is diffusionally controlled, is increasing the stirring rate. The stirring rate influences the mass transfer rate of the gas phase to the liquid phase and from the organic liquid phase to the water liquid phase and not the transfer in the water liquid phase to the catalyst. For this reason, improvement of the partial hydrogenation of benzene in a four-phase system is limited in a stirred batch reactor. According to Struijk et al. the catalyst particles are crushed at higher stirring rates [4]. The consequences of the crushing is discussed above.

As shown by the simulations it is very important to know more about the adsorption processes of the organics at the surface of the catalyst. To develop a better system it is necessary to understand and to quantify the effect of parameters, which influence the adsorption equilibria, like temperature, additives, and catalyst preparation methods.

Finally, it will be very important to investigate the influence of the temperature on the cyclohexene selectivity, and as a consequence also the heat-transfer effects. It is remarkable that the cyclohexene selectivity increases when the hydrogen pressure is raised.

Two explanations can be given. Firstly, a higher hydrogen coverage influences the cyclohexene adsorption strength; this is unlikely due to the low concentrations of hydrogen and organics in the water phase. In Table 6 the estimated hydrogen concentrations in the gas phase and the water phase are given at the applied reaction conditions. Secondly, an increased cyclohexene desorption rate is established by an increase of the temperature of the catalyst particles. It should be noted, to the best of our knowledge, that the last explanation has never been observed earlier in slurry-phase reactions and probably the heat-transfer coefficients are clearly underestimated. Nevertheless, the heat effects during the benzene hydrogenation reaction is a point of concern and further research on this topic is necessary.

<table>
<thead>
<tr>
<th>Table 6: Estimated hydrogen concentration in the water phase and the gas phase at 4 MPa hydrogen pressure and T=423 K.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen concentration (mol/m³)</td>
</tr>
<tr>
<td>Gas phase</td>
</tr>
<tr>
<td>Water phase</td>
</tr>
</tbody>
</table>

In conclusion, the model can be improved at several points, but this is only useful when the reaction system is understood at a much more detailed level. Determinations of adsorption equilibria in combination with catalyst preparation methods, solubility data and basic reaction kinetics are desired. Up to now the used model is satisfactory and the aim to get more insight into the optimum conditions and possibilities for the partial hydrogenation of benzene is realized.
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Modelling of the partial hydrogenation of aromatics
Chapter 8

Process development and future outlook

Process development

The production of cyclohexene

It has been shown that it is possible to prepare cyclohexene by partial hydrogenation of benzene. In this thesis maximum cyclohexene yields up to 30% are reported, but, on the basis of the results from other researchers, it can be stated that in practice maximum yields up to 60% are possible. A process scheme which can be used for the production of cyclohexene is depicted in Figure 1.

![Diagram](image)

Figure 1: Process scheme for the production of cyclohexene: R1 = Hydrogenation of benzene to cyclohexene and cyclohexane; R2 = Dehydrogenation of cyclohexane to benzene; S1 = Separation of gaseous, organic, and aqueous phase; S2 = Separation of cyclohexene from the organic phase.

Process development and future outlook
Hydrogenation of benzene to cyclohexene and cyclohexane (R1)

The first question is which type of reactor is optimal. The reaction has to be performed at a temperature between 403 K and 453 K and at a total pressure between 3.0 MPa and 9.0 MPa. On a laboratory scale a stirred autoclave is very convenient. Scaling up of such reactors is troublesome, for instance, due to poor heat removal. The system comprises a continuous aqueous phase, having the catalyst particles suspended therein; an organic phase, and a gaseous phase containing hydrogen gas, water vapour, and benzene vapour. To prevent gas/liquid mass-transfer limitation high shear rates are necessary, by which the interfacial area is enlarged. Also liquid/liquid mass-transfer limitation has to be prevented. The reaction requires good mixing conditions resulting in a high energy input.

Yamashita et al. [1] studied different reactor systems. A good dispersion was shown to be essential to obtain high selectivities and yields. Therefore, in a stirred tank reactor the use of baffles can be required. They observed that the use of two tank reactors in series yields higher selectivities in a continuous process. The reason is that the concentration of benzene can be maintained at a maximum level, thereby facilitating the formation of cyclohexene, and further conversion of cyclohexene is held down. The effect of two or more tanks in series could also be obtained by using a reactor which is partitioned into a plurality of chambers so that each chamber contains a stirring blade set and baffles. Another possibility is the use of a bubble reactor, but in this case it is almost impossible to obtain a good dispersion of hydrogen gas in the liquid phases and mixing of the organic and aqueous phase. Slugging will occur and, therefore, good operation seems to be troublesome. By use of a jet loop reactor a good dispersion of hydrogen gas in the liquid phase and proper mixing of the two liquid phases could be obtained [2]. The use of such a reactor seems to be attractive.

Separation of gaseous, organic, and aqueous phase (S1)

After reaction the desired product cyclohexene has to be isolated. Firstly, the organic phase has to be separated from the gaseous phase and the water phase, which contains the solid catalyst particles. When the reaction mixture is allowed to
stand still in a stationary zone of the reactor, the gas phase will be separated from
the liquid phase and, furthermore, the organic droplets are caused to ascend thereby
forming a continuous organic phase as an upper layer and a continuous aqueous
phase as a lower layer in the stationary zone. Then, the continuous organic phase can
be withdrawn by an outlet pipe and the continuous aqueous phase will descend due
to its specific gravity and will be mixed up again in the reactor [1].

However, when the separation is carried out at high hydrogen pressures, a
relative large amount of hydrogen will dissolve in the liquid phases. Therefore, it is
to be preferred to perform the separation outside the reactor at a low pressure: the
reaction mixture has to be flashed. Afterwards, a gas/liquid separator and an
organic phase/aqueous phase separator can be used. It is desirable that the liquid
introduced from the gas-liquid separator to the organic phase/aqueous phase
separator contains no gas bubbles. The catalyst particles can be swept away to the
organic phase due to the raising gas bubbles.

It has to be noticed that the time to reach complete separation of the different
phases, will be larger when the dispersion in the hydrogenation reactor is higher.
The dimensions of the settler have to be adapted to the conditions in the
hydrogenation reactor.

*Separation of cyclohexene from the organic phase (S2)*

The organic phase contains cyclohexene, cyclohexane, and the unreacted
benzene. Their boiling points are very close (at atmospheric pressure 356 K, 354 K,
and 353.3 K, respectively) and, therefore, it is difficult to isolate cyclohexene from the
organic phase by simple distillation. Extractive distillation can advantageously be
used for isolating cyclohexene. In extractive distillation, a solvent, in which one of
the organics is more soluble than the other, is introduced close to the top of and
extraction column. The solvent extracts one of the organics and passes from the
bottom of the column to a second column where the organic is separated from the
solvent as a distillate. Appropriate solvents can be adiponitrile, sulfolane, dimethyl
malonate or dimethylacetamide.

*Dehydrogenation of cyclohexane to benzene (R2)*

The dehydrogenation of cyclohexane can be performed over a platinum catalyst.
At atmospheric pressure the thermodynamically attainable conversion is essentially
100% at temperatures above 620 K [3]. At higher pressure much higher temperatures
are required for high conversions. However, to prevent coke formation,
dehydrogenation in the presence of hydrogen is preferred. Therefore, the
dehydrogenation is operated at 800-900 K and a pressure of 3 MPa.

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The production of cyclohexanol via cyclohexene

Cyclohexene has no direct use on a large scale; it can be an intermediate for other chemicals; the most important application being the production of cyclohexanol. A The cyclohexene production was integrated in a study for the production of cyclohexanol. A process by which cyclohexanol (total production 50 kton/year) is formed by hydration of cyclohexene might be an option [4]. In this study it is assumed that a maximum cyclohexene yield of 45% is possible at a temperature of 423 K and a total pressure of 5.0 MPa. Before the hydration of cyclohexene is performed, cyclohexene is isolated by extractive distillation with dimethyl malonate. The cyclohexene hydration is performed over a ZSM-5 catalyst at a temperature of 393 K and a total pressure of 0.5 MPa. It is assumed that in this reaction a selectivity >99% can be obtained at 10% conversion. The low conversion leads to a large recycle, but the product selectivity is high. Disadvantage of this process is the high energy input necessary for extractive distillation [4]. A cost price of Dfl.2.7 per kg cyclohexanol has been calculated, while the market price is approximately Dfl.2.7-3.0 per kg [5]. The cost price of the starting material benzene is Dfl.0.40 per kg [5].

To by-pass the cyclohexene separation step, which wastes energy, selective reaction of cyclohexene out of the organic phase to a desired product and afterwards distillation might be more attractive. Hydration to cyclohexanol is once again a possibility, but also esterification with acetic acid to cyclohexyl acetate is an option, e.g. over an Amberlyst-15 catalyst at 363 K and a pressure of 0.5 MPa is an option [6]. After distillation cyclohexyl acetate can be hydrolyzed to cyclohexanol and acetic acid. A preliminary study of Van der Berg et al. showed that this process is economically not viable at a total production of 5 kton/year [7]; a cost price of Dfl 4.5 per kg cyclohexanol has been calculated. At first sight this price might be considered to be too high, but it can be supposed that the cost price will be reduced when the production is enlarged.

From the above it can be concluded that the production of cyclohexanol via cyclohexene is economically competitive to commercial processes. The two studies, which have been discussed above, are both performed as a stand-alone operation. When the cyclohexanol production plant is integrated within a refinery the economic evaluation will be more favourable. Asahi Chemical Industry in Japan have commercialized this process in 1991, total production 60 kton/year [8].
Figure 3: Flow sheet for the production of cyclohexanol via the partial hydrogenation of benzene.

On the basis of the discussion above and the results reported in this thesis the flow sheet presented in Figure 3 is proposed. The benzene is hydrogenated in two consecutive reactors. After hydrogenation the phases are separated at low pressure in a gas/liquid and a liquid/liquid separator. The gas phase is recirculated and to prevent a build-up of products like methane in the gas phase, the gas stream is vented partly. The water phase including the catalyst is recirculated to the hydrogenation reactors. It might be possible that the catalyst particles have to be regenerated.

By reactive distillation it is possible to convert cyclohexene selectively to cyclohexanol and to isolate simultaneously cyclohexanol. From the bottom of the reactor a cyclohexanol/water mixture will be isolated and an additional distillation step is necessary. The low-boiling organic fraction will come over the top of the column and is led over a dryer to remove remaining amounts of water.

After drying, the low-boiling organic fraction is led through a reformer. In this reformer the produced cyclohexane will dehydrogenate to benzene. In the described processes no attention has been paid to the presence of small amounts of by-products, like methylcyclopentane, n-pentane, cyclopentene, and n-hexane, but in Chapter 4 it is shown that during one batch-cycle ~0.9% of the benzene is converted.
to these products. When these by-products are recycled to the hydrogenation reactor after distillation, a build-up to a steady-state level in the reactor will occur. This can influence the performance in the partial hydrogenation. These products have to be excluded from the process. Reforming to benzene will be a possibility, but will be troublesome for by-products like n-pentane and methane. The dehydrogenation of cyclohexane and the reforming of by-products are processes which should be easily integrated in a refinery plant.

FUTURE OUTLOOK

The following statement is published recently by Döbert and Gaube [9]:

"The history of catalyst development for the partial benzene hydrogenation reminds to old days of alchemy."

This thesis is a contribution to the knowledge about the development of ruthenium catalysts for the partial hydrogenation of benzene. Nevertheless, some questions still remain unanswered and new questions have been arisen. One of the most important conclusions of this thesis is that the partial hydrogenation of benzene in a four-phase reaction system is very complicated.

In Chapter 2 of this thesis a new method for the reduction of the catalyst is proposed, but further optimization of the catalyst preparation is possible. An additional reduction of the catalyst particle in a stream of hydrogen at elevated temperatures showed to have a beneficial influence on the cyclohexene selectivity, see Chapter 3. This additional reduction step has not been investigated extensively. When more is known about the effect of pore diffusion limitation on the cyclohexene selectivity it should be possible to prepare a tailor-made catalyst.

Another topic for further research is the study of the influence of the modifiers on the adsorption/desorption equilibria of the substrates and the products. To develop a good kinetic model it will be necessary to know more about the adsorption/desorption processes. In line with this, the solubilities of the substrates and products in water at the applied conditions have to be investigated. Also the influence of modifiers on the solubilities have to be taken into account because of ‘salting-in’ and ‘salting-out’ effects [10]. Alternative methods for the use of modifiers would be very desirable. Opportunities to improve the model presented in Chapter 8 are present.
A very interesting phenomenon in the partial benzene hydrogenation is that the cyclohexene selectivity increases when the pressure is raised. In Chapter 8 several explanations are given for this effect. One of the reasons given for this phenomenon is the heat-transfer limitation from the catalyst surface to the bulk fluid. In gas-phase hydrogenation reactions this effect is observed commonly, but in general not in liquid-phase hydrogenation reactions. Due to the very exothermic hydrogenation reaction and the high reaction rates it is however difficult, if not impossible, to perform the reaction at a constant reaction temperature. Calculations showed that heat-transfer limitation might take place. At first sight this result is surprising and, for this reason, the conversion rates, expressed in moles substrates converted per gram catalyst per second, of several industrial related reactions are compared. The rates are depicted on a logarithmic scale in Figure 4. It is clear that the benzene conversion rate is relatively high. Therefore, it is well conceivable that also during the benzene hydrogenation warming-up of the catalyst particles can occur, although in general it is found that in liquid/solid catalyst reactions this does not take place. In Chapter 4 and 8 it is shown that the selectivity of the catalyst increases when the temperature is raised. More research has to be carried out to elucidate this phenomenon. Heat-transfer coefficients should be determined and, if possible, the temperature of the catalyst particles during the benzene hydrogenation should be measured directly.

\[ \text{EO} = \text{Ethene epoxidation} \]
\[ \text{Wacker} = \text{Wacker oxidation of butene} \]
\[ \text{HDS} = \text{Hydrodesulfurization of gasoils} \]
\[ \text{HDM} = \text{Hydrodemetallization of nickel and vanadium in crude oil} \]
\[ \text{CH}_4 = \text{Carbon dioxide reforming of methane} \]
\[ \text{FCC} = \text{Fluid Catalytic Cracking} \]
\[ \text{CFC} = \text{Catalytic conversion of CFC-12} \]
\[ \text{BALD} = \text{Selective hydrogenation of benzaldehyde over a Ni-monolith} \]
\[ \text{PHB} = \text{The partial hydrogenation of benzene} \]

**Figure 4:** Window of catalyst activities for different commercial or in development stage processes. Source: Industrial Catalysis group Delft University of Technology.
From the process studies it is clear that a three-phase system for the partial hydrogenation of benzene has some benefits. The mixing in the reactor would be much easier and reproducibility might well be improved. Recently, Döbert and Gaube have developed a new method for measurement of reaction rates in a continuously operated slurry reactor in the absence of a liquid benzene/cyclohexene phase [9]. The vapour pressure of the hydrocarbon mixture is kept below the saturation vapour pressure. A gas flow consisting of benzene, nitrogen, and hydrogen was led through an aqueous zinc chloride solution, which contained a Ru/La$_2$O$_3$ catalyst. Cyclohexene selectivities up to 60% were achieved at a benzene conversion rate of 0.02 mmol/s/g$_\text{cat}$. The selectivity is comparable with the initial selectivities of the reaction systems described in this thesis, but the activity is considerably lower. Based on this reactor concept, a monolith reactor can also be of interest to develop a three-phase system. A monolith consists of a large number of parallel channels. The channel walls can be covered with a thin layer of a hydrophilic porous oxide, which will serve as the catalyst support. When water is pumped through the monolith a homogeneous water layer with variable thickness can be established over the catalyst layer. When this can be realized a benzene/hydrogen gas mixture can be led through the monolith. Advantages are a low pressure drop, a large external surface area, and the benzene/hydrogen ratio in the gas phase can be regulated very easily. It will be very important that the total surface of the monolith will be wetted by the water liquid phase. If not, formed cyclohexene will be further hydrogenated very easily.

From both a scientific and industrial point of view the partial hydrogenation is interesting. Opportunities for further research are present and when the yield to cyclohexene can be enlarged the partial benzene hydrogenation will be an elegant route for the production of a broad range of chemicals.
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Samenvatting

In de scheikundige technologie staat de ontwikkeling van nieuwe en de verbetering van bestaande chemische producten en/of processen centraal. Belangrijke drijfveren voor onderzoek zijn naast het economische belang (lagere productiekosten), ook veiligheid en zorg voor het milieu.

Dit proefschrift beschrijft de partiële hydrogenering van aromaten, en in het bijzonder die van benzeen. Aromaten hebben een welriekende geur en de molekuulstructuur bevat 'een ring met dubbele bindingen'. Bij een hydrogeneringsreactie worden waterstofatomen aan de molekuulstructuur toegevoegd en daarbij worden 'dubbele' bindingen omgezet in een 'enkele' binding. Bij de partiële hydrogenering van benzeen wordt dan cyclohexeen gevormd. Cyclohexeen kan als basisgrondstof dienen voor andere chemische stoffen, bijv. Nylon. Het huidige proces voor de bereiding van Nylon kent als nadeel dat bijproductvorming gemakkelijk kan optreden en in het verleden zijn herhaaldelijk ernstige ongelukken gebeurd bij dit proces. De veiligheid van het proces is inmiddels sterk verbeterd, maar een alternatief proces, welke mogelijk gebaseerd is op cyclohexeen, is nog steeds zeer aantrekkelijk.

Het bereiden van cyclohexeen vanuit benzeen is echter geen gemakkelijke opdracht. Benzeen kan tot cyclohexeen gehydrogeneerd worden, maar bij deze reactie wordt bij voorkeur cyclohexaan gevormd. Dit is eenvoudig voor te stellen. Benzeen bevat drie dubbele bindingen, zoals te zien is in het onderstaande reactieschema.

\[
\text{Benzeen} \quad 2 \text{H}_2 \quad \text{Cyclohexeen} \quad \text{Cyclohexaan} \quad \text{Waterstof}
\]

Voor de vorming van cyclohexeen is het alleen nodig om twee van de drie dubbele bindingen om te zetten. Wanneer de reactie echter eenmaal loopt dan is de drijvende kracht om de derde binding om te zetten enorm groot en dat betekent dat cyclohexaan wordt gevormd. Ter vergelijking: wanneer je een grote bal van de trap af laat rollen, is de kans dat deze op een van de treden blijft liggen erg klein. Vrijwel altijd rolt de bal helemaal naar beneden.

Al vanaf het begin van deze eeuw zijn onderzoekers met de hydrogenering van benzeen bezig geweest. Om de reactie te laten verlopen bleek dat een katalysator
noodig is. (Wanneer de bal boven aan de trap ligt moet deze eerst een zetje krijgen voordat die naar beneden rollt.) Een katalysator kan ervoor zorgen dat de reactie gemakkelijk verloopt. Vrijwel iedere chemische reactie heeft zijn eigen katalysator. De optimale katalysator is die stof die ervoor zorgt dat de reactie relatief snel verloopt (=activiteit) en dat de gewenste producten worden gevormd (=selectiviteit). Verder dient de werking van de katalysator niet te veranderen bij gebruik (=stabiliteit).

Een rutheniumpkatalysator is zeer geschikt voor de hydrogenering van benzeen. Wanneer benzeen en waterstof over deze katalysator geleid worden, ontstaat alleen cyclohexaan. Wanneer echter een oplossing van zinksulfaat (= een zout) in water aan het benzeen wordt toegevoegd, blijkt dat het gewenste product cyclohexeen gevormd wordt. Verschillende onderzoekers hebben geprobeerd de selectiviteit naar cyclohexeen te verbeteren, door andere reactiecondities (d.w.z. temperatuur, druk, type zout) te kiezen of de structuur of samenstelling van de katalysator te veranderen.

In het onderzoek naar de bereiding van cyclohexeen met rutheniumpkatalysatoren bleek dat het moeilijk was om resultaten van andere onderzoekers goed te reproduceren. Onlangs schreven twee Duitse onderzoekers: “de bereiding van rutheniumpkatalysatoren voor de partiële hydrogenering van benzeen doet ons herinneren aan de tijden van alchemie!” Waarom? Doel van mijn onderzoek was daarom te achterhalen waarom de reproduceerbaar niet goed was. Verder was het doel de opbrenst aan cyclohexeen te vergroten en een antwoord te formuleren op de vraag waarom cyclohexeen gevormd kan worden. De resultaten van het onderzoek zijn in dit proefschrift beschreven.

In Hoofdstuk 1 wordt een inleiding gegeven over de katalytische hydrogenering. Er wordt verder ingegaan op de toepassingen van aromaten en (methyl-)cyclohexenen, het mechanisme van de katalytische benzeenhydrogenering, de thermodynamica en een uitgebreid, maar niet compleet, overzicht wordt gegeven van resultaten in het verleden op het gebied van de partiële benzeenhydrogenering. Het blijkt dat hoge opbrengsten mogelijk zijn wanneer de reactie wordt uitgevoerd over een rutheniumpkatalysator die gedispergeerd is in een waterige zoutoplossing. De hydrogenering dient dan bij voorkeur uitgevoerd te worden bij temperaturen variërend van 120 tot 180 °C en bij totaaldrukken variërend van 30 tot 80 bar.

In Hoofdstuk 2 wordt uitvoerig ingegaan op de katalysatortbereiding en de uitvoering van de hydrogeneringsreacties. Diverse maatregelen zijn getroffen om externe factoren die de katalysator en de testreactie beïnvloeden in beeld te krijgen en daarna uit te sluiten.

Om een goed beeld te kunnen krijgen van het reactiemechanisme is een goede beschrijving van de katalysator vereist. De resultaten van diverse karakteriserings-
technieken, welke gegeven zijn in *Hooftstuk 3*, laten zien dat de textuur van de katalysator complex is. De katalysator is opgebouwd uit rutheniunkorstallieten met een doorsnee van ongeveer 5 nm. Het bouwwerk van rutheniunkorstallieten heeft een gemiddelde doorsnee van ongeveer 25 μm en vertoont sterke gelijkenissen met een kaartenhuis. De textuur kan gemakkelijk verstoord worden. De hydrogeneringsreactie moet in een waterig zoutoplossing uitgevoerd worden. Het blijkt dat een gedeelte van het zout geadsorbeerd wordt door de katalysator. Daardoor blijven de katalysatordeeltjes in de waterfase en komen niet in de organische fase. Dit heeft een gunstig effect of de selectiviteit naar cyclohexeen.


Aangezien de reactie in de waterfase plaatsvindt, spelen de oplosbaarheden van de uitgangsstoffen benzeen en waterstof en van de producten cyclohexeen en cyclohexaan een rol in de reaktiekinetiek en de selectiviteit. Om dit te verifiëren is ook de hydrogenering van tolueen en p-xyleen bestudeerd, waarvan de resultaten beschreven worden in *Hooftstuk 5*. Uit de resultaten blijkt inderdaad dat de oplosbaarheden van belang zijn.

De textuur van de rutheniunkatalysator is niet stevig en daarom is geprobeerd het rutheniun aan te brengen op een drager. Een bijkomend voordeel kan zijn dat wanneer de drager hydrofiel is, de katalysator zich direct in de waterfase zal bevinden en het gebruik van zout niet meer noodzakelijk is. Verschillende dragermaterialen zijn geprobeerd en een verhoogde cyclohexeenselectiviteit werd gevonden bij hydrofiel macroporeuze katalysatoren. De selectiviteit naar cyclohexeen kon bij de gedragen katalysatoren nog vergroot worden, wanneer een zout aan de waterfase werd toegevoegd. Dit geeft aan dat het geadsorbeerde zout niet alleen zorgt voor het hydrofiel worden van ongedragen katalysatoren, maar dat het ook het oppervlak zodanig kan modifieren dat cyclohexeen minder snel zal doorreageren naar cyclohexaan. Het bleek dat ook organische additieven gebruikt konden worden om de selectiviteit naar cyclohexeen van gedragen rutheniun-katalysatoren te vergroten. De resultaten van het gebruik van gedragen katalysatoren bij de partiële benzenehydrogenering worden beschreven in de *Hooftstukken 6 en 7*.

In *Hooftstuk 8* wordt een overzicht gegeven van de reactiveregelkingen en massatransportregelkingen die van belang zijn om de kinetiek van de partiële
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hydrogenering goed te beschrijven. Een model is geschreven, waarin deze vergelijkingen zijn geïntegreerd. Met behulp van het model konden verkregen data goed beschreven worden en kon bijvoorbeeld de invloed van temperatuur op de cyclohexene selectiviteit voorspeld worden. Het model maakt duidelijk dat kleine verschillen in de adsorptie-energieën van de substraten en producten (~2 kJ/mol), een groot verschil in de cyclohexeenopbrengst kan betekenen. Kleine verschillen in de bereiding van de katalysatoren of de uitvoering van de hydrogeringsreactie kunnen daarom een totaal andere selectiviteit geven.

Zoals genoemd kan cyclohexeen gebruikt worden voor de productie van andere chemicaliën. In Hoofdstuk 9 wordt ingegaan op de mogelijke productie van cyclohexeen via de partiële hydrogenering van benzeen. De productie van zuiver cyclohexeen is economisch gezien niet rendabel vanwege de moeilijke benzeen/cyclohexeen/cyclohexaan scheiding. Indien cyclohexeen in een eventuele vervolgstap in het proces direct kan doorreageren en niet eerst geïsoleerd hoeft te worden zal het proces economisch gezien interessanter zijn. Cyclohexanol is gemakkelijk van benzeen/cyclohexaan te scheiden en daarom wordt een productieproces waarin cyclohexeen direct doorreageert naar cyclohexanol beschreven en geëvalueerd. Een dergelijk proces lijkt economisch gezien concurrerend te kunnen zijn met bestaande processen. Verder onderzoek naar de partiële hydrogenering van benzeen is vanuit dit oogpunt nodig en daarom wordt in Hoofdstuk 9 een aantal voorstellen gedaan voor verder onderzoek.
Een woord van dank.....

.....aan al die mensen die in de afgelopen jaren een bijdrage hebben geleverd aan de totstandkoming van dit proefschrift. Velen hebben op de een of andere manier wel hun steentje bijgedragen. Een dankwoord betekent terugkijken op vijf jaar onderzoek. Wanneer je terugblikt komen dezelfde randverschijnselen naar voren die je ook aantreft bij een sportwedstrijd.

Ruim vijf jaar geleden werd het beginsignaal gegeven. Jaap Struijk had al voorbereidend werk gedaan en maakte mij duidelijk wie de tegenstander was, welke hulpmiddelen je kon gebruiken en wat het doel was. Jaap, bedankt voor je steun en betrokkenheid bij het werk. Met veel plezier kijk ik terug naar die tijd en naar de discussies en gesprekken die we toen hebben gevoerd.

Een aantal afstudeerders kon ik als medespeler begroeten. Emile van de Sandt, Martin Smith, Alexander Eulenpesch en Ron Dhauri, er is door jullie hard gewerkt. Bedankt voor jullie inzet. Ook de researchpracticanten Johan Goudzwaard en Stefan Musch moet ik bedanken voor hun bijdrage. Ook jullie inzet was prima.

Een bijzonder medespeler was Andrzej Cybulska. Andrzej, jouw kennis en ervaring hebben zeer goed geholpen. Bedankt.

Prestaties kunnen geleverd worden wanneer het speelmateriaal en de verzorging goed is. Daarom een woord van dank aan: de bibliotheek die ervoor zorgde dat de ‘spelregelkennis’ op peil bleef, het O&O-lab en Materiaalkunde voor de analyses van de ‘tegenspeler’, de instrumentmakerij voor de hulp bij de vele ‘blessures’, de glasblazerij voor het nodige glaswerk, Bart Boshuizen voor de data-acquisitie en data-verwerking, Jan Smit voor de kopietjes, Theo Hunnego voor de broodnodige chemicaliën, Dolf Pruisken voor het kunnen werken op het hoge-druk lab en tot slot Thom van Velzen die niet alleen voor wat extra pressie zorgde, maar ook voor de doping (=koffie+taart).

Zonder sponsoring is het vrijwel niet meer mogelijk om een goede prestatie neer te zetten. Daarom wil ik Frank van den Brink, Andrzej Stankiewicz, Ruud van Hardeveld en Wim Glasz van DSM Research in Geleen van harte bedanken. Bedankt voor de sponsoring, maar ook voor het meedenken en meedoen.

Als tweede, dr. ir. M. Makkee. Michiel, je lette niet alleen op de punten en de komma’s, maar ook op een eerlijke weergave van de feiten en je gaf het onderzoek een extra dimensie met je eigen industrial point of view.


Dan blijft er nog een groep van mensen over die op een heel andere manier hebben meegewerkt: de toeschouwers. Hierbij denk ik eerst aan de toeschouwers die heel dicht op het veld zaten: André, Emile, Koen, Niek, John, Ronald, Anja, Ahmed, Jan-Baptist, Jean-Paul, Jan-Remmert, Mark, Annelies, Wridzer, Guido, Xander, Rob, Bastiaan, Freek, Dick, Sytze, Adriëtte, Jolinde, Hank, Marco, Maurice, Xiao Ding, Qwen, Marion, Theo, Paul, Gerard, Bas en ..... nog vele anderen. Jullie zorgden niet alleen voor een continue evaluatie van het ‘katalyse’-spel maar ook voor vele zeer plezierige randverschijnselen. Bedankt!

Er waren nog veel meer toeschouwers die belangstellend toekijken en enthousiast aanmoedigen. Wat verder van het speelveld, maar zeer zeker aanwezig. Vrienden, vriendinnen en familieleden, bedankt voor jullie aandacht en aanmoedigingen!

Tot slot nog een zeer belangrijke toeschouwer. Nynke, bedankt voor je steun en ik hoop dat we in de toekomst meer tijd met elkaar zullen doorbrengen.

De tegenstander is taai. Het kost moeite om door de verdediging heen te komen, maar toch...., het lukt! En dan klinkt het eindsignaal: Hora est! Promotie!!


Matthys
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