## Abstract

This project treats the subject of development of microsystems for hydrogen production. The aim of the project is to determine a new catalyst incorporation method for microreactors and investigate hydrogen producing reactions using these microsystems.

Initially a description of the theory behind three hydrogen producing processes is given. The processes are steam reforming, partial oxidation, and ammonia decomposition. In particular ammonia decomposition is explained, as it is the preferred hydrogen source.

The microreactor, anodic bonding, and the experimental setup for partial oxidation of methane and ammonia decomposition is presented.

For carrying out experiments for both partial oxidation of methane and ammonia decomposition in microsystems, a catalyst incorporating method of the microreactors is determined. The support material is synthesized from water, nitric acid, and boehmite giving aluminum oxide (Al<sub>2</sub>O<sub>3</sub>), which is impregnated with Pd for the partial oxidation experiment and with 1.3% Ru, 1.0% Fe, 0.4% Co, 0.9% Pd, and 1.9% Cu for the ammonia decomposition experiments.

Partial oxidation of methane experiments are performed. The influence of temperature and methane-to-oxygen ratio is investigated, and shows that a temperature above 590°C gives complete conversion of oxygen and a large hydrogen production. It is found that the optimal methane-to-oxygen ratio is 2:1 as expected from the reaction equation.

Ammonia decomposition experiments on the five mentioned catalysts show that Co, Fe, and Ru gave significantly higher ammonia conversion than Pd and Cu. At a temperature of 680°C conversion was 97% on Fe and 88% on Ru. They also show that a low flow gives the largest conversion, but for Co, Fe, and Ru also a lower catalyst activity. To get high activity of Ru the flow should be 8 ml/min ammonia, and higher for Fe and Co. Furthermore, a large ammonia concentration inhibits the decomposition reaction.

The ammonia decomposition experiments suggested mass transport limitations. A characterization of the microsystem shows that at low flows the reactor behaves like a number of tanks in series, but as a plug flow at higher flows.

# Resumé på dansk

Nærværende projekt omhandler udviklingen af mikrosystemer til hydrogen fremstilling. Formålet med projektet er dels at udvikle en ny metode til at loade katalysator i mikroreaktorer, dels at undersøge hydrogenproducerende reaktioner i de dannede mikrosystemer.

Som introduktion beskrives teorien bag tre forskellige hydrogenproducerende processer; steam reforming, partiel oxidation og dekomponering af ammoniak. Særligt vægt er lagt på dekomponering af ammoniak, da det er den foretrukne proces for hydrogen fremstilling.

Mikroreaktoren, anodisk bonding og forsøgsopstillingen til partiel oxidation af methan og dekomponering af ammoniak er omtalt.

For at kunne udføre hhv. partiel oxidation af methan og dekomponering af ammoniak forsøg i mikroreaktorer er en ny metode til loading af katalysator udviklet. Supportmaterialet består af vand, salpetersyre og boehmite som, ved opvarmning, giver aluminium-oxid (Al<sub>2</sub>O<sub>3</sub>). Det er imprægneret med Pd til partiel oxidation forsøgene og med 1.8% Ru, 1.0% Fe, 0.4% Co, 0.9% Pd and 1.9% Cu til dekomponering af ammoniak forsøgene.

Partiel oxidation af methan forsøgene undersøger afhængigheden af temperaturen samt methan-oxygen forholdet. Resultaterne viser, at ved temperature over 590°C opnås fuld oxygen omsætning, samt en stor hydrogenproduktion. Det optimale methan-oxygen forhold er til 2:1, som forventet ud fra reaktionsligningen.

Forsøgene med dekomponering af ammoniak viser, at Co, Fe og Ru giver signifikant højere ammoniakomsætning end Pd og Cu. Ved 680°C er omsætningen 97% på Fe og 88% på Ru. Desuden viser de, at et lavt flow giver den største omdannelse dog med en lavere aktivitet for Co, Fe og Ru. For at få høj aktivitet på Ru skal flowet være 8ml/min ammoniak, og højere for Fe og Co. Yderligere viser forsøgene at en høj ammoniakkon-centration hæmmede dekomponeringen.

Dekomponering af ammoniak forsøgene indikerer massetransport begrænsning. En karakterisering af mikrosystemet viser, at ved lave flows opfører reaktoren sig som en række serieforbundne tank reaktorer, mens det for høje flows opfører sig som en plug-flow reaktor.

# Preface

This project is submitted in partial fulfillment of the requirements for the degree in Master of Science in Engineering at the Technical University of Denmark (DTU). The project was carried out at the Interdisciplinary Research Center for Catalysis at DTU from primo October 2003 to ultimo February 2004 and corresponds to 30 ETCS points.

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# List of Symbols

А	:	compound A
$\mathbf{A}_E$	:	preexponential factor
$A_{eff}$	:	cross section area $(m^2)$
$A_s$	:	activated compound A
В	:	compound B
$\mathbf{B}_s$	:	activated compound B
b	:	width of reactor (m)
$C_{A0}$	:	initial concentration of compound A (mol/L)
$C_j$	:	concentration of compound j (mol/L or mol/m <sup><math>3</math></sup> )
$D_a$	:	dispersion coefficient $(m^2/s)$
$\mathbf{D}_{AB}$	:	diffusion coefficient of A in B $(m^2/s)$
$\mathbf{D}_H$	:	hydraulic diameter (m)
$\mathbf{E}_A$	:	apparent heat of adsorption (kJ/mol)
$\mathbf{E}_a$	:	activation energy (kJ/mol)
$\mathbf{E}_R$	:	apparent activation energy (kJ/mol)
$F_{A0}$	:	initial molar flow of compound A (mol/min or mol/s)
$\mathbf{F}_{j}$	:	molar flow of compound j (mol/min or mol/s)
h	:	height of reactor (m)
$I_j$	:	mass spectrometer signal for compound j (A)
$K_{A0}$	:	equilibrium constant for compound A at initial the temperature $(atm^2 \text{ or } mol^2)$
$\mathbf{K}_A$	:	equilibrium constant for compound A at specific temperature $(atm^2 \text{ or } mol^2)$
$\mathbf{k}_A$	:	specific reaction rate of compound A, (mol/s)
$\mathbf{k}_a$	:	rate constant for adsorption (unit depends on reaction order)
$k_d$	:	rate constant for desorption (unit depends on reaction order)
$k_{R0}$	:	rate constant for reaction at initial temperature (unit depends on reaction order)
$k_R$	:	rate constant for reaction (unit depends on reaction order)
k"	:	constant
$\mathbf{L}$	:	reactor length (mm or cm)
$L_p$	:	length of circumference (m)
m	:	mass (g or kg)
$N_{Pe}$	:	Peclet number
$N_{Re}$	:	Reynolds number

$n'_A$	:	reaction order for compound A
$\mathbf{n}_j$	:	amount of compound j (mol)
$p_{A0}$	:	initial partial pressure of compound A (atm or Pa)
$\mathbf{p}_A$	:	partial pressure of compound A (atm or Pa)
$\mathbf{p}_{c}$	:	mixture critical pressure (bar or atm)
$\mathbf{p}_{cA}$	:	critical pressure of compound A (K)
$\mathbf{p}_r$	:	reduced pressure
R	:	gas constant $(J/(mol \cdot K) \text{ or } (L \cdot atm/(mol \cdot K))$
R	:	radius (m)
r	:	reaction rate (mol/s or molecules/s)
$\mathbf{r}_A$	:	reaction rate for compound A (mol/s or molecules/s)
$\mathbf{S}$	:	cross section area $(m^2)$
Т	:	temperature ( $^{\circ}C$ or K)
$T_c$	:	mixture critical temperature (K)
$T_{cA}$	:	critical temperature of compound A (K)
$\mathbf{T}_r$	:	reduced temperature
u	:	linear velocity (m/s)
V	:	volume (L or $m^3$ )
$V_{eff}$	:	effective reactor volume (ml or $m^3$ )
$V_{freecat}$	:	pore volume of catalyst (ml or $m^3$ )
Vsolidcat	:	solid volume of catalyst (ml or $m^3$ )
$V_{totalcat}$	:	total volume of catalyst (ml or $m^3$ )
$v_0$	:	entering volumetric flow rate (ml/min)
$\mathbf{X}_A$	:	conversion of compound A (mol A converted per s)
YA0	:	initial mol fraction of compound A in gas phase
$y_j$	:	mol fraction of compound j in gas phase
*	:	free active site

Greek symbols :

	-	
$\beta$	:	constant
$\delta$	:	stoichiometric coefficient
ε	:	expansion coefficient
$\varepsilon'$	:	porosity
$\mu$	:	viscosity $(kg/m \cdot s)$
$\mu_c$ '	:	mixture critical viscosity $(kg/m \cdot s)$
$\mu_{cA}$	:	critical viscosity of compound A (K)
$\rho$	:	density $(g/ml \text{ or } kg/m^3)$
Θ	:	ratio parameter

# Chapter 1

# Introduction

Today fossil fuels are one of the main sources for generating energy. Oil is raffinated to gasoline/fuel for cars, making it a key to transportation, natural gas is burned for electric generation and industrial feedstock, and coal dominates the electricity production. Both oil and gas are also used for domestic heating. When oil, natural gas and coal are burned CO and CO<sub>2</sub> is formed, polluting the environment. To reduce the use of fossil fuels and thereby also protect the environment, alternative energy sources are exploited intensively.

One alternative could be hydrogen driven fuel cells. This kind of fuel cell transforms chemical energy to electrical energy by reacting hydrogen and oxygen forming heat and water

 $2\mathrm{H}_2(g) + \mathrm{O}_2(g) \rightarrow 2\mathrm{H}_2\mathrm{O}(l)$ 

The oxygen used for the fuel cell can come directly from air, while hydrogen can be supplied indirectly from e.g. ammonia decomposition

$$2\mathrm{NH}_3(g) \rightarrow \mathrm{N}_2(g) + 3\mathrm{H}_2(g)$$

or partial oxidation of methane

$$\operatorname{CH}_4(g) + \frac{1}{2}\operatorname{O}_2(g) \to \operatorname{CO}(g) + 2\operatorname{H}_2(g)$$

Both these reactions require a catalyst to occur.

Micro fabricated reactors are promising tools when investigating catalytic reactions. A microreactor is a reaction chamber etched into a silicon chip. It can be incorporated with a catalytic material, making it a catalytic microsystem. These systems are presently used for e.g. investigating highly exothermic reactions. Due to their small size, microreactors are promising as mobil hydrogen producing devices for fuel cells in e.g. mobile phones or laptops.

## 1.1 Problem Specification

The overall objectives of this project is to determine an incorporation method for microreactors, which are to produce hydrogen and to experimentally investigate hydrogen producing processes.

Initially, a literature survey will be performed to investigate fuel cells, hydrogen producing processes, and microreactors. Based on the literature survey, the optimal hydrogen producing process is determined and investigated more thoroughly.

Presently there are several procedures for incorporating catalyst in microreactors. A goal in this project is to develop a new method using boehmite as the support material. The method will be determined on the ground of experiments.

Using the incorporated microsystems, partial oxidation of methane and ammonia decomposition will be investigated experimentally. In addition the experimental setup for these experiments will be presented.

Finally the results of the experiments will be the basis for a characterization of the microsystems.

## Chapter 2

# Hydrogen for Fuel Cells

Fuel cells could be a good alternative for reducing the still growing use of fossil fuels when generating electricity for both domestic and industrial applications. Fuel cells cannot replace fossil fuel all at once, but over several years e.g. battery driven machines - such as mobile phones, bicycle lights, cars, etc - could get their energy from fuel cells instead of batteries. In the future they could furthermore replace coal as the main energy source for electricity, and one day sun cells, wind mills, and fuel cells may be the main energy source.

## 2.1 Principles of the Hydrogen Fuel Cell

A fuel cell converts chemical energy directly to electricity by an electrochemical process. This means that no unwanted byproducts such as  $NO_x$  or particles are produced, which is the case when fossil fuels are burned. Another advantage is the fact that this method can theoretically convert over 80% of chemical energy directly to electricity, and it avoids the Carnot efficiency limitation known from combustion motors [1].

The principle of the fuel cell was first discovered in 1839 by judge and scientist Sir William Grove, when he was experimenting with decomposition of water. After turning off the power to his setup, he saw bobbles of oxygen and hydrogen still present on the electrodes. He discovered that these could produce electricity and steam, if the electric circuit was held closed. This was the beginning of the fuel cell, which basically works the same way [2, 3].

There are many types of fuel cells, but the two most often used are the Polymer Electrolyte Membrane Fuel Cell (PEMFC) and the Solid Oxide Fuel Cell (SOFC) [4]. Common for the these two fuel cell types, is that they both run on hydrogen and oxygen.

## 2.1.1 Polymer Electrolyte Membrane Fuel Cell

The polymer electrolyte membrane fuel cell is also called proton exchange membrane fuel cell. A PEMFC consists of a cathode, an anode, and a solid electrolyte membrane separating the two, similar to an electrochemical cell.



Figure 2.1: Principle of the PEMFC [5]

Figure 2.1 shows how hydrogen is led to the anode where it is dissociated and ionized to  $\operatorname{protons}(\mathrm{H}^+)$  and  $\operatorname{electrons}(\mathrm{e}^-)$ . The protons migrate through the electrolyte membrane, while the electrons pass around it through an external circuit, producing electricity. The protons and electrons are reunited at the cathode, where oxygen is present. The electrons ionize the oxygen, and water is formed when  $\mathrm{O}^{2-}$  react with  $\mathrm{H}^+$ .

The electrodes are usually  $\rm Pt$  or  $\rm Pt/Ru$  nano-particles deposited on a conductive graphite support.

The following reactions take place in a PEMFC [4]:

Anode  $: 2H_2(g) \to 4H^+ + 4e^-$  (2.1)

Cathode :  $O_2(g) + 4e^- \to 2O^{2-}(aq)$  (2.2)

Overall reaction in cell : 
$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$
 (2.3)

The cell reaction is exothermic with a reaction enthalpy of  $\Delta_r H^\circ = -572 \text{kJ/mol}$ , [6].

A single fuel cell will only give a few volts, and therefore several cells are often stacked together to reach a larger voltage.

The PEMFC is very sensitive towards CO, which contaminates and poisons the platinum electrodes in the cell [7].

## 2.1.2 Solid Oxide Fuel Cell

In the SOFC the temperature is raised to 600–1000°C [4, 8] to increase the mobility of the  $O^{2-}$ -ions and give the electrolyte sufficient conductivity, to let the  $O^{2-}$  pass through the electrolyte membrane.

At temperatures between 600–800°C Ni, Pd, Pt, and Co are used as anode catalyst, while at 800–1000°C the temperature is high enough for the anode reaction to happen without the presence of catalyst[8, 9].

The design of the SOFC is similar to the design of the PEMFC. Figure 2.2 shows how the hydrogen is led to the anode, and oxygen to the cathode. The two electrodes are separated by an electrolyte membrane, which lets oxygen-ions diffuse through to the anode side where it reacts with the hydrogen. The electrolyte most common is yttria-stabilized zirconia (YSZ).



Figure 2.2: Principle of the SOFC [9]

In the SOFC the following reactions take place [9]:

Anode 
$$: 2H_2(g) + 2O^{2-}(aq) \to 2H_2O(l) + 4e^-$$
 (2.4)

Cathode : 
$$O_2(g) + 4e^- \rightarrow 2O^{2-}(aq)$$
 (2.5)

Overall reaction in cell :  $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$  (2.6)

The cell reaction is thus the same as the one taking place in a PEMFC.

## 2.1.3 Other Types of Hydrogen Driven Fuel Cell

There are several other kinds of fuel cell types e.g. alkaline, direct methanol, molten carbonate, and phosphoric acid fuel cells. The latter two do not, however, run on hydrogen.

The alkaline fuel cell, AFC, is not a very often used fuel cell because  $CO_2$  destroys the electrolyte when it is present in greater amounts than a few ppm [10].  $CO_2$  is a problem because it reacts with  $OH^-$  formed at the cathode.  $CO_2$  is a byproduct from steam reforming and partial oxidation, which are typical hydrogen production processes [3].

The principle of the direct methanol fuel cell, DMFC, is similar to the principle of the PEMFC. The DMFC converts methanol, ethanol, and methane to hydrogen directly in the fuel cell, resulting in a yield of 1 to 70 W [3]. This makes them suitable for smaller electronic devices. The DMFC has the disadvantage of being very sensitive to CO, since CO contaminates the electrodes.

## 2.2 Hydrogen Sources for Fuel Cells

As described in the previous section, hydrogen and oxygen are the reactants in fuel cells. Oxygen is easy to get a hold of, since it is present in air, while hydrogen is somewhat more difficult to handle. It is very reactive and does therefore not exist in its pure form under normal/standard conditions [11].

Some commonly used and relatively easily decomposed substances for producing hydrogen are ammonia (NH<sub>3</sub>), methanol (CH<sub>3</sub>OH), methane (CH<sub>4</sub>), and other alcohols and hydrocarbons. Hydrogen is produced from these compounds according to the processes described below.

### 2.2.1 Steam Reforming

Steam reforming is a process producing hydrogen from both hydrocarbons and alcohols. In the reaction equations (2.7)-(2.9) steam reforming reactions of methane, n-heptane, and methanol are shown [12, 13, 14, 15]

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2$$
 (2.7)

$$C_7H_{16} + 7H_2O \approx 7CO + 15H_2$$
 (2.8)

$$2CH_3OH + 2H_2O \rightleftharpoons 2CO_2 + 6H_2$$

$$(2.9)$$

A competing reaction is the exothermic water gas shift reaction stated in equation (2.10)[12, 13, 14, 15]

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$
 (2.10)

The main steam reforming reactions (2.7)-(2.9) are reversible. However, under correct conditions the thermodynamic equilibrium can be made irreversible for reactions (2.8) and (2.9).

Steam reforming of methane is an endothermic process,  $\Delta H^{\circ} = 198 \text{ kJ/mol} [12, 13, 14]$ , taking place at high temperature, low pressure, and a high steam-to-methane ratio. The process is, for hydrocarbons, catalyzed by group VIII metals, of which Ni is the most cost effective.

Steam reforming of higher hydrocarbons also lead to endothermic reactions. The steam reforming reaction for n-heptane (2.8) has an enthalpy of  $\Delta H^{\circ} = 1175 \text{ kJ/mol}$  [12, 14]. The higher hydrocarbons are reformed as irreversible adsorptions on nickel surfaces. There is a significant difference in reaction rate from one particular hydrocarbon to another; high order hydrocarbons usually react faster than the low order ones. The high order hydrocarbons are furthermore able to crack with no catalyst present. This means that at higher temperatures 600–650°C, catalytic steam reforming reaction competes with the thermal reactions of the higher hydrocarbons, resulting in a decrease in catalyst activity.

Steam reforming of methanol (2.9), with an enthalpy of  $\Delta H^{\circ} = 49 \text{ kJ/mol}$  [12, 13, 14], is less endothermic than the reforming of hydrocarbons. When Cu is used as catalyst a conversion of more than 99% has been observed at temperatures as low as 200–300°C. The low temperatures result in a product gas with a high hydrogen concentration but low CO concentration, as the forward reaction in (2.10) proceeds at high temperatures. Ethanol can also be steam reformed, as can higher alcohols. This process, however, requires higher temperatures than steam reforming of methanol, making them less favorable as hydrogen sources. Steam reforming of ethanol and higher alcohols is usually carried out with Ni or Cu as catalysts [12].

#### 2.2.2 Partial Oxidation

Partial oxidation is another well known process for producing hydrogen. The process can occur with or without the presence of a catalyst, but also as a combination of a non-catalytic oxidation and steam reforming.

#### Autothermal Reforming

The latter method is called autothermal reforming, ATR, and is performed in two steps; a steam reforming stage according to reactions (2.7)[14] for steam reforming of methane and (2.9) [16] for methanol

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2$$
$$CH_3OH + H_2O \rightleftharpoons CO_2 + 3H_2$$

and a catalytic stage [14, 16]

$$CH_4 + \frac{3}{2}O_2 \rightleftharpoons CO + 2H_2O \tag{2.11}$$

$$CH_3OH + O_2 \rightleftharpoons CO + 2H_2O$$
 (2.12)

as for steam reforming, the water shift reaction (2.10) is the competitive reaction.

The total thus becomes [14, 16]

$$2CH_4 + \frac{3}{2}O_2 \approx 2CO + 3H_2 + H_2O$$
 (2.13)

$$2CH_3OH + O_2 \quad \rightleftharpoons \quad CO_2 + 3H_2 + CO + H_2O \tag{2.14}$$

### Non-Catalytic Partial Oxidation

Non-catalytic partial oxidation is made under very high temperatures to obtain complete methane conversion. The high temperatures prevents large amounts of soot being produced which, however, cannot be prevented completely. The H<sub>2</sub>-to-CO ratio produced from non-catalytic partial oxidation is usually 1.7-1.8 [12].

#### **Catalytic Partial Oxidation**

In contrast to both autothermal reforming and non-catalytic oxidation, catalytic partial oxidation is first of all a catalytic reaction. The exothermic reaction of partial oxidation of methane,  $\Delta H^{\circ} = -35.6 \text{ kJ/mol} [12, 17, 18]$ , is shown in reaction (2.15)

$$CH_4 + \frac{1}{2}O_2 \rightleftharpoons 2H_2 + CO \tag{2.15}$$

Reaction (2.15) is the overall reaction of several stages. In the first stage methane is converted to  $CO_2$  and  $H_2O$ 

$$CH_4 + 2O_2 \rightleftharpoons CO_2 + 2H_2O \tag{2.16}$$

The reaction continues until the limiting reactant, oxygen, has been completely converted. Any unreacted methane will react with both  $H_2O$  and  $CO_2$ , mainly giving the overall reaction (2.15), according in the following reaction steps

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$$
 (2.17)

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2$$
 (2.18)

$$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2$$
 (2.19)

Reactions (2.17) and (2.18) are both endothermic with enthalpies of respectively  $\Delta H^{\circ} = 226 \text{ kJ/mol}$  and  $\Delta H^{\circ} = 261 \text{ kJ/mol}$  [17]. At higher temperatures these reactions are favored, compared to reaction (2.19), mainly giving CO and H<sub>2</sub>.

Carbon forming reactions can also occur but will not be described here.

The catalysts most often used for partial oxidation are Ni and Rh in a temperature range of 873-1023K (600- $800^{\circ}$ C)[19]. They have resulted in methane selectivities and corresponding conversions as high as 90% [12, 18].

Initially partial oxidation investigations have mainly been performed at atmospheric pressure, but experiments made at higher pressures do not show any significant changes in conversion.

Methanol can also be partially oxidized according to reaction (2.20)

$$CH_3OH + \frac{1}{2}O_2 \rightleftharpoons 2H_2 + CO_2 \tag{2.20}$$

The reaction is exothermic with an enthalpy of  $\Delta H^{\circ} = -192.3 \text{ kJ/mol} [16]$ .

### 2.2.3 Ammonia Decomposition

The decomposition of ammonia proceeds according to reaction (2.21)

$$2\mathrm{NH}_3 \rightleftharpoons 3\mathrm{H}_3 + \mathrm{N}_2 \tag{2.21}$$

For the reaction to take place a catalyst must be present. The reaction is endothermic with  $\Delta H^{\circ}=92 \text{ kJ/mol} [6, 20, 21]$ . Many different catalysts have been used for the decomposition process, among others; Ni, Pt, V, Fe, Ru, Rh, Ir, and Pd. A number of oxides are well known subjects as support material, but also activated carbon has been used successfully [22, 23].

The reaction of ammonia decomposition takes place at high temperatures and at atmospheric pressure. Only  $N_2$  is produced as byproduct since no competing reactions are known to occur.

## 2.3 Choice of Hydrogen Source

When choosing which process is the optimal for producing hydrogen for fuel cells, several aspects must be considered as presented in the following.

CO in PEMFCs is unwanted because it contaminates and poisons the electrode catalyst. The tolerance level for CO in a feed gas going in the fuel cell is therefore very low, only 5-50ppm [10]. The CO concentration in the product from steam reforming, partial oxidation, or autothermal reforming of hydrocarbons can be reduced by e.g. temperature shifts [10, 21]. A temperature shift is a relatively expensive process, where the temperature of a product gas containing CO is changed resulting in a reduction in the CO concentration.

As a result of the CO issue a general comparison of hydrocarbons and ammonia as hydrogen source speaks in favor of ammonia.

From an environmental point of view ammonia is furthermore the preferred substance. This is the case because the byproduct from ammonia decomposition  $N_2$  is already present in air, while both CO and CO<sub>2</sub> are environmental problems.

Experiments made by Metkemeijer and Achard [24], show that catalytic decomposition of ammonia is an appealing process for clean hydrogen production, as concluded above.

Unfortunately any trace of ammonia, as low as 13 ppm [25], in the hydrogen fed to the fuel cell, will lower the efficiency of the cell. This is due to ammonia reacting with  $H^+$  to form  $NH_4^+$ .  $NH_4^+$  seems to contaminate the catalyst on the anode side of the fuel cell, but also decrease the conductivity in the membrane. A solution to the problem could be adsorption of product gas of ammonia decomposition with e.g. sulfuric acid. Sulfuric acid is known to be able to reduce an ammonia concentration from 2000-3000ppm to less than 200ppb [25].

It should be noted that 30-90ppm [25] ammonia is present in hydrogen gas from autothermal reforming and partial oxidation of hydrocarbons, since there are some impurities in the reactant gas. Therefore both problems regarding  $NH_3$  and CO poisoning the catalyst are results of steam reforming and partial oxidation as oppose to only  $NH_3$ -poisoning for ammonia decomposition.

Based on the facts stated above, the optimal hydrogen source is ammonia. Ammonia only forms  $N_2$  as byproduct, and  $N_2$  does no harm to the fuel cell. Furthermore any unwanted ammonia in the hydrogen feed gas for the fuel cell is easily removed using by e.g. adsorbing using sulfuric acid.

## 2.4 Theory of Ammonia Decomposition

In the previous section ammonia was found to be the optimal hydrogen source compared to steam reforming and partial oxidation of hydrocarbons and alcohols. In the present section a more thorough investigation regarding the decomposition of ammonia is made.

## 2.4.1 Mechanism

The mechanism of ammonia decomposition is the revers mechanism for synthesis of ammonia [26]. The mechanism for ammonia synthesis is [27]

$$N_2(g) + * \rightleftharpoons N_2 * \tag{2.22}$$

$$N_2 * + * \rightleftharpoons 2N *$$

$$N * + H * \rightleftharpoons NH * + *$$
(2.23)
(2.24)

$$NH * + H* \rightleftharpoons NH_2 * + *$$

$$(2.24)$$

$$(2.24)$$

$$NH_2 * + H * \rightleftharpoons NH_3 * + *$$
 (2.26)

$$NH_{3}* \rightleftharpoons NH_{3}(g) + *$$
 (2.27)

$$H_2(g) + 2* \rightleftharpoons 2H* \tag{2.28}$$

where \* is a free active site, N\* and H\* are respectively nitrogen and hydrogen bonded to the surface of an active site.

#### 2.4.2 Kinetics

In 1996 Papapolymerou et al. [20] decomposed ammonia in the presence of either Pd, Ir, Pt, or Rh, and compared the results of the experiments. The decomposition rates were found to follow the Langmuir-Hinshelwood unimolecular rate expression, with a 80% precision at all conditions for an ammonia pressure of 0.01 and 1 torr

 $(1.3 \cdot 10^{-5} \text{ to } 1.3 \cdot 10^{-3} \text{ atm})$ , a total pressure of  $10^{-3} \text{ to } 10 \text{ torr } (1.310^{-6} \text{ to } 1.310^{-2} \text{ atm})$ , and a temperature of 500 to 1900K (227 to 1627°C). The Langmuir-Hinshelwood mechanism for e.g.  $A_g \to B_g$  consists of the following elementary steps [4, 20]

$$A + * \frac{\overset{k_a}{\overleftarrow{k_d}}}{A*} \tag{2.29}$$

$$A \ast \xrightarrow{\kappa_R} B \ast \tag{2.30}$$

$$B^* \to B + * \tag{2.31}$$

A and B refer to species A and B, \* a free active site, and A\* and B\* the surface absorbed species A and B respectively.  $k_a$  is the absorption rate coefficient,  $k_d$  is the desorption rate coefficient, and  $k_R$  is the "actual" reaction rate coefficient corresponding to the rate coefficient of the rate limiting step [4]. The adsorption equilibrium constant is determined as [20]

$$K_A(T) = \frac{k_a}{k_d} = K_{A0} \exp \frac{E_A}{RT}$$
 (2.32)

where  $K_A$  is the adsorption equilibrium constant at temperature T,  $K_{A0}$  is the absorption equilibrium constant at an initial temperature,  $E_A$  is the apparent heat of adsorption, and R is the gas constant. When the desorption reaction (2.31) is the rate limiting step, the rate expression derived for Langmuir-Hinshelwood will be [4]

$$r_A = \frac{k_R K_A p_A}{(1 + K_A p_A)} \tag{2.33}$$

as also stated by Papapolymerou et al. [20]. In (2.33)  $r_A$  is the reaction rate and  $p_A$  is the partial pressure of species A.  $k_R$  is the rate coefficient defined as [4, 20]

$$k_R(T) = k_{R0} \exp \frac{-E_R}{RT} \tag{2.34}$$

where  $k_{R0}$  is the rate coefficient at a given temperature and  $E_R$  is the apparent activation energy.

The reaction order of the decomposition can be derived from the rate expression using the following derivation [4]

$$n'_{A} \equiv \frac{\partial \ln r}{\partial \ln |A|} = |A| \frac{\partial \ln r}{\partial |A|}$$
(2.35)

where  $n'_A$  is the reaction order of species A, r is the reaction rate, and |A| is the concentration of species A. Inserting equation (2.33) in equation (2.35) and replacing the concentration of e.g. species A with the partial pressure of A gives

$$n'_A = p_A \frac{\partial \ln r_A}{\partial p_A} = \frac{1}{K_A} - \frac{K_A}{1 + K_A \cdot p_A}$$

This result shows that the reaction order is dependent of both the equilibrium constant  $K_A$  and the partial pressure  $p_A$ , and since the equilibrium constant is dependent of the temperature, see equation (2.32), the order of the reaction will change with temperature. This corresponds to what Chellappa et al.[25] found when they investigated the kinetics of ammonia decomposition using Ni-Pt supported on Al<sub>2</sub>O<sub>3</sub>. They found that when the ammonia pressure is below 1 Torr ( $1.3 \cdot 10^{-3}$  atm) and the temperature is below 500°C, the reaction rate with respect to ammonia is zero ordered. Papapolymerou et al. [20] found that at low temperatures (below 600°C) the reaction rate is independent of the pressure. Both Papapolymerou et al. [20] and Chellappa et al. [25] discovered that at high temperatures the reaction rate depends on both the pressure and temperature, and the reaction is of first order. An expression for the reaction rate is therefore [25, 28, 40]

$$r = k_0 \exp\left(\frac{-E_a}{RT}\right) p_{NH_3}^{n'} \tag{2.36}$$

where n'=1 for T > 500-520°C. Here  $k_0$  is the preexponential coefficient and  $p_{NH_3}$  is the partial pressure of ammonia. Chellappa et al. [25] have found values for the preexponential factor and the activation energy when using Ni-Pt as catalyst to give the following expression

$$r = 3.639 \cdot 10^{11} \exp\left(\frac{-46897}{RT}\right) p_{NH_3}$$

In addition Chellappa et al. found that at low temperature and high hydrogen pressures, hydrogen acts as an inhibitor towards the decomposition. The reaction can then be described by the Temlin-Pyzhev expression [25]

$$r = k'' \left(\frac{p_{NH_3}^2}{p_{H_2}^3}\right)^{\beta}$$
(2.37)

Here k'' and  $\beta$  are constants.

Arabczyk et al. [28] have decomposed ammonia over a Fe catalyst. They determined a reaction order at a temperature above 500°C to be first order corresponding to the orders found for other catalysts at temperatures above 500°C.

## 2.4.3 Catalysts

When a catalyst is to be used in a reaction, there are several important properties to respect [4]

- A high activity
- A high selectivity, if several side reactions occur
- Slow deactivation
- Possible to regenerate after deactivation
- Preparation reproducibility possible
- Thermally stabile thus avoiding sintering
- High mechanical strength (e.g. crushing and wear)

As mentioned earlier many different catalysts - Ni, Pt, V, Fe, Ru, Rh, Ir, and Pd - have been tested for ammonia decomposition. The condition for the decomposition plays an important role in the choice of catalyst as do the properties of the support material. Furthermore promoting of the catalyst has an effect on the activity. Some common promoters regarding ammonia decomposition are Ba and K.

The influence of the Ru particle size on carbon was investigated by Rarog-Pilecka et al.[22], and showed that a particle of 8nm in diameter gave an eight times higher turnover frequency, TOF, than a fine particle, 1.2nm. This indicates that a particle with a larger diameter is more active than a smaller particle. This does not correspond with the theory stating that small particles give a high specific surface area, and thereby a higher activity than larger ones.

Raróg-Pilecka et al. [22] experiments showed that the presence of chlorine reduces the reaction rates, because the presence of chlorine is known to be a severe contamination agent to all ammonia synthesis catalysts. The experiments, however, also showed that catalyst deactivated faster in the presence of oxygen-containing groups, e.g.  $CO_2$ , than

by contamination by chlorine.

Papapolymerou et al. [20] have found that ammonia decomposition on Ir is very fast even at low temperatures varying significantly from Pt, Rh, and Pd.

To determine the reaction rate for the ammonia decomposition, equation (2.36), the activation energy must be known or determined. Table 2.1 shows activation energies determined for different catalysts together with the experimental conditions.

Catalyst	Activation Energy (kJ/mol)	Experimental conditions
Fe/Al <sub>2</sub> O <sub>3</sub> /CaO/K <sub>2</sub> O	87	360-560°C, 1bar [28]
$Fe/Al_2O_3/CaO/K_2O$	96	K present $360-560^{\circ}$ C, 1bar [28]
Pt wire/foil	88	$230-1625^{\circ}C, 0.01-1 \text{ Torr } [20]$
Rh wire/foil	88	$230-1625^{\circ}C, 0.01-1 \text{ Torr } [20]$
Ir wire/foil	131	$230-1625^{\circ}C, 0.01-1 \text{ Torr } [20]$
Pd wire/foil	110	$230-1625^{\circ}C, 0.01-1Torr [20]$
Ni-Pt/Al <sub>2</sub> O <sub>3</sub>	197	520-690°C, 50-780Torr [25]
$V_2O_5$	100-165	$525-570^{\circ}C$ , $101kPa$ [29]
Ru/C	138	400-800°C, 152-760Torr [30]
Ru/C	130	350-400°C, 600-800Torr [30]

Table 2.1: Experimentally determined activation energy for different catalysts

Boisen et al. [45] have made ammonia decomposition experiments using Ru, Co, Cu, Ni, Fe, and  $Co_3Mo_3N$  as catalysts. The results showed that Ru was the most active of the five followed by  $Co>Co_3Mo_3N>Ni>Fe>Cu$ . Cu being significantly lower than the others. This corresponds to the activation energies for Ru and Fe listed in table 2.1, since Ru has a higher activation (138 kJ/mol) than Fe (88 kJ/mol) in the temperature range 400-800°C.

Both the activation energies listed in table 2.1 and the activity order found by Boisen et al. suggest that metal from the lower transition metal groups give both higher activation energies and activities.

#### 2.4.4 Support Materials

The support material also plays a role in catalytic reactions. The active metal is applied to a support material to stabilize the catalyst particles and prevent them from sintering at higher temperatures. Oxides and activated carbon are well-known support materials and alumina or silica oxides along with carbon are the most common.

Alumina oxides can e.g. be made from boehmite (AlOOH) typically forming three oxides,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and  $\eta$ -Al<sub>2</sub>O<sub>3</sub>.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as support material has a specific surface area between 50 and 300 m<sup>2</sup>/g [4], is thermally stabile, and can be formed into stable extrudates and pellets.

Raróg-Pilecka et al.[22] have investigated ammonia decomposition with ruthenium on activated carbon. When prepared according to three different procedures the carbon gave different surface areas of respectively 66, 440, and 435 m<sup>2</sup>/g. The one with the lowest surface area was during preparation heated to 1900°C, while the other two were only heated to 600 and 840°C. This is a strong indication that the carbon particles have sintered due to the high temperature (1900°C).

## 2.5 Microreactors for Catalytic Reactions

A microreactor is defined as having at least one dimension in the  $\mu$ m range. The reactor is usually etched into a thin silicon chip, making them heat conductive and thereby thermally stable up to the Si(s) melting point of 1410°C [31]. Combined with the fact that they have high surface/volumen ratios, this makes the microreactors ideal for thermally unstable reactions such as partial oxidation of methane and other exothermic reactions producing explosive mixtures, due to rapid heat transfer from the silicon surface [32, 33]. In addition exposure regarding toxic fumes or hazardous materials is reduced due to the closed nature of the microreactor [32].

Another advantage of microreactors compared to e.g. industrial or pilot scale reactors, is the quick response to operation changes. The reaction chamber is so small that it only takes a short time to get the system to reach steady state when changing e.g. the temperature or gas flow [33].

The type or amount of catalyst needed if a specific or several reactions are to be investigated is also reduced compared to the industrial or pilot scaled reactors [32].

Compared to a pilot scale setup, the microreactor needs significantly less energy when e.g. an endothermic reaction is to be investigated. The chip is so small that only a small amount of energy is needed for the reaction chamber to reach a wanted temperature.

Despite the small size of the microreactors, it has been shown that only 1000 microreactors processing continuously can produce 1 kg material per day [32]. This is a strong indicating that up-scaling to pilot or full-scale is no problem, in addition it shows that the microreactors can maintain selectivity and high level of control.

Finally microreactors allows preparation of chemicals in the exact volume and location of which they are needed, making transportation and storage of hazardous materials unnecessary [34].

## 2.5.1 Catalyst Incorporation in Microreactors

When microreactors are incorporated with catalyst they become microsystems. There are several alternatives for incorporating catalyst in a microreactor and some of these methods will be described in the following.

The catalyst can be placed in the reactor as a metal wire. This makes it easy to change catalyst between experiments and thereby reuse the reactor. The catalyst surface as well as the surface/volumen ratio can be varied by changing the wire diameter. Another advantage when using wires is that it is easy to examine the catalyst after a reaction [32].

Many catalysts can be deposited directly onto the reactor walls as a thin film, either directly as the active metal or as a metal oxide giving a porous surface. However, this method does not always result in the sufficient surface area, leading to an increase in surface/volume ratio, despite the small dimensions.

An expensive incorporation method is to fabricate the microreactor using the catalyst as reactor material [35].

A newer method for incorporation of catalyst is flame spray pyrolysis. A microreactor is placed in a flame containing two organic precursors, one giving the support material and one giving the active metal. The microreactor is kept cold making the support and active metal stick to it [35].

## 2.6 Summary

Fuel cells are an interesting alternative to the fossil fuels used today as energy source worldwide. Hydrogen and oxygen is used as fuel for hydrogen driven fuel cells. Oxygen can be obtained directly from ordinary air, while hydrogen can be extracted from e.g. ammonia and hydrocarbons. For environmental reasons but also to avoid destruction of the fuel cell, ammonia is preferred since no  $CO_x$  is formed during the decomposition.  $CO_x$  is formed when hydrocarbons are decomposed and is unwanted because it contaminates and poisons the electrodes in the fuel cells.

Ammonia decomposition has been investigated more thoroughly. The ammonia decomposition reaction has through experiments been determined to be zero ordered at temperatures below 500°C and first ordered above 500°C. Ni, Pt, V, Fe, Ru, Rh, Ir, and Pd on both carbon and oxide support have been tested earlier as catalysts for the decomposition. The particle size of ruthenium seems to have an influence in the turn over frequency, giving large TOF-values for larger ruthenium particles. The presences of chlorine reduces the decomposition rate significantly, but oxygen-containing groups are even more deactivating than chlorine.

Microreactors are good experimental tools for investigating specific reactions. Due to their small size steady state is easily reached when an operation condition is changed. Furthermore microreactors are optimal for studies regarding high-temperature and explosive reaction due to their high thermal conductivity.

There are several catalyst incorporation methods e.g. coating of reactor walls or metal wires in the reaction chamber, resulting in microsystems which can be used for investigations of different synthesis'.

## Chapter 3

## **Experimental Equipment**

In chapters 5 results of partial oxidation of methane experiments are used as introductory experiments, while results of ammonia decomposition in microsystems experiments are presented in chapter 6. In the present chapter the microreactors, anodic bonding and the experimental setup used for these experiments are described.

## 3.1 The Microreactor

A microreactor is a small reaction chamber etched into a silicon chip. The dimensions of the chips are 1.5 cm x 2.0 cm x 350  $\mu m$ . There are many different reactor designs available, but for the introductory experiments of this project only four designs are used. Of these, two of the designs have one reaction chamber while the other two designs have two chambers. The width of the reaction chambers are either 1 or 1.5 mm but all are 200  $\mu$ m deep (vertical height) and 1.5 cm long. The dimensions of the channels leading to and from the reaction chamber are 200  $\mu$ m in both width and depth.

To seal the reactor a glass lid is bonded to the reactor when catalyst has been incorporated into the reaction chamber. The lid has three holes, two for inlet flows and one for the outlet flow.



Figure 3.1: A microreactor with two wide reaction chambers, has been bonded with a pyrex glass lid.

Figure 3.1 shows a picture of a microreactor chip with two 1.5 mm reaction chambers (yellow frame). Two red arrows show the inlet holes in the lid and a blue arrow points away from the outlet hole. The picture also shows the bonded pyrex glass lid.

The procedure for fabricating a catalytic microsystem can be seen in details in appendix A.

## 3.2 Anodic Bonding

When catalyst has been loaded into the reactor, see detailed procedure in section 4.4, the system is ready to be bonded, as the catalytic system has to be sealed. The glass plate used as lid is made of pyrex glass, and is anodically bonded to the reactor. The principle of anodic bonding, also known as glass-silicon sealing, is to mobilize ions in the glass. The principle shown in figure 3.2



Figure 3.2: The principle of anodic bonding

Using a high voltage supplier the glass lid is made anodic by placing an anodic electrode on the glass surface. When the temperature of the glass lid is raised, Na<sup>+</sup> ions become more mobile and are therefore attracted to the negative electrode. They migrate to the surface and are removed while the negative ions in the glass form a layer near the chip surface. The silicon surface away from the pyrex is made cathodic, resulting in a positive charge on the silicon surface in contact with the pyrex [36].

Initially there is a uniform potential in the glass, but as Na<sup>+</sup> ions move to the glass surface, a large decrease in potential occurs at the glass/anode interface. This results in an electrical field between the two surfaces, which pulls them into contact. When the voltage is removed, the glass and the silicon chip are held together by covalent bonds.

#### 3.2.1 Procedure

The reactor is placed on a heating plate attached to the cathodic side of a power supplier. A lid is placed on top of the chip, with the in- and outlet holes placed at the ends of the channels. In figure 3.3 the reactor and lid cannot be seen due to their small sizes, but the figure shows the anodic needle placed on the pyrex lid, and the cathode metal plate.



Figure 3.3: The experimental setup for the anodic bonding of the pyrex glass lid to the silicon microreactor

The voltage is applied from a high voltage power supplier. The temperature at which the bonding takes place is controlled with a thermometer and changed using a transformer.

Figure 3.4 shows a rainbow pattern that forms between two surfaces which are in close contact. When a rainbow pattern is seen between the lid and the reactor before the bonding, a sufficient bonding is usually obtained. A sufficient bonding means a bonding which makes the reactor and the channels all completely air tight.



Figure 3.4: The rainbow pattern appears when there is very close contact between the lid and the reactor.

When the lid has been bonded, the rainbow pattern disappears leaving the reactor system colorless.

## 3.3 The Experimental Setup

When a sufficient bonding has been made, the micro reactor is ready for the partial oxidation of methane and ammonia decomposition experiments. A flow sheet illustrating the experimental setup for these experiments is shown in figure 3.5



Figure 3.5: Flow sheet of the experimential setup

The reactant gas is lead to the microreactor mounted on the microreactor setup from the gas bottle in the right in the figure. The flow of the gas is varied by flow controllers, which are controlled by the program LabVIEW<sup>TM</sup>. By supplying power to a heating element in contact with the microreactor, the temperature of the microsystem can be varied. The reactor temperature is measured by an infrared sensor and stored in LabView<sup>TM</sup>. The outlet gas is mainly sent to waste, but a small fraction is lead to a mass spectrometer for the composition to be analyzed. The data from the mass spectrometer is collected by a second computer and viewed in the program Quadstar.

#### Microreactor Setup

Figure 3.6 illustrates the microreactor setup more clearly. The microreactor setup is designed by Jakob Svagin [37] and was operational from the beginning of this project.



Figure 3.6: Closeup of the microreactor setup

The microreactor, which cannot be seen in the figure, is placed with the glass lid downwards on the white ceramic block. On top a silicon heating element is placed. Initially a piece of canthal thread/wire is attached to each end of the heating element. Alligator beaks with connection to a power supply are pinched around the threads so current can be passed through the heating element, thereby raising the temperature of the reactor.

The inlet flows are indicated by the two red arrows leading to the aluminum block. In the block, channels lead the gas flows to and through the white ceramic block as illustrated by the two thinner red arrows. From the ceramic block the gas flows enters the channels in the silicon chip. They are led to the reaction chamber where they react to form the product gas. The product exits the microsystem, goes through the ceramic block (thin blue arrow), and out through the aluminum block (thick blue arrow).

A more detailed description of the microreactor setup can be seen in appendix B.

#### **Heating Element**

As mentioned canthal thread was initially used for connecting the alligator beaks to the heating element. This gave problems when the temperature was raised because the thread broke when it was heated above 600°C. Therefore alumina foil was used for a short time. This too gave problems at the high temperatures, because the foil traveled across the heating element causing a short-circuit. For the final experiments a 'sandwich' of two gold coated silicon pieces on each side of the heating element was used as shown in figure 3.7. This method would, however, only work when the heating element was warm, but when this was the case it worked irreproachable



Figure 3.7: The new heating element

## Flow Controllers

For the ammonia decomposition experiments two inlet gasses will be used; ammonia and argon. The gas flows are regulated with HI-TEC flow controllers from Bronkhorst. The flow controller for the ammonia gas can give a maximum flow of 20 ml/min while the argon flow controller gives a maximum flow of 45 ml/min. The flows are regulated using the program LabVIEW<sup>TM</sup>. LabVIEW measures in voltage, with a maximum voltage of 10 V corresponding to the maximum velocity of the flow controller.

Both flow controllers have been calibrated to determine their exact maximum flow. The results are shown in appendix C.

### 3.3. THE EXPERIMENTAL SETUP

#### Infrared Temperature Sensor

The temperature inside the reactor is measured using an infrared temperature sensor. The sensor is placed under the aluminum block, as shown in figure 3.8.



Figure 3.8: Closeup of the infrared temperature sensor

The infrared sensor measures the temperature of the silicon chip by irradiation through a hole in the aluminum block and through the glass lid. The measured temperature along with the time of the measurement is sent to a computer and collected by a LabVIEW program.

#### Mass Spectrometer

As mentioned previously the product gas is continuously analyzed using a mass spectrometer. The QMG 420 mass spectrometer is manufactured by Balzers and determines the amount of the different species in the product gas.

To get the product gas to the mass spectrometer, it is sucked from the outlet pipe due to vacuum. The gas to be analyzed is sucked through a quarts tube capillary also called a sniffer tube. The sniffer tube is a thin glass pipe where one end has been almost completely closed, leaving only a very small hole. Figure 3.9(a) shows the tip of a sniffer tube, while figure 3.9(b) shows how the sniffer tube is mounted on the aluminum block



Figure 3.9: (a) Closeup and (b) placement of the sniffer tube

The sniffer tube enters the setup through a hole in the aluminum block. The sniffer is mounted so the tip is just below the outlet stream coming from the reactor making it possible to suck product gas through the sniffer into the mass spectrometer.

In the mass spectrometer the product gas is led into a vacuum chamber, where it is ionized by ion bombardment. The ions are separated according to mass-to-charge ratios by an electrical field, and then led to a detection system, where they are identified according to their molecular weight. The corresponding partial pressures of the gas components are determined and shown in the DOS program Quadstar measured in current.
## Chapter 4

# **Incorporation of Catalyst**

Different catalyst incorporation methods for loading catalyst into microreactors were presented in chapter 2. These methods are, however, not optimal due to the fact that they are difficult to control with respect to e.g. amount of catalyst. In the present chapter a new method for loading catalyst into microreactors will be determined based on experimental trials. It has been decided that the support material to be used is  $Al_2O_3$  synthesized from boehmite (AlOOH).

## 4.1 Loading of Support Material

When a microsystem is to be sufficiently bonded, it must be completely free of any particles larger than 0.1  $\mu$ m [36]. Therefore cleaning of the reactor must be possible. Cleaning of the microreactor chip surface is done by wetting an ordinary piece of white printing paper with acetone. The reactor chip is placed face down on the paper, and pushed through the area wetted with acetone. This is done till there is no visual appearance of any particles left on the chip. As the chip is turned upside down, it is of importance that the support sticks to the silicon surface in the reaction chamber. Furthermore the support material must not fall out of the reaction chamber when the chip is pushed through the acetone on the paper. However, it must be possible during the cleaning to remove any support residues which are not in the reacting chamber but on the chip surface.

Initially it is tried to place a couple of drops of water in the reacting chamber and add untreated AlOOH to this. The reactor is heated to  $99.3-104^{\circ}$ C so the water evaporates. Jakob Svagin [37] has successfully used this method for loading MgCo on Al<sub>2</sub>O<sub>3</sub>, though not when using AlOOH to form Al<sub>2</sub>O<sub>3</sub>. The AlOOH does not stick to the reactor after the water is evaporated, and the method is therefore discarded.

In the second attempt untreated AlOOH is calcinated by heating  $5^{\circ}C$  per minute. When the temperature reaches  $600^{\circ}C$  it is held constant for three hours. When AlOOH is heated above  $500^{\circ}$ C it evaporates 30(w/w)% water, which might have an effect on the sticking ability of AlOOH. Calcination, however, has no effect on the sticking ability, when the loading method described above is used.

Support material fabricated for the industry can be produced as a gel, so it can be formed to any shape wanted for a specific process. This gave the idea to the following experiments, where recipes for gels inspired by Clar et al. [39] are tried. The recipe Clar et al. suggests, contains AlOOH with water and either formic acid (HOOCH) or glacial acid (HOOCCH<sub>3</sub>). In this project the original recipe is used only with the modification of the acid being nitric acid.

In the initial gel experiment it is tried to produce a brick of support material which can be laid directly into the reactor. This will make cleaning of the reactor unnecessary, and thereby simplify the bonding procedure.

An amount of AlOOH is added to 1 ml HNO<sub>3</sub> and a small amount of water to make the mixture just liquid enough to press through a syringe tip (no needle). The gel is made with both the calcinated and the untreated AlOOH. This gives two cylindrical pieces of support material which both are calcinated by heating to  $600^{\circ}$ C,  $5^{\circ}$ C per minute, as above. The calcination makes the two support pieces quite robust, and therefore also easy to handle. Unfortunately their diameter is much larger than the height of the reacting chamber, and the pieces can therefore not be used, since it will be impossible to bond the reactor. If a syringe with a smaller tip is available, or if another way of making these support material 'bricks' is found, this could be an easy and effective procedure for loading reactors, since the support material simply could be laid into it.

In the following experiments different recipes for synthesis' of gels are tried. A requirement for the gel is that it can be pressed out through a hypodermic needle, since this seems to be an ideal way of getting gel mainly into the reaction chamber. The composition of some of the tested gels made can be seen in table 4.1.

Number	$H_2O$ amount	$HNO_3$ amount	AlOOH amount
	(ml)	(ml)	(g)
1.	10	1.88	4
2.	10	0.50	5
3.	11	0.50	2.5
4.	10	0.25	2.5
:	:	:	÷
n	10	1.25	0.50

Table 4.1: Different compositions of water, acid and boehmite for the gel synthesis

All experiments are carried out by placing some gel in a 100°C warm microreactor. When all water has evaporated another layer of gel is put in. This procedure is repeated till there is five layers in the reactor.

The first and second gels are very thick, too thick to get through a hypodermic needle, which is the suggested method for handling the gel into the reactor. Therefore these recipes are discarded.

In the third gel the amount of AlOOH is reduced compared to the water and acid content. This gives a more liquid gel which, however, does not stick to the silicon.

A large amount of acid gives a thicker gel and therefore a smaller amount of acid is added with a smaller amount of AlOOH. This results in an even more liquid gel, but it still does not stick.

After several compound combinations a usable gel is found. This is gel number n in table 4.1. The gel is synthesized by stirring the three compounds in a beaker for 15-20 minutes. This results in a gel that sticks nicely to the silicon and stays in the reaction chamber even during cleaning.

The BET surface area of the support material formed from the gel is measured to be  $135.0 \text{ m}^2/\text{g}$  on a Micromeritics, Gemini apparatus.

## 4.2 Behavior of the Gel

The gel behaves as a thixotropic material. A thixotropic material is a material which become thick when it is left with no stirring or other movement, while when it is stirred it becomes liquid like. This behavior is shown in figure 4.1, where (a) is the gel just after stirring and (b) is after some time without stirring. It is later found that if the gel is left still for several days it becomes almost as liquid as water.



Figure 4.1: The thixotropic behavior of the pseudoboehmite gel

When the loaded reactor chip is dried on a hotplate, the gel cracks up into smaller flakes (figure 4.2 (a)). When the chip is cleaned, these flakes seem to get pressed together, forming a more homogenous porous phase (figure 4.2 (b)).



Figure 4.2: A one time loaded reactor before and after cleaning

Figure 4.3 (a) shows the reactor after five loadings. When a five times loaded and cleaned reactor is left on a 300°C hotplate for 15 minutes, the support material gets a yellowish color as shown in figure 4.3 (b).



Figure 4.3: Five times loaded reactor before and after heating

When the reactor is cleaned, small fragments of support material may come into the gas channels (figure 4.4(a)). This, however, does not seem to give any problems in the microsystem, and therefore nothing is done about it.

During cleaning one should be careful not to press the chip down too hard. This can result in the support material falling out of the reaction chamber (figure 4.4 (b)).



Figure 4.4: Consequences of cleaning

## 4.3 Impregnation and Preactivation

The support material alone cannot activate a reaction and therefore an active metal must be added to the support. How this metal is impregnated in the support material and how the catalyst is preactivated is described in the present section.

When catalytic reactions are performed, it is of interest to know the amount of active metal in the catalyst. It is therefore important to know both the weight of the support material placed in the reactor but also the amount of metal put on the support.

In the following ammonia decomposition experiments Ru(III), Fe(III), Co(III), Pd(II), and Cu(II) are to be investigated for ammonia decomposition. The precursor for these metals is acetyle acetonate ( $H_3CCOCHCOCH_3^-$ ), in short (acac), which is dissolvable in acetone.

Five acetone solutions containing each of the five precursors are made. To know the exact metal concentration of the solution, the exact amount of both precursor and acetone in the solution must be known.

The solutions are prepared according to the following procedure:

- 1. place a beaker on a scale, reset the scale
- 2. put a small amount of precursor in the beaker, note the weight
- 3. reset the scale
- 4. put about 1 ml acetone in the beaker, note the weight
- 5. stir the acetone till all solid is dissolved
- 6. suck up the solution with a hypodermic needle

the solution is now ready to be put on the support material.

When impregnating the support material with the metal-acetone solution, the amount of metal in the catalyst is controlled by the amount of acetone solution put on the support material. This is done by the following procedure:

- 1. place the reactor chip on a scale, reset the scale
- 2. put a drop of acetone solution onto the support material, note the weight
- 3. wait till all acetone has evaporated (the scale is zero again)
- 4. put an new drop of acetone solution onto the support material, note the weight
- 5. repeat this till a wanted metal concentration is reached

This procedure is necessary because it is not possible to weigh the small amount of precursor impregnated in the support on a scale which only goes down to 0.1 mg.

For the ammonia decomposition experiments five reactors, with single wide reaction chambers, are made. They are loaded with the five metals mentioned above. Table 4.2 shows the reactor names, the metals added, the weights of the support material loaded into the reactors(after heating), the weight of the metal acac for the metal-acetone solution, the weight of acetone for the solution, the weight of solution added to the support, the weight of metal on the support, and the weight percent of the metal in each of the reactors compared to the support material.

Reactor	Metal	Support	Metal acac	Acetone	Solution	Metal	Metal
Letter		weight	weight	$\mathbf{weight}$	$\mathbf{weight}$	added	percent
		(mg)	(mg)	(mg)	(mg)	(mg)	((w/w) %)
А	Ru	1.33	4.8	663.0	9.5	0.017	1.3
D	Pd	1.33	3.7	1229.6	11.7	0.012	0.9
Е	Cu	0.9	2.7	636.9	16.9	0.017	1.9
F	Fe	1.96	24.0	1318.7	6.9	0.020	1.0
G	Co	0.84	2.4	704.5	5.7	0.003	0.4

Table 4.2: Metal content in the reactors for ammonia decomposition experiments

A detailed calculation example for the reactor support material loading and impregnation of the active metal is shown in section 4.4.

When the support material is being impregnated, the chip should be of room temperature. Too high temperature will make the acetone evaporate rapidly which tends to loosen the catalyst from the reactor. Figure 4.5 shows a reactor where a metal (Pd) acetone solution has been added while the reactor was hot.



Figure 4.5: Pd catalyst in microreactor

The thermal, preactivation of the catalyst is done automatically when the reactor is anodically bonded, since the reactor is heated to 400-450°C during this procedure. When the reactor is placed on the heating plate a clear sintering of the catalyst is seen as a reduction in volume. Furthermore the catalyst is loosened from the silicon surface, but because the chip is already cleaned and ready for bonding, this is not a problem. However, when the catalyst loosens, some particles can go out of the reactor onto the chip. This causes problems bonding wise, since particles are difficult to remove when the catalyst no longer sticks to the silicon.

## 4.4 Summary: Example of Catalyst Loading

To illustrate the catalyst loading procedure, a detailed description of the catalyst loading into reactor F is made. The loading procedure is made over two stages. In the first stage the support material gel is synthesized and loaded into the reactor, while in the second stage impregnation of the active metal to the support is performed.

#### Synthesis and Loading of the Support Material Gel

- $10 \text{ ml H}_2\text{O}$ ,  $1.25 \text{ ml HNO}_3$  and 0.5 g AlOOH is stirred in a beaker for 15-20 minutes
- reactor chip F is weighed, weighs 349.1 mg empty, and is placed on a hotplate (100-120°C)
- gel is transferred to a syringe with a hypodermic needle on the tip
- using the syringe, some gel is placed in the reaction chamber and dried. The procedure is repeated three or four times
- the reaction chip is cleaned on a piece of printer paper wetted with acetone. The cleaning is repeated till the chip is completely free for dust or support residues

- the reactor chip is again placed on the hotplate for 5 minutes
- the reaction chip is weighed again, weighs 351.9 mg

#### **Impregnation of Active Metal**

- 24.0 mg  $Fe(acac)_3$  is placed in a beaker
- 1318.7 mg acetone is added to the beaker
- the  $Fe(acac)_3$  is dissolved and transferred to a syringe
- the support material loaded reactor is placed on a scale, which is set to zero
- a drop of Fe(acac)<sub>3</sub>-acetone solution are put on the support, the weight is noted, the acetone evaporates, and the procedure repeated. This is repeated three times giving a total weight of 6.9 mg
- the reactor chip is carefully cleaned
- the reactor is ready for bonding

To determine the amount of metal in the reactor, the following calculations are made:

Reactor F is loaded with 351.9 mg - 349.1 mg = 2.8 mg support material. When the support material is heated above 500°C it (actually it is AlOOH) evaporates 30(w/w)% water giving a support material weight of  $0.7 \cdot 2.8$  mg = 1.96 mg.

Of the 24 mg  $Fe(acac)_3$  the accurate amount of Fe found:

$$n_{Fe(acac)} = \frac{m_{Fe(acac)}}{M_{Fe(acac)}}$$
  
=  $\frac{24 \cdot 10^{-3} \text{g}}{(55.85 + 3 \cdot 99.106) \text{g/mol}}$   
=  $6.8 \cdot 10^{-5} \text{mol}$ 

So in the 24 mg  $Fe(acac)_3$  the Fe mass is

$$m_{Fe} = n_{Fe} \cdot M_{Fe} = 6.8 \cdot 10^{-5} \text{mol} \cdot 55.85 \text{g/mol} = 3.8 \cdot 10^{-3} \text{g} = 3.8 \text{mg}$$

This means that the  $Fe(acac)_3$ -acetone solution contains

$$\frac{3.8 \text{mg}}{24 \text{mg} + 1318.7 \text{mg}} \cdot 100\% = 0.28 (\text{w/w})\%$$

Fe.

When 6.9 mg Fe(acac)<sub>3</sub>-acetone solution is added to the support, the Fe content in the catalyst is

$$\frac{0.0028 \cdot 6.9 \text{mg}}{0.0028 \cdot 6.9 \text{mg} + 1.96 \text{mg}} \cdot 100\% = 1.0\%$$

The catalyst is thermally activated when it is placed on the heating plate before being anodically bonded.

## Chapter 5

# **Partial Oxidation of Methane**

In chapter 2 different methods for producing hydrogen are mentioned, namely steam reforming and partial oxidation of hydrocarbons and alcohols, and ammonia decomposition. A literature survey determined ammonia decomposition to be the preferable process for producing hydrogen. As the introductory experiments, however, partial oxidation of methane is made, because it is known to work on the setup. The introductory experiments are made to get familiar with the experimental setup described in chapter 3, in addition to investigating if the new incorporation method works. The results of these experiments will be presented and discussed in the present chapter.

## 5.1 Results

In partial oxidation of methane experiments, methane and oxygen are the reacting compounds, but in the following experiments also argon is used to dilute the reactant gas. The gasses are sent through the reactor and the data from the mass spectrometer is used to investigate the reaction under different operation conditions. For partial oxidation of methane, the variable parameters are the reactor temperature, the reactant gas flow, and the methane-to-oxygen ratio. In the following only results from a temperature experiment and from a methane-to-oxygen ratio experiment are investigated. The catalyst used in both experiments is Pd on  $Al_2O_3$  made as described in chapter 4

The data given from the mass spectrometer is a current measure with unit Ampere (A). An increase in amount of a specific species will result in a higher current, so a current measurement can be interpreted as a concentration or mol fraction.

The current data is not treated quantitatively but only a qualitative interpretation of the oxidation reaction is performed.

#### 5.1.1 Influence of the Temperature

To investigate the influence of the temperature, the current of a power supply is altered manually to vary the temperature. The resulting temperature is noted. The flow of the inlet gas is 1.0 ml/min oxygen, 2.0 ml/min methane, and 3.0 ml/min argon throughout the experiment. The result can be seen in figure 5.1



Figure 5.1: Influence of temperature. Flow: 2 ml/min methane and 1 ml/min oxygen with 3 ml/min argon

The figure shows the reaction progress when the temperature is altered. Table 5.1 summarizes the effect a temperature change has on the process. A green arrow symbolizes a change according to the wanted overall partial oxidation reaction (2.15)

$$CH_4 + \frac{1}{2}O_2 \rightleftharpoons 2H_2 + CO \tag{2.15}$$

while a red arrow symbolizes a change according to the unwanted first stage oxidation reaction (2.16)

$$CH_4 + 2O_2 \rightleftharpoons CO_2 + 2H_2O$$
 (2.16)

<b>Temperature</b> (°C)	$\mathbf{H}_2$	$\mathbf{CH}_4$	$\mathbf{O}_2$	CO	$\mathbf{CO}_2$
330	$\rightarrow$	$\downarrow$	$\downarrow$	↑	1
412	↑ followed by ↓	↓	$\downarrow$	↑	↑ followed by ↓
505	$\rightarrow$	Ļ	$\rightarrow$	$\rightarrow$	$\downarrow$
590	1	Ļ	$\rightarrow$	1	$\downarrow$
350	$\downarrow$	↑	$\rightarrow$	↓	1
Lower		1	1	$\rightarrow$	

Table 5.1: Influence of temperature. Flow 2 ml/min methane and 1 ml/min oxygen with 3 ml/min argon

Table 5.1 shows that the only temperature at which the wanted oxidation reaction occurs is when the temperature is 590°C. There is, however, a small production of hydrogen and CO but a decrease in CO<sub>2</sub> when the temperature is above 412°C, indicating that reaction (2.17)

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$$
 (2.17)

takes place, since this is the only reaction where  $CO_2$  is a reactant producing hydrogen and CO.

In the beginning of the experiment the reactor temperature is  $170^{\circ}$ C and no reaction takes place. As the temperature is raised to  $412^{\circ}$ C the only reaction taking place is reaction (2.16). This can be concluded from figure 5.1 because no significant amount of hydrogen and only little CO is formed. It is further confirmed by the rapid raise in the CO<sub>2</sub> signal. CO<sub>2</sub> is only formed in reaction (2.16) and (2.19)

$$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2 \tag{2.19}$$

but in the latter reaction, hydrogen is also one of the products and since there is no change in the hydrogen signal, the significant reaction taking place must be reaction (2.16).

Reaction (2.16) also produces water, so a water measurement could have been a further confirmation. Unfortunately the mass spectrometer is not able to give a reliable measure for water, since water condenses in the pipes resulting in a misguiding signal. Therefore the water content is not analyzed.

When the temperature is raised above  $412^{\circ}$ C, the hydrogen signal increases significantly. However, the signal decreases again and stabilizes at a lower current. CO is also produced indicating that reaction (2.15) now takes place. This corresponds to what is expected because reactions (2.17) and (2.18)

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \tag{2.18}$$

giving reaction (2.15), are favored at higher temperatures. This is clearly seen when the temperature is raised to 590°C giving a clear increase in hydrogen and a continuing decrease in  $CO_2$ .

A decrease in temperature gives a rapid decrease in both hydrogen and CO, while methane and  $CO_2$  increase. This indicates that reaction (2.16) becomes significant once more, and is furthermore confirmed by the increase in the methane signal indicating surplus methane.

Further cooling of the system gives a decrease in all product signals, while the reactant signals increase. This indicates, as expected, that the reactions only take place at high temperatures.

After the system is heated to 412°C and until it is cooled, the oxygen signal completely disappears, indicating instantaneous oxygen conversion. The methane signal shows a clear decrease in signal, but never full conversion. This also suggests that reaction (2.16) is the dominating reaction, since the methane to oxygen is 2:1. If reaction (2.15) is the dominant one, methane should also have been near complete conversion.

Unfortunately the different temperatures were not held constant long enough for the signals to stabilize. Had this been the case, the signals had been more reliable and easier to interpret.

Figure 5.1 shows that each time the temperature is raised, both the hydrogen and the methane signals first increase but decreases just after. The reason for this is transient.

#### 5.1.2 Influence of Methane-to-Oxygen Ratio

To investigate the influence of the methane-to-oxygen ratio, a constant total flow of 10 ml/min is sent through the reactor. Initially as 3.34 ml/min methane, 1.66 ml/min oxygen, and 5 ml/min argon corresponding to a methane-to-oxygen ratio of 2:1 is sent to the reactor, but through the experiment the ratio is changed. At the starting temperature of 200°C no reaction occurs, but when the reactor is heated to 300°C products are formed. The temperature is raised further to 650°C where it is held constant through the remaining time of the experiment.

Figure 5.2 shows the change in reactant and product concentrations, when the methaneto-oxygen ratio is varied.



Figure 5.2: Methane-to-oxygen ratio influence

Table 5.1 summarizes the effect the ratio has on the reaction. Again a green arrow indicates a change according to the wanted overall partial oxidation reaction (2.15), while a red arrow indicates a change according to the unwanted first stage oxidation reaction (2.16).

$\mathbf{CH}_4$ to $\mathbf{O}_2$ Ratio	$\mathbf{H}_2$	$\mathbf{CH}_4$	$\mathbf{O}_2$	CO	$\mathbf{CO}_2$
2:1	1	$\downarrow$	$\rightarrow$	1	$\downarrow$
2.5:1	Ļ	$\downarrow$	$\rightarrow$	$\rightarrow$	$\downarrow$
3.3:1	↑	1	$\rightarrow$	1	$\downarrow$
5:1	$\downarrow$	1	$\rightarrow$	$\rightarrow$	↓
10:1	$\downarrow$	1	$\rightarrow$	$\rightarrow$	$\downarrow$
2:1	1	$\downarrow$	$\rightarrow$	$\downarrow$	1
1.4:1	1	Ļ	$\rightarrow$	$\rightarrow$	1

Table 5.2: Influence of methane-to-oxygen ratio,  $T = 650^{\circ}C$ 

As for the experiments where the influence of temperature was investigated, the signals have not had time to stabilize in this experiment either. This makes interpretation of the results rather difficult and only tendencies can be discussed.

Figure 5.2 shows that most hydrogen is produced when the methane-to-oxygen ratio is

3.3:1. It is, however, difficult to conclude if this is the optimal ratio, because the signals have not had time to stabilize when the other ratios are changed. The methane-to-oxygen ratio of 2:1 in both the beginning and end of the experiment tends to result in quite high hydrogen signals. Neither of the two points where the ratio is changed to 2:1 tend to stabilize, indicating that they might give hydrogen signals as high as for the ratio of 3.3:1.

As stated in chapter 2 but also as seen from the experiment investigating temperature influence above, reaction (2.15) is preferred at high temperatures. The present experimental results also show that reaction (2.15) is the reaction mainly taking place. This is the case because a significant amount of both hydrogen and CO is present throughout the experiment after the temperature has reached 650°C.

## 5.2 Discussion and Conclusion

The temperature and methane-to-oxygen ratio influence regarding partial oxidation of methane has been experimentally investigated. This has been done by two experiments; one where the reactor temperature is varied and another where the methane-to-oxygen ratio is varied.

Figure 5.1 indicates that when partial oxidation of methane is used to produce hydrogen, the temperature must be above 590°C. This corresponds well to what is expected from the statement in section 2.2.2, saying that at higher temperatures reactions (2.17) and (2.18) are favored, in addition to the temperature range Mallens et al. [19] found was optimal for partial oxidation. They made their experiments in a temperature range of 600-800°C. Both reactions (2.17) and (2.18), the main hydrogen and CO forming reactions, lead to the overall reaction (2.15).

At the lower temperatures  $CO_2$  is produced indicating that reaction (2.16) is the dominant reaction. This is confirmed by the small amount of hydrogen present at the lower temperatures.

According to reaction (2.15) the methane-to-oxygen ratio should be 2:1. To investigate if a different ratio can give a more favorable product stream, an experiment where the methane-to-oxygen ratio is varied has been carried out.

Figure 5.2 shows that a methane-to-oxygen ratio of 2:1 at a temperature of 650°C, gives a high hydrogen signal and a significant rapid decrease in methane. Unfortunately the reactions are not given time to stabilize. If they had been given time to stabilize, full conversion of methane would very likely have been obtained.

When the ratio is set to 3.3:1 steady state is obtained, seen by the fact that all signals stabilize. Oxygen is completely converted while methane is still present. This corresponds well with the expected because methane is surplus according to reaction (2.15). It also indicates that full conversion of both methane and oxygen could be possible if the system is just given time to stabilize.

The experiment with varied temperature showed that at temperatures above  $590^{\circ}$ C the overall reaction for partial oxidation of methane reaction (2.15) is preferred. This corresponds well to the results of the experiments investigating ratio influence, as a significant amount of hydrogen is produced at all ratios at a temperature of  $650^{\circ}$ C.

Based on the results of the experiment concerning temperature, the operation temperature should be held above 590°C if partial oxidation of methane is the desired hydrogen producing process. At this temperature all oxygen is converted forming CO and  $CO_2$ . The methane to oxygen ratio should be 2:1.

Both experiments show that partial oxidation of methane can produce hydrogen, which is the wanted fuel for fuel cells. Unfortunately partial oxidation also produces CO as a byproduct. CO is very unwanted in fuel cells, because it contaminates and poisons the catalyst electrodes in the fuel cell, and over time makes them inactive. Therefor the CO content in the product gas from partial oxidation must be minimized to 5-50 ppm before using it in a fuel cell. This CO reduction can be carried out by performing temperature shifts, a resourceful and costly process, and alternative hydrogen sources are therefore of interest.

An alternative to partial oxidation is ammonia decomposition, producing hydrogen and nitrogen, neither of which are damaging towards fuel cells. Any unreacted ammonia can contaminate the electrolyte, but is easily and cheaply removed by adsorption.

Adsorption could be necessary anyway as it is not unknown to have 30-90 ppm ammonia in hydrogen produced by partial oxidation due to reactant contamination.

The ammonia content in any hydrogen fuel stream for a fuel cell must be below 13 ppm. Adsorption using sulfuric acid is known to reduce an ammonia concentration to less than 200 ppb, making it an optimal solution to the ammonia problem.

Based on the correspondence between results from earlier partial oxidation of methane experiments and the results of the above mentioned experiments, microreactors seem to be ideal systems for investigating partial oxidation. The fact that the above mentioned experiments have been performed in microreactors does not seem to affect the oxidation reaction significantly. Furthermore the newly developed incorporation method turned out to be satisfactory, giving reasonable results for partial oxidation.

## Chapter 6

# Ammonia Decomposition

In chapter 2 ammonia decomposition was found to be the optimal hydrogen producing process compared to steam reforming and partial oxidation of hydrocarbons and alcohols. In the present chapter experiments and results regarding ammonia decomposition in microreactors are presented and discussed. The catalysts to be used for the ammonia decomposition experiments are 1.9(w/w)% Cu/Al<sub>2</sub>O<sub>3</sub>, 1.0(w/w)% Fe/Al<sub>2</sub>O<sub>3</sub>, 0.9(w/w)% Pd/Al<sub>2</sub>O<sub>3</sub>, 0.4(w/w)% Co/Al<sub>2</sub>O<sub>3</sub>, and 1.3(w/w)% Ru/Al<sub>2</sub>O<sub>3</sub>, according to the five reactors incorporated in chapter 4. These active metals are chosen partly because they represent metals from four transition metals groups, partly because they are metals commonly used in the literature.

## 6.1 Presentation of Experiments

To investigate the influence of experimental conditions regarding the conversion of ammonia, the catalyst, the temperature, the ammonia flow, and the argon concentration in the inlet gas have been varied in different experiments. All experiments are carried out at atmospheric pressure, but the pressure could also be a variable parameter. In the following the changes in operation conditions will shortly be described.

#### Influence of Temperature

To investigate the temperature effect on the ammonia conversion, each of the five catalysts have been tested at three different temperatures. A program is used to make temperature ramps so it is possible to see at exactly which temperature the reaction begins. In the program a set point temperature is entered. The three set point temperatures used here are 500, 600 and 700°C. These temperatures are chosen, because earlier ammonia decomposition experiments typically were operated at temperatures above  $400^{\circ}$ C (see table 2.1 in chapter 2).

#### Influence of Flow

One would think that a lower gas flow, resulting in a higher residence time, will give the ammonia more time to convert. To see if this is the case, the gas flow is varied to investigate an eventual effect. For each of the three above mentioned temperatures, two different gas velocities; 0.4 ml/min and 2 ml/min are investigated for each of the five catalysts.

#### Influence of Argon Concentration

To investigate if ammonia inhibits the decomposition reaction, experiments with respectively 50 and 100% ammonia are made. The above mentioned experiments are all made with approximately 50% argon, while the experiments for 100% ammonia are only carried out at a set point temperature of  $600^{\circ}$ C and 2 ml/min ammonia.

## 6.2 Introductory Experiment

Ruthenium is a well known catalyst for ammonia decomposition, and therefore this is the catalyst used in the introductory experiment of ammonia decomposition.

As mentioned, a temperature ramp is used to control the temperature in the reactor. The ramp is run by the LabVIEW<sup>TM</sup> program, which is programmed to heat the reactor to a specific temperature, hold the reactor at this temperature for a specific time, and then cool the reactor again to a specific temperature. The program is set to respectively heat and cool 2°C per second. Figure 6.1 shows a temperature ramp with a maximum temperature set point of 600°C. The actual reactor temperature is usually  $30-50^{\circ}$ C lower than the set point temperature which is seen in the figure.



Figure 6.1: Example of a temperature ramp with set point 600°C and an increase of 2°C per second

When using the ruthenium catalyst, the ammonia decomposition should start at 623-673K (350-400°C) [21, 10], so in the first experiment the temperature set point is set to 600°C. This is a high set point, which is chosen to ensure reaction. The ammonia and argon flows are 2 ml/min and 2.52 ml/min respectively. Figure 6.2 shows the mass spectrometer (MS) signals for ammonia, hydrogen, and nitrogen during this temperature ramp program



Figure 6.2: Hydrogen, nitrogen, and ammonia MS signals for Ru catalyst and 2 ml/min ammonia and 2.52 ml/min argon

The figure shows that at about 380°C the decomposition reaction begins. The hydrogen signal shows a significant increase in hydrogen, while the nitrogen signal is not so clear. When the temperature of the reactor again is decreased the signals return to their initial positions almost immediately. This indicates that the reaction is endothermic, since the reaction does not happen when the temperature is lowered.

According to the reaction scheme for ammonia decomposition, reaction (2.21)

$$2\mathrm{NH}_3 \rightleftharpoons 3\mathrm{H}_2 + \mathrm{N}_2 \tag{2.21}$$

the increase in hydrogen should be three times that of nitrogen. This is not indicated by the MS signals suggesting that the mass spectrometer is more sensitive toward hydrogen than nitrogen. A reason could be that the hydrogen molecule is so small that the mass spectrometer has difficulty pumping it from the vacuum chamber, making hydrogen accumulate here, resulting in the high hydrogen signal.

There also seems that there are problems with the ammonia signal. Even at the maximum temperature of 550°C there is only little change in the ammonia signal, which seems strange, since a clear production of especially hydrogen but also nitrogen is observed. When the temperature is decreased again the ammonia signal is not at the initial current indicating stabilization problems. To see if the problem with the signal is slow stabilization, argon and ammonia is sent to the spectrometer in equal velocities. Figure 6.3 shows how the argon and ammonia signals change when the ammonia flow is changed.



Figure 6.3: Change in argon and ammonia signals when the ammonia velocity is changed

During the experiment the argon flow is held constant. The argon signal stabilizes almost immediately, while the ammonia signal is not finished stabilizing when the velocity again is lowered.

It turns out that if the pipe going from the setup to the mass spectrometer is hand heated, the ammonia signal raises significantly when ammonia is sent through the reactor. This indicates that the ammonia condensates in this pipe making the signal misleading. A result to the problem could therefore be heating of the pipe using e.g. a rope heater, but this has not been done in these experiments. This indicates that the mass spectrometer measurements regarding ammonia are not reliable, and will not be analyzed further.

In the following result treatment only the nitrogen signal is analyzed, because both the hydrogen and the ammonia signals are unreliable. How the signal is calibrated to a concentration is described in appendix D.

### 6.3 Treatment of Results

For evaluating a reaction, the *conversion* of reactants is a very descriptive value. The conversion quantifies how far a reaction has progressed, or how much of a basis reactant has reacted to form product. The conversion can also be used to investigate the activity of a catalyst.

Another interesting value is the theoretical equilibrium constant. The theoretical equilibrium constant gives an indication of the maximum fraction of reactant which converts at a specific temperature, if the reaction is allowed to reach equilibrium, i.e. the residence time is large enough.

Finally the activation energy can give an indication of the activity of a catalyst, and is a good measure when the results are to be compared with results from earlier experiments.

#### 6.3.1 Conversion

To determine the activity of a catalyst, the conversion of the reactant must be found. This can be done by using the following equation from Fogler [40]

$$C_{j} = \frac{C_{A0} \left(\Theta_{j} + \nu_{j} X\right)}{1 + \varepsilon X} \frac{p}{p_{0}} \frac{T_{0}}{T}$$
(6.1)

where  $C_j$  is the concentration of species j,  $C_{A0}$  is the initial concentration of species A,  $\nu_j$  is a stoichiometric coefficient, X is the conversion of species A,  $p_0$  and p are the initial and present pressures, and  $T_0$  and T are the initial and present temperatures.  $\Theta$  and  $\varepsilon$  are constants corresponding to the specific reaction. When they are determined, as described in appendix E, equation (6.1) can be solved with respect to the conversion X, giving equation (6.2)

$$X = \frac{2C_{N_2}T}{C_{NH_{3,0}}T_0 - 2y_{NH_{3,0}}C_{N_2}T}$$
(6.2)

when  $y_{NH_{30}}$  is the initial mol fraction of ammonia.

The activity can now be found as the amount of ammonia converted per unit time per mass catalyst or active metal, e.g. mol NH<sub>3</sub> converted per second per gram metal. The conversion of ammonia is found as  $F_{NH_{3},0} - 2 \cdot X \cdot F_{NH_{3},0}$ , where X is determined by the nitrogen signal.

A calculation example for finding conversion based on the nitrogen signal can be seen in appendix E.

#### 6.3.2 Chemical Equilibrium

To get an idea of the maximum fraction of ammonia possible to decompose, the theoretical equilibrium is determined. This is done by finding the equilibrium constant, K, defined as

$$K \equiv \exp\left(\frac{-\Delta G^{\circ}}{RT}\right) \tag{6.3}$$

where  $\Delta G^{\circ}$  is Gibb's free energy, R is the gas constant, and T the temperature. Equations and calculations for finding Gibb's free energy,  $\Delta G^{\circ}$  and thereby also the equilibrium constant at different temperatures can be seen in appendix F. The theoretical equilibrium constants at a range of temperatures can be seen in table 6.1

Table 6.1: The equilibrium constant at different temperatures for ammonia decomposition

Temperature	K
(K)	
298	$0.17 \cdot 10^{-5}$
523	29
563	153
603	657
643	2383
683	7523
723	21125
763	53698
803	125292
823	271431
923	1436137

The values in table 6.1 show that as the temperature is raised the ammonia decomposition reaction is shifted to the right, meaning the higher the temperature the more ammonia is decomposed, corresponding to an endothermic reaction.

#### 6.3.3 Activation Energy

The activation energy of a reaction can be determined by the Arrhenius equation [40], equation (6.4)

$$k_A(T) = A_E \exp\left(\frac{-E_a}{RT}\right) \tag{6.4}$$

where  $k_A(T)$  is the specific reaction rate,  $A_E$  is a preexponential factor,  $E_a$  is the activation energy, R is the gas constant, and T the temperature.

By plotting e.g. the logarithm of ammonia converted per second as a function of inverse temperature, the activation energy can be determined from the slope of the straight line regressed to the data points. This can be seen by taking the logarithm to the Arrhenius equation and getting

$$\ln(k_A(T)) = \ln(A_E) - \frac{E_a}{R} \frac{1}{T}$$
(6.5)

## 6.4 Results

As mentioned in section 6.1 ammonia decomposition experiments on the five catalysts will investigate the influence of the temperature, the total inlet flow, and the ammonia concentration in the inlet flow.

For each of the experiments the steady state conversion and the corresponding amount of ammonia decomposed per second per gram metal is found. Calculation methods are summarized in appendix E.

Due to measuring errors, not all the data points obtained in the different experiments give reasonable results (negative conversions and conversions above 1) and therefore these results are not shown in the result presentation.

#### 6.4.1 Influence of Temperature

The influence of temperature is tested by making three experiments for each of the catalysts. The ramp set point temperatures for the three experiments are 500, 600, and  $700^{\circ}$ C respectively.

Figure 6.4 illustrates the conversion of ammonia at different steady state temperatures. The maximum conversion expected from the equilibrium constant is also shown in the figure.



Figure 6.4: Influence of temperature on ammonia conversion. Flow: 2 ml/min ammonia and 2.25 ml/min argon

The figure shows a general tendency of increasing conversion for increasing temperature for all five catalysts. At the lower temperatures all five catalysts vary from equilibrium, while Fe and Ru are close to equilibrium at  $675^{\circ}$ C.

To investigate the drop at  $560^{\circ}$ C in conversion for the Ru catalyst, figure 6.5 illustrates the temperature influence for a flow of 0.4 ml/min ammonia and 0.45 ml/min argon. The lower flow will of course have an influence on the conversion, but it is assumed that the tendencies are the same for the two flows.



Figure 6.5: Influence of temperature on ammonia conversion. Flow: 0.4 ml/min ammonia and 0.45 ml/min argon

The figure shows that conversion on Ru is not significantly higher than on the other four metals at a temperature of about 480°C, opposed to what figure 6.4 shows. This indicates that the observed Ru conversion at 480°C in figure 6.4 is a measuring error. The conversion rank at 650°C is similar for the two figures, Fe>Co>Pd.

The metal content in the catalyst is not the same for the five reactors but has an effect on the conversion, and therefore the metal mass is taken into account. Figure 6.6 illustrates the amount of ammonia converted per second per gram metal at the three steady state temperatures. The ammonia converted per second per gram metal is an expression for the activity of a metal.



Figure 6.6: Influence of temperature on the mol of ammonia converted per second per gram metal. Flow: 2 ml/min ammonia and 2.25 ml/min argon

Figure 6.6 shows that the activity of Co is higher than the activity of the other four metals. The decreasing activity order of these four is Ru>Fe>Pd>Cu. The activity of all the metals but Ru increase with increasing temperature. The Ru activity decreases at 560°C but increases again at 680°C, similar to what is observed in figure 6.4, most likely due to a measuring error.

The activity investigation is based on results of the high flow shown in figure 6.4 because an interesting result for the conversion on Ru at 680°C is obtained in the high flow experiment opposed to for the low flow. This conversion is of interest because it shows that the equilibrium determined maximum is nearly reached.

#### 6.4.2 Influence of Flow

The influence of the ammonia flow is tested by making two experiments on each of the catalysts. The flows investigated are 0.4 ml/min ammonia with 0.45 ml/ml argon and 2.0 ml/min with 2.25 ml/min argon. More flows have been tested on the Ru catalyst. The temperature ramp has a set point of 600°C for all the experiments.



Figure 6.7: Influence of flow on the ammonia conversion. Temperature: 570°C, equal flows of ammonia and argon

Figure 6.7 illustrates the conversion of ammonia at a steady state temperature of  $570^{\circ}$ C under different reactant gas flows. It shows that a higher flow gives a lower conversion as expected, due to a decrease in residence time. Pd is the most sensitive to a flow change, while Fe is only slightly affected.

On Ru five different flows have been tested; 0.4 ml/min, 2.0 ml/min, 4.0 ml/min, 8 ml/min, and 16 ml/min ammonia, all with 53% argon. The Ru experiments indicate that when the flow goes toward infinity, the conversion goes toward a very low conversion.

Figure 6.8 illustrates the amount of ammonia converted per second per gram metal for different flows at a temperature of  $570^{\circ}$ C.



Figure 6.8: Influence of flow on the mol of ammonia converted per second per gram metal. Temperature: 570°C, equal flows of ammonia and argon

The figure shows that when the residence time and metal mass is taken into account, the activities increase for Ru, Fe, and Co with increasing flows. The Ru activity seems to follow an asymptote when the ammonia flow reaches 8 ml/min, indicating a maximum activity at the present temperature.

The Pd and Cu conversions at the low flow are significantly higher than the conversions at the higher flow. Therefore a decrease in residence time gives a decreased in activation. In addition the figure shows that Pd is the most active of the five metals regarding ammonia decomposition at the lowest flow. The decreasing activity order of the remaining four is Co>Ru>Fe>Cu. The tendency in figure 6.8 shows that the activity order is Co>Fe>Ru>Pd>Cu.

### 6.4.3 Influence of Argon Concentration

To investigate the effect of a large ammonia concentration, a 4.0 ml/min flow of 100% ammonia is decomposed on the five catalysts. The temperature ramp set point is  $600^{\circ}\text{C}$  for all experiments.

Figure 6.9 illustrates the conversion of ammonia at a steady state temperature of  $570^{\circ}$ C and an inlet flow of 47% and 100% ammonia. The total flows are 4.5 ml/min ammonia



with argon and 4.0 ml/min pure ammonia

Figure 6.9: Influence of the ammonia concentration at 570°C

The figure clearly shows a decrease in conversion when the ammonia concentration is raised. This indicates that a large ammonia concentration inhibits the decomposition reaction.

#### 6.4.4 Determination of Activation Energy

Figure 6.10 shows Arrhenius plots for Ru and Fe at a flow of 2 ml/min ammonia and 2.25 ml/min argon. The set point temperatures are 500 and 600°C respectively.



Figure 6.10: Arrhenius plot for (a) Ru and (b) Fe

From the regressed lines the activation energy can be determined by multiplying the slopes of the lines with the negative gas constants giving respectively

Ru : 
$$E_a = -(-14.78 \cdot 10^3 K) \cdot 8.31451 \text{J/(mol} \cdot \text{K}) = 122888 \text{J/mol} = 123 \text{kJ/mol}$$
  
Fe :  $E_a = -(-18.68 \cdot 10^3 K) \cdot 8.31451 \text{J/(mol} \cdot \text{K}) = 155315 \text{J/mol} = 155 \text{kJ/mol}$ 

For Ru only the activation energy for the lower temperatures is determined. At the higher temperatures the slope decreases, giving approximately  $\frac{1}{2}E_a$ , which is an indication of diffusion [4].

In the literature survey activation energies for Ru, Fe, and Pd has been found, therefore the activation energies for Co and Cu are not determined. Unfortunately only the steady state temperatures for the Pd experiments was noted, and therefore the activation energy for Pd is not determined either.

### 6.5 Discussion

Based on results from the above performed ammonia decomposition experiments, the influence of temperature, flow, and ammonia concentration in the inlet stream is investigated. The activity of the five catalysts is compared and the activation energy for Ru and Fe is determined.

An investigation of the temperature influence regarding the ammonia decomposition shows that an increase in temperature gives an increase in both conversion and activity. This corresponds well to what is expected, since the equilibrium constants increases with temperature. At 680°C and with a flow of 2 ml/min ammonia, the equilibrium conversion is 99.0% and the conversions for Ru and Fe are 88.4% and 97.5%, respectively, showing that there is not reason to operate at higher temperatures than 680°C. when high conversions are wanted. However, when the conversion is compared directly to the corresponding equilibrium expected conversion, there is a significant difference at the lower temperatures. A reason for this could be that the reaction is activity limited below a certain temperatures, corresponding to what figure 6.5 shows. Despite a lower flow of 0.4ml/min ammonia giving a higher residence time, the conversion on Fe only reaches 61.6% at a temperature of  $650^{\circ}$ C, indicating that the activation temperature of Fe is above  $650^{\circ}$ C. A closer look at Ru shows that at temperatures below  $580^{\circ}$ C, the catalyst does not vary from the other four. However, when the temperature was raised above  $580^{\circ}$ C the conversions on Ru increases significantly compared to Co, Pd, and Cu. The reason for this could be that Ru too is not activated at the lower temperatures. Bradford et al. [30] investigated ammonia decomposition on Ru/Al<sub>2</sub>O<sub>3</sub> i a temperature range of  $623-723^{\circ}$ C. They observed conversions between 9 and 32% corresponding both the conversions obtained on Ru illustrated in figures 6.4 and 6.5, indicating that the high conversion on Ru seen in figure 6.4 is not a measuring error.

The equilibrium maximum showed that complete conversion (100%) is not possible at 680°C. This means that if the hydrogen produced is to be used for fuel cells, the decomposition product gas must be absorbed before being led to the fuel cell.

Based on the conversion and mass of active metal, the activities of the catalysts are found. As for the conversion, the activity increases with increasing temperature. At a temperature of  $680^{\circ}$ C the decreasing activity order of the five catalysts is Co>Ru>Fe>Pd>Cu. A comparison to the order Boisen et al. [45] found shows similarity. Boisen et al. found the activities in decreasing order to be Ru>Co>Co<sub>3</sub>Mo<sub>3</sub>N>Ni>Fe>Cu. Except for a change in Ru and Co, this is the same as found above. Although Ni and Pd are in the same transition metal group, Ni seems a better choice for ammonia decomposition since it is more active than Fe.

An investigation of the flow influence regarding the ammonia decomposition reaction shows that a lower flow gives a higher conversion. This is as expected, since a lower flow will give a longer residence time. When the flow is raised the conversion decreases for all the catalysts.

The activities do not show a similar tendency as the conversions when the flow is increased. The reason for this could be the reaction rates on the different catalysts resulting in decreasing activities of Pd and Cu with increasing flows. The activities of Co, Fe, and Ru all increase with increasing flows.

From a catalyst activity view Co again shows the highest activity followed by Pd>Fe>Ru>Cu at a flow of 2 ml/min ammonia. The reason that Ru is not very active could be due to the temperature which is only 570°C. For higher flows (above 2 ml/min ammonia) the decreasing activity order seems to be Co>Fe>Ru>Pd>Cu, because the activity of both Pd and Cu decrease with increasing flow, while Co, Fe, and Ru increase. The activity of Co increases faster than the activity of Fe. The activity of Ru seems to stabilize at 0.02 mol ammonia converted per second per gram Ru at a flow of 8 ml/min ammonia,

while the activities of both Co and Fe are above this value at 2 ml/min ammonia.

A more thorough investigation of the flows tested on Ru shows that an increase in flow gives a decrease in conversion as expected due to the residence time. When the flow is raised, the conversion decreases and tends to follow an asymptote going towards zero. This does not mean that no ammonia is decomposed, but compared to the amount entering the system, it is only a small fraction.

The Ru activity shows that for increasing flows, the activity also increases till it reaches 0.02 mol ammonia converted per second per gram Ru, where it tends to follow an asymptote. The reason the activity is low for the lower flows is mass transport limitations due to diffusion. An investigation of these transport limitations will be investigated in chapter 7.

To investigate if a large ammonia concentration in the inlet flow inhibits the reaction, experiments with a pure ammonia flow are made. The result of these all show a decrease in conversion when the ammonia concentration in the inlet flow in increased. This is a strong indication that a high ammonia does inhibit the decomposition reaction.

The activation energies for Ru and Fe are determined to be 123 kJ/mol and 155 kJ/mol, respectively. In earlier performed experiments Bradford et al. [30] and Arabczyk et al. [28]. have determined the activation energies for Ru and Fe.

Bradford et al. found an activation energy for Ru to 130 kJ/mol in a temperature range of 350-400°C. This is in good agreement with the 123 kJ/mol in the temperature range of 350-450°C found above.

The change to a lower activation energy for the Ru catalyst, seen in figure 6.10(a), occurs when the conversion of ammonia is 30%. At this temperature the activity of the catalyst is so high that reaction takes place faster than transportation of reactant to the site, giving a concentration gradient inside the particle causing pore diffusion.

Araczyk et al. found that the activation energy for Fe is 87 kJ/mol in a temperature range of 360-560°C. This is approximately half the activation energy determined above for Fe in a temperature range of 450-570°C. Had the experiments of Araczyz et al.'s been carried out in a temperature range of 570-670°C the two activation energies would have been in good agreement, as the experiments investigating the temperature influence performed above, showed that when the temperature is at 670°C, almost complete conversion is observed on Fe. A reduction in activation energy would thus have been expected. This is, however, not the case. Araczyk et al. performed a literature survey and discovered that the activation energy at normal pressure varied from 150 to 240 kJ/mol. This is in quite good agreement with the activation energy determined above.

## 6.6 Conclusion

A number of experiments have been made to investigate the influence of temperature, flow and ammonia concentration in the inlet stream with respect to ammonia decomposition.

The influence of temperature experiments showed that the high temperature,  $680^{\circ}$ C, gave the highest conversion. Both Ru and Fe gave near the maximum conversion expected from an equilibrium point of view. This was, however, only at the highest tested temperature  $680^{\circ}$ C. The activity of the catalysts showed that Co was significantly more active than the other five catalysts at the high temperature, followed by Ru>Fe>Pd>Cu.

The experiments investigating the influence of flow showed that low flows gave high conversions. These experiments were made at a temperature of  $570^{\circ}$ C, which is below the temperature where almost full conversion of Ru and Fe was seen, and therefore full conversion was not reached for any of the metals. The activity of the metals indicated that Co again was the most active followed by Fe>Pd>Ru>Cu at flows above 2 ml/min ammonia.

An investigation of the ammonia concentration in the inlet stream showed that a large ammonia concentration inhibits the decomposition reaction.

An estimation of the activity energies from the experimental data gave an activity energy for Ru to 123 kJ/mol and for Fe to 155 kJ/mol. They corresponded well with the earlier determined activation energies.

The results from the experiments show that the catalysts to use, when a large hydrogen concentration is wanted, should be either Co, Fe, or Ru. The temperature should be 680°C and the flow above 2 ml/min diluted with 2.25 ml/min argon. Unfortunately, it is not possible to convert all ammonia in the inlet stream, so absorption must be performed, before the hydrogen stream can be led to the fuel cell.

## Chapter 7

# Analysis of the Microsystems

In chapter 6 the experiments investigating the influence of flow indicate mass transport limitations at low flows. In the present chapter the behavior of the microsystem will be investigated more thoroughly and the reason for mass transport limitation described.

Initially the space velocity is determined. The space velocity is an alternative to the flow, and is usually the given description of flow in literature. The space velocity is found so comparisons to the literature can be made.

The reciprocal Peclet number can give an indication of the behavior of a reactor and is therefore determined for the different tested flows.

Throughout the chapter the microreactor impregnated with Ru will be the reference system. The calculations are made for a temperature of 25°C, so no reaction takes place. Therefore, the only gases present in the system are ammonia and argon.

## 7.1 Space Velocity

The mean residence time,  $\tau$ , is the time it takes for one reactor volume fluid with a specific volumetric velocity to pass through a reactor. The space velocity is the reciprocal of the mean residence time and therefore tells how many reactor volumes can be processed per time unit. The space velocity is defined as [40]

$$SV \equiv \frac{v_0}{\mathcal{V}_{eff}} = \frac{1}{\tau} \tag{7.1}$$

where  $v_0$  is the entering volumetric flow rate and  $V_{eff}$  is the effective reactor volume both at standard pressure (1 atm) and temperature (25°C). For a catalytic system, the effective volume is the reactor volume not containing the porous catalyst.

The porous catalyst volume can be found from the definition of porosity

$$\varepsilon' = \frac{\mathcal{V}_{free\ cat}}{\mathcal{V}_{total\ cat}} \tag{7.2}$$

where  $\varepsilon'$  is the porosity of the catalyst,  $V_{free\ cat}$  is the pore volume of the porous catalyst, and  $V_{total\ cat}$  is the total volume of the catalyst.

The space velocity can thus be found as a function of the porosity (see detailed considerations and calculations in appendix G)

$$SV = \frac{v_0}{V_{total} - \frac{m_{catalyst}}{\rho_{solid\ catalyst}} \cdot \frac{1}{1 - \varepsilon'}}$$
(7.3)

where  $V_{total}$  is the total reactor volume,  $m_{catalyst}$  is the mass of the catalyst, and  $\rho_{solid\ catalyst}$  is the density of the solid catalyst (here Al<sub>2</sub>O<sub>3</sub>).

Figure 7.1 illustrates the space velocity for the Ru system with a total flow of  $v_0=0.85$  ml/min (0.4 ml/min ammonia and 0.45 ml/min argon at 1 atm and 25°C) corresponding to the lowest flow tested when the flow influence was investigated on Ru. The space velocity corresponding to higher flow tested, 2 ml/min ammonia and 2.25 ml/min argon, only varies from 998 per minute for a porosity of 0 to 999.0 per minute for the maximum porosity of 0.8.



Figure 7.1: Space velocity as a function of porosity for a total flow of 0.85 ml/min

The figure corresponds to a numerical expression for equation (7.3) of the form
$$SV = \frac{0.85ml/min}{0.0045ml - \frac{1.9 \cdot 10^{-3}g}{3.87g/ml} \cdot (\frac{1}{1 - \varepsilon'})}$$

The maximum porosity possible is 0.89 because a larger porosity will give a total catalyst volume larger than the volume of the reaction chamber.

Figure 7.1 shows that when the porosity increases, the space velocity also increases, though faster when the porosity is above about 0.5.

In chapter 4 it is described how the catalyst sinters when it is heated during anodically bonded. This gives a reduction in the total catalytic volume, compared to the catalyst volume immediately after the loading. The exact catalyst volume is not known, so the following calculations are performed for three different porosities 20, 50, and 80%.

#### 7.2 Investigation of the Peclet Number

The Peclet number can be used to describe the behavior of a fluid in a reactor. It can be found as [40]

$$N_{Pe} = \frac{\text{rate of conversion by convection}}{\text{rate of transport by diffusion or dispersion}} = \frac{uL}{D_a}$$
(7.4)

where L is the length of the reactor, u is the linear velocity in the reactor, and  $D_a$  is the dispersion coefficient. When the flow in the reactor is laminar, the dispersion coefficient can be found using the Aris-Taylor approximation [40]

$$D_a = D_{AB} + \frac{u^2 R^2}{48 D_{AB}}$$
(7.5)

where  $D_{AB}$  is the diffusion coefficient of compound A in compound B, here ammonia in argon since no reaction occurs, and R is the radius of the reactor. The dispersion coefficient describes the effective downstream diffusion coefficient.

To investigate if the flow is laminar, the Reynolds number can be found [43]

$$N_{Re} = \frac{\mathrm{u}\mathrm{D}_{H}\rho}{\mu} \tag{7.6}$$

where  $D_H$  is the hydraulic diameter of the reactor,  $\rho$  is the density of the fluid, and  $\mu$  is the viscosity of the fluid. When a stream is laminar, the Reynolds number is less than 2100 [43].

Table 7.1 shows the space velocity, the Reynolds number, and reciprocal Peclet number for the tested flows. The Reynolds number has been determined to ensure that the flow is laminar.

Total flow	Space velocity	Reynolds number	1/Peclet number
(ml/min)	$(1/\min)$		
$\varepsilon' = 0.2$			
0.85	218	0.7	0.0264
4.50	1158	3.8	0.0054
9.00	2315	7.6	0.0034
18.00	4630	15.1	0.0030
36.00	9260	30.3	0.0042
$\varepsilon' = 0.5$			
0.85	242	0.7	0.0241
4.50	1278	3.8	0.0049
9.00	2556	7.6	0.0031
18.00	5114	15.3	0.0028
36.00	10222	30.6	0.0039
$\varepsilon' = 0.8$			
0.85	415	0.8	0.0139
4.50	2195	4.0	0.0029
9.00	4390	8.0	0.0018
18.00	8781	15.9	0.0017
36.00	17561	31.8	0.0029

Table 7.1: The space velocity, the Reynolds number and reciprocal Peclet number for different porosities and flows

Figure 7.2 illustrates the reciprocal Peclet number for the three different porosities and the flows investigated on  ${\rm Ru}$ 



Figure 7.2: The reciprocal Peclet number for different porosities and flows

The figure shows that a higher flow and porosity gives a lower reciprocal Peclet number.

The reciprocal Peclet number is also known as the *vessel dispersion number*. Figure 7.3 illustrates the influence of the vessel dispersions number on a trace pulse.



Figure 7.3: The effuent concentration-time curve in closed vessels for various extents of back-mixing as predicted by the dispersion model [40]

Low values of the vessel dispersion number indicate a perfect pulse output corresponding to an ideal plug flow reactor, while large number correspond to the reaction behaving as a stirred tank reactor (CSTR continuously stirred tank reactor).

The vessel dispersion number indicates how diffusion influences the concentration of a specific compound. If the concentration stays as a pulse or if the concentration of the compound spreads out.

If the concentration spreads out, the absolute mean length of diffusion from the pulse inject can be determined as [35]

$$\bar{l} = \sqrt{2 \cdot D_{AB} \cdot t} \tag{7.7}$$

where  $\bar{l}$  is the mean distance the peak spreads in the time interval t and  $D_{AB}$  is the diffusion coefficient.

The mean length is used to describe the axial mixing in the reactor. Using the reciprocal space velocity (the residence time), the mean length for the different porosities can be calculated. The results are summarized in table 7.2

Inlet flow $(ml/min)$	$l(\mathrm{mm})$		
	$\varepsilon' = 0.2$	$\varepsilon' = 0.5$	$\varepsilon' = 0.8$
0.85	0.057	0.055	0.042
4.5	0.027	0.027	0.027
9.0	0.019	0.019	0.019
18.0	0.013	0.013	0.013
36.0	0.009	0.009	0.009

Table 7.2: The mean distance a peak will spread at different flow and porosities  $\overline{\mathbf{x}}$ 

Corresponding to what table 7.1 showed, the table shows that a higher flow gives a shorter mean distance spreading of the impulse peak, meaning the higher the flow, the closer to plug flow behavior.

#### 7.3 Discussion and Conclusion

Arabcyk et al. obtained a conversion on Fe of approximately 23% at 500°C and a space velocity of 5.3 Ndm<sup>3</sup>/(g·h). Their porosity was 0.5 and the experiment was carried out in an internal tank reactor and catalyst fixed in baskets. This space velocity corresponds to the low flow (0.85 ml/min) tested in the performed ammonia decomposition experiments, which gave a conversion on Fe of 13.2% at 580°C. There is some variation between these two conversions, and the fact that the activation energy determined by Arabcyk et al. is lower than the one determined in the present project does not correspond to the higher conversion.

Bradford et al. performed their experiments on Ru in a microreactor system with a flow rate of 1900 cm<sup>3</sup>/(g · h), but have unfortunately not noted their conversion. This flow corresponds to a flow of 2 ml/min ammonia with 2.25 ml/min argon investigated in the present project. The activation energies of the experiments performed by Bradford et al. and the present experiments showed good agreement.

As mentioned the Ru curve in figure 6.8 indicated mass transport limitations. This is the case because the activity of Ru does not stabilize till the flow is above 8 ml/min ammonia. The reason for this is most likely due to the high conversion giving diffusion problems. When the conversion is high, there can be mass transport limitations of the reactants to and the product from the active sites of a Ru particle. This causes a product concentration gradient in the particle giving pore diffusion. When the reactant cannot come in contact with the active sites, the possible activity of the catalyst is not reached. Furthermore, when the flow is low, diffusion in the radial direction, rather than in the axial direction, can act as mixing.

To investigate the latter, the dispersion number for the used to characterize the behavior of the system. The dispersion number is quite small for all the tested flows. Both figure 7.2 and table 7.1 show that the dispersion number goes toward zero. Figure 7.3 shows that when this is the case, the reactor behaves as a plug flow reactor.

A plug flow reactor can be seen as an infinity number of tank reactors in series. When a defined number of tanks are in series, the dispersion number can go towards a more defined number, as is seen in table 7.1 at a total flow of 0.85 ml/min and porosity 0.5, where the dispersion number is 0.0264. Figure 7.3 shows that a dispersion number of 0.02 indicates a small amount of dispersion. This means that the pulse concentration will spread some compared to in a plug flow reactor, table 7.2 shows that a peak spread of 0.05 mm in the 15 mm long reaction chamber. There is, however, not complete mixing as in a tank reactor. Based on the fact that a plug flow reactor behaves as an infinite number of tank reactors, therefore suggests that at low flows the system behaves as a defined number of tank reactors in series.

For the higher flows, above 4.5 ml/min, the dispersion number indicates pure plug flow behavior.

In conclusion the dispersion numbers of the different flows show that at low flows, below 4.5 ml/min, some diffusion takes place in radial direction, making the system behave as a number of tanks in series, while at the higher flows, only very little or no diffusion takes place in radial direction and the reactor behaved as a plug flow reactor.

# Chapter 8 Conclusion

The aim of this project was to develop a microsystem which could produce hydrogen for fuel cells. A literature survey was carried out to find common hydrogen producing processes, and to determine the conditions under which they progressed.

From the literature survey it was found that ammonia decomposition was the preferred hydrogen producing process, when the produced hydrogen was to be used in fuel cells. Ammonia has the advantage of only producing nitrogen as a byproduct as opposed to steam reforming and partial oxidation of hydrocarbons and alcohols. Both steam reforming and partial oxidation produce CO and  $CO_2$ , two compounds that are unwanted in fuel cells, because they contaminate and poison the electrodes.

A new incorporation method of the microreactor was to be determined. A gel containing 10 ml water, 1.25 ml nitric acid, and 0.5 g boehmite was prepared and loaded into the reaction chamber of a microreactor using a hypodermic needle. When the water was evaporated by heating the reactor on a heating plate and the support material,  $Al_2O_3$ , was doped with an active metal, the reactor was anodically bonded, giving a microsystem. The catalysts used to develop the microsystems for the ammonia decomposition experiments were aluminum oxide doped with 1.3% ruthenium, 1.0% iron, 0.4% cobalt, 0.9% palladium, and 1.9% cobber as these metals were found to be efficient in earlier ammonia decomposition experiments.

To get familiar with the experimental setup and to test if the new incorporation method worked partial oxidation of methane experiments were initially made. Using a palladium on aluminum oxide microsystem the influence of temperature and methane-to-oxygen ratio were investigated. The experiments showed that the temperature should be above 590°C, while the methane-to-oxygen ratio should be 2:1, for optimal hydrogen production. These results showed good agreement to what was theoretically expected, indicating that the incorporating method worked and that microsystems give reasonable result despite their size.

To investigate the ammonia decomposition reaction under different operation conditions, experiments for each of the five mentioned catalysts were made. In these experiments the temperature, the inlet flow, and the inlet ammonia concentration were varied. On the basis of the results, conversions and catalyst activities for each of the experiments were calculated. It was found that high temperatures gave high conversions and activities as expected from an equilibrium point of view. The conversions on Fe and Ru at 680°C were 97.5% and 88.4%, respectively, compared to 99% which is the theoretical maximum conversion. The flow experiments showed that a high flow gave a low conversion, corresponding with the reduced residence time. The activities for high flows approached an asymptote. The asymptote for Ru was lower than the one for Fe, which was lower than the one for Co. The investigation of the inlet ammonia concentration indicated that ammonia inhibited the reaction. The activation energies for ruthenium and iron were found and showed good agreement with similar values from the literature.

The flow experiment results indicated mass transport limitation, and therefore a characterization of the microsystem was performed. This investigation showed that at low flows diffusion took place in the radial direction making the system behave as a series of tank reactors, but at the higher flows, the reactor behaved as a plug flow reactor.

#### 8.1 Future works

This thesis gives reason for a number of questions. The following will shortly summarize these:

- **Incorporation** The catalyst loosens when the reactor is heated for the anodic bonding. This can give some problems concerning the bonding, and a more stable method should be determined. If this is possible, a hole wafer of reactors could be incorporated and bonded simultaneously, instead of one at a time.
- **Partial oxidation of methane** The experiments performed in the present project should be repeated and be given time to reach steady state.
- Ammonia decomposition A more thorough investigation of ammonia decomposition on Co, Fe, and Ru should be made. The maximum activity of Co and Fe should be determined.

In addition an article for *Chemical Communications* is being written.

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### Appendix A

## Fabrication of Catalytic Micro Systems

A microreactor is made by etching channels and reactions chambers into a silicon chip. Figure A.1 shows the procedure from the untreated silicon chip to the ready to use reactor.



a. A 10  $\mu \mathrm{m}$  thick silicon wafer is cleaned with a cetone

b. 1.5  $\mu$ m photoresist is spun on the wafer. The wafer is dried 1 minute on a 90°C hotplate. Irradiation with UV light through a hole mask, patterns the photoresist

c. The photoresist is developed in NaOH which removes the photoresist that has been exposed to UV irradiation

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Figure A.1: Fabrication of microsystems

# Appendix B

## The Microreactor Setup

The following figure illustrates the microreactor setup in details.



a. The alumina block where the in- and outlet gas tubes are attached. The red arrows indicate the inlet gas and the green arrows the outlet gas. The picture also shows a larger hole in the center of the block, through which the temperature of the reactor is measured.

b. To make the system as leak free, rubber rings are placed in the gas in- and outlet gas holes. The holes in the right side of the block, are not used in these experiments and have no influence on the setup.

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c. Because alumina has a melting point of 660°C, a ceramic brick with in- and outlet holes is placed on the alumina block. Each hole is made air tight with a gold O-ring (marked with a red circle).

d. A reactor is placed faced down over the holes in the ceramic brick. It is important to make sure that the holes in the glass lid are placed exactly above the holes in the brick, so the gas can flow both in and out of the reactor.

e. A small ceramic brick is placed to press down the reactor tightly over the holes in the larger ceramic brick.

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f. A brass brick is placed on top of the small ceramic brick.

g. Perpendicularly to the brass brick another longer brass brick is placed. In the longer brick a small screw is mounted to tighten the smaller brass brick and the ceramic brick to the reactor, making the system air tight.

h. Each end of the long brass brick is stabilized by nuts.

Figure continuing on page 80

g



Continued from page 79



f. A heating element is placed on the reactor. The temperature is altered by a power supplier (reason for the alligator beaks).

g. An overview of the experimental setup. Under the alumina block the infrared sensor for temperature measurements can be seen as the gray cylinder, and to the left the mass spectrometer wrapped in cellophane. The exit tube for the mass spectrometer under the reactor can dimly be seen.

Figure B.1: Detailed description of the experimental setup

### Appendix C

## **Flow Controller Calibration**

#### C.1 Calibration of the Argon Flow Controller

The argon flow controller is calibrated with a "bubble meter" to determine the connection between the voltage setting in LabVIEW and the actual flow through the reactor. Figure C.1 illustrates different voltage settings with corresponding actual flows through the reactor.



Figure C.1: Correlation between voltage and measured gas flow velocity

Regressing a straight line with intercept 0.02 shows that the maximum voltage corre-

sponds to a velocity of approximately 45 ml/min. It should be noted that the straight line is forced through the point (0,0.02), because a voltage of 0.02 V is the minimum voltage setting possible.

#### C.2 Calibration of the Ammonia Flow Controller

The ammonia flow controller cannot be calibrated using the "bubble measuring meter", since the detergent used to make bubbles contains water, in which ammonia is very soluble. Instead the outlet gas pipe is put into a glass of water. At a chosen gas velocity it is timed how long it takes to blow a specific number of bubbles.

This calibration showed that when the flow was doubled, so were the number of bubbles blown. It should be noted that the flow controller is made special for ammonia, and therefore calibrated with ammonia by the manufacture.

### Appendix D

## Calibration of the Mass Spectrometer Signals

Due to the misleading signals of hydrogen and nitrogen in the introductory experiment a sensitivity investigation regarding these compounds is made. At the same time a factor for converting the mass spectrometer signals to partial pressures or concentrations of the different species is determined. Both the sensitivity investigation and the factor for signal conversion can be found by sending a gas with known species and concentrations through the mass spectrometer.

For ammonia decomposition the gasses of interest are ammonia, nitrogen, and hydrogen. A premixed gas with the following composition is used to determine the hydrogen and nitrogen factors for conversion:

- 1% CO
- $2\% N_2$
- 2% O<sub>2</sub>
- 25% H<sub>2</sub>
- 70% He

The gas is passed through a reactor into the mass spectrometer until all signals stabile. One could thing that CO and H<sub>2</sub> could reacts with  $O_2$ , but this does not happen because of the high activation energy at 25°C. Had the metal in the reactor been gold (Au) reaction would have happened even at low temperatures.

The resulting currents for the five compounds can be seen in table D.1

Table D.1: Fractions and corrected fractions corresponding to the signals of the calibration gas

	CO and $N_2$	O <sub>2</sub>	$H_2$	He
Signal	$6.7 \cdot 10^{-8}$	$1.0 \cdot 10^{-8}$	$1.6 \cdot 10^{-6}$	$9.6 \cdot 10^{-7}$
Actual fraction	0.01 + 0.02	0.02	0.25	0.7
Fraction according to MS	0.025	0.004	0.607	0.364
Corrected fraction according to MS	0.012	0.001	0.445	0.542
Sensitivity for base peak	14	13	20	6.4

Both CO and  $N_2$  have atomic masses of 28 g/mol. Therefore the mass spectrometer cannot distinguish between the two and shows them as one signal.

To find if it is possible to directly convert the signals to concentrations, the 'signal fraction' is determined. This fraction is found for each of the species using equation (D.1)

fraction of component 
$$A = \frac{I_A}{I_{total}}$$
 (D.1)

where  $I_A$  is the current signal for component A and  $I_{total}$  is the sum of all current signals.

The corrected fractions have also been found as in equation (D.1) but the specific signal have been divided by a correction factor given in the mass spectrometer manual [38]. These correction factors are given in the lowest line of table D.1 as the 'Sensitivity for base peak'.

Neither the fractions nor the corrected fractions are in agreement with the actual component fractions of the gas. They both show too high hydrogen contents compared to the nitrogen-CO signal, since the ratio is not 3:1.

Based on experience from earlier experiments, where the mass spectrometer also was used, it is decided that the signal to rely on is the nitrogen-CO signal, which will be the reference signal in all further calculations.

This means that all nitrogen-CO signals in the further experiments will be multiplied by a conversion factor of the form

$$\frac{\frac{3\%}{100\%} \cdot 1 \text{atm}}{6.7 \cdot 10^{-8} \text{A}} = 5 \cdot 10^5 \frac{\text{atm}}{\text{A}}$$

to find the nitrogen partial pressure. 3%/100% corresponds to the nitrogen and CO content in the gas, 1 atm corresponds to the total pressure of the system when the gas was analyzed, and  $6.7 \cdot 10^{-8}$ A is the current measured by the mass spectrometer. It is

assumed that there is no significant pressure change.

In the ammonia experiments the initial nitrogen signal should show zero, since only ammonia and argon are present at the beginning of the experiments. This is not the case, and to rectify for this, the nitrogen signals from each experiments are subtracted the initial nitrogen signal before the nitrogen pressures are determined.

For a reliable comparison the data is normalized by the argon signal. This is done by multiplying the determined nitrogen pressure with a reference steady state argon current divided by the measured steady state argon current of the present experiment. Because the normalization is based on a steady state signal, the currents used to determine have not been normalized, and therefore the preexponential factors cannot be interpreted.

To sum up, to translate the nitrogen signal to a corresponding partial pressure the following calculation must be made

$$p_{N_2} = (I_{N_2,0} - I_{N_2}) \cdot 5 \cdot 10^5 \text{atm} / \text{A} \cdot \frac{I_{Ar \ ref}}{I_{Ar}}$$
(D.2)

here  $p_{N_2}$  is the nitrogen concentration,  $I_{N_2,0}$  and  $I_{N_2}$  are respectively the initial and following nitrogen signals,  $I_{Ar ref}$  is the reference argon signal (2.88·10<sup>-7</sup>), and  $I_{Ar}$  the measured argon signal.

A calibration was also made on air. This gave a 'translation factor' very different from the one found above. However, the gas above determined factor will be the one used in the result treatment, since the gas contain hydrogen. If hydrogen should have an influence on the mass spectrometer measurements, this should be avoided when the gas is used as the calibration reference.

# Appendix E Calculations for Conversion

To determine the activity of a catalyst, the conversion of the reactant must be found. This can be done by using equation (6.1) from Fogler [40]

$$C_{j} = \frac{C_{A0} \left(\Theta_{j} + \nu_{j} X\right)}{1 + \varepsilon X} \frac{p}{p_{0}} \frac{T_{0}}{T}$$
(6.1)

here  $C_j$  is concentration of species j at pressure p and temperature T,  $C_{A0}$  is the initial concentration of species A at pressure  $p_0$  and temperature  $T_0$ ,  $\nu_j$  is a stoichiometric coefficient, and X is the conversion of species A.  $\Theta_j$  is defined as

$$\Theta_j = \frac{F_{j0}}{F_{A0}} \tag{E.1}$$

$$= \frac{C_{j0}}{C_{A0}} \tag{E.2}$$

$$= \frac{y_{j0}}{y_{A0}} \tag{E.3}$$

(E.4)

where  $F_{j0}$  and  $F_{A0}$  are the initial mol flows of j and A and  $y_{j0}$  and  $y_{A0}$  are the initial mol fractions of species j and A.

When nitrogen is the reference component,  $\Theta$  becomes:

$$\Theta_{N_2} = \frac{F_{N_2}}{F_{A0}} = \frac{0}{F_{A0}} = 0$$

because there is no nitrogen present in the inlet gas.  $\nu = \frac{1}{2}$  because of stoichiometric.

The expansion factor  $\varepsilon$  is found as

$$\varepsilon = y_{A0}\delta$$
 (E.5)

where  $\delta$  relates to a reaction scheme of the form

as

$$\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1 \tag{E.6}$$

For the ammonia decomposition reaction (2.21)

$$2\mathrm{NH}_3 \rightleftharpoons 3\mathrm{H}_2 + \mathrm{N}_2 \tag{2.21}$$

giving

$$\delta = \frac{3}{2} + \frac{1}{2} - \frac{0}{2} - 1 = 1$$

 $A + \frac{b}{a}B \to \frac{c}{a}C + \frac{d}{a}D$ 

This means that  $\varepsilon$  equals  $y_{NH_3,0}$ .

Inserting in equation (6.1) will for j~nitrogen and A~ammonia give

$$C_{N_2} = \frac{C_{NH_3,0} \left(0 + 0.5 \cdot X\right)}{1 + y_{NH_3,0} X} \frac{T_0}{T}$$

 $\frac{p}{p_0}$  is neglected because there is no pressure change in the system. Isolating X gives equation (6.2)

$$X = \frac{2C_{N_2}T}{C_{NH_{3,0}}T_0 - 2y_{NH_{3,0}}C_{N_2}T}$$

From the mass spectrometer data the partial pressures of the different species can be determined, and using the ideal gas law

$$pV = nRT$$

$$\Downarrow \qquad (E.7)$$

$$\Downarrow \qquad C = \frac{p}{RT}$$

the concentration of the species in the out gas can be found, and thereby the conversion by inserting into equation (6.2). For nitrogen the pressure is found as

$$C_{N_2} = \frac{I_{N_2} \cdot 5 \cdot 10^5 \frac{\text{atm}}{\text{A}}}{RT} \cdot \frac{I_{Ar \ ref}}{I_{Ar}} \tag{E.8}$$

Using the conversion, the ammonia converted per time can be found by the help of a stoichiometric table

Table E.1: Stoichiometric table for  $2NH_3 \rightarrow 3H_2 + N_2$ 

Species	Symbol	Initial	Change	Remain
NH <sub>3</sub>	А	$F_{A0}$	$-2XF_{A0}$	$\mathbf{F}_A = \mathbf{F}_{A0} - 2\mathbf{X}\mathbf{F}_{A0}$
$H_2$	В	0	$3F_{A0}$	$F_B = F_{A0}$
$N_2$	С	0	$F_{A0}$	$F_C = F_{A0}$

There is some variation in the mass of metal in the five different reactors. To normalize the mol ammonia converted per second is divided by the gram metal in catalyst giving

$$\frac{n_A \ converted}{sec \cdot g \ metal} = \frac{F_{A0} - 2XF_{A0}}{m_{metal}} \tag{E.9}$$

where  $F_{A0}$  is the initial mol flow of compound A, X is the conversion of compound A, and  $m_{metal}$  is the mass of catalyst in a specific reactor.

#### E.1 Conversion Calculation Example

For a Ru experiment with a flow of 2 ml/min NH<sub>3</sub> and 2.25 ml/min Ar and a steady state temperature of 596°C measures a nitrogen signal of  $7.81 \cdot 10^{-8}$ A. The initial nitrogen signal is  $6.70 \cdot 10^{-9}$ A while the steady state argon signal is  $4.30 \cdot 10^{-7}$ A. The reference steady state argon signal is  $2.88 \cdot 10^{-7}$ A.

The nitrogen concentration is found using equation (E.8)

$$C_{N_2} = (7.81 \cdot 10^{-8}A - 6.7 \cdot 10^{-9}) \\ \cdot \frac{5 \cdot 10^5 a tm/A}{0.08206L \cdot a tm/(mol \cdot K) \cdot (596^{\circ}C + 273)K} \\ \cdot \frac{2.88 \cdot 10^{-7}A}{4.30 \cdot 10^{-7}A} = 3.35 \cdot 10^{-4} mol/L$$

While the initial ammonia concentration is determined using the ideal gas law (E.7)

$$C_{NH_{3},0} = \frac{p_{NH_{3},0}}{RT}$$
  
=  $\frac{y_{NH_{3},0} \cdot p_{total,0}}{RT}$   
=  $\frac{\frac{2ml/min}{(2+2.25)ml/min} \cdot 1atm}{0.08206L \cdot atm/(mol \cdot K) \cdot 298K}$   
=  $0.019mol/L$ 

Using equation (6.2) the conversion can now be found

$$X = \frac{2 \cdot 3.35 \cdot 10^{-4} mol/L \cdot 869K}{0.019 mol/L \cdot 298K - 2\frac{2ml/min}{(2+2.25)ml/min} 3.35 \cdot 10^{-4} mol/L \cdot 869K}$$
  
= 0.11

All conversion calculations have been made in Excel.

### Appendix F

## Calculations of Equilibrium Constant

To get an idea of the fraction of ammonia which can be expected to decompose, the theoretical equilibrium is determined. This is done by finding the equilibrium constant defined as in equation (6.3)

$$K \equiv \exp\left(\frac{-\Delta G^{\circ}}{RT}\right)$$

Gibb's free energy,  $\Delta G^{\circ}$ , is temperature dependant and can be found as

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} \tag{F.1}$$

From Smith et al.[41] values for Gibb's free energy and enthalpy are given for the formation of gaseous ammonia at the standard temperature 298 K. These are respectively -16450 J/mol and -46110 J/mol. Because both H<sub>2</sub> and N<sub>2</sub> are in their ideal state  $\Delta G_f(298)_{H_2} = \Delta H_f(298)_{H_2} = \Delta G_f(298)_{N_2} = \Delta H_f(298)_{N_2} = 0$  J/mol. Both the reaction Gibb's free energy and the reaction enthalpy can be determined in terms of the formation Gibb's free energy and the formation enthalpy using equations (F.2) and (F.3) from Atkins [6]

$$\Delta_r G^\circ = \sum_{Products} \nu \Delta_f G^\circ - \sum_{Reactant} \nu \Delta_f G^\circ$$
(F.2)

and

$$\Delta_r H^\circ = \sum_{Products} \nu \Delta_f H^\circ - \sum_{Reactant} \nu \Delta_f H^\circ$$
(F.3)

When Gibb's free energy and enthalpy are known at a specific temperature, entropy at the same temperature can be determined using equation (F.1).

All three of the above mentioned thermodynamic properties are dependent on the temperature. For the Gibb's free energy, this can be seen in equation (F.1). The connection between the temperature and the enthalpy is as follows

$$\Delta H_T^{\circ} = \Delta H_{298}^{\circ} + R \int_{298}^T \frac{\Delta C_p^{\circ}}{R} dT$$
 (F.4)

and for the entropy

$$\Delta S_T^{\circ} = \Delta S_{298}^{\circ} + R \int_{298}^T \frac{\Delta C_p^{\circ}}{R} \frac{dT}{T}$$
(F.5)

From Smith et al. [41] an expression for  $\Delta C_p^{\circ}$  is given for the three species as

$$\frac{C_p^{\circ}}{R} = A + B \cdot T + C \cdot T^2 + D \cdot T^{-2}$$
(F.6)

$$\frac{U_p^o}{R}(NH_3) = 3.578 + 3.02 \cdot 10^{-3} \cdot T + 0 \cdot T^2 - 0.186 \cdot 10^5 \cdot T^{-2}$$
(F.7)

$$\frac{C_p^{\circ}}{R}(H_2) = 3.249 + 0.422 \cdot 10^{-3} \cdot T + 0 \cdot T^2 + 0.083 \cdot 10^5 \cdot T^{-2}$$
(F.8)

$$\frac{C_p^{\circ}}{R}(N_2) = 3.280 + 0.593 \cdot 10^{-3} \cdot T + 0 \cdot T^2 + 0.04 \cdot 10^5 \cdot T^{-2}$$
(F.9)

The temperatures are entered in Kelvin.

 $\mathbf{C}_p$  for the reaction can be found using equation (F.10) from Atkins [6]

$$\Delta_r C_p^\circ = \sum_{product} \nu C_{p,m}^\circ - \sum_{reactant} \nu C_{p,m}^\circ$$
(F.10)

When Gibb's free energy is determined at a wanted temperature, the equilibrium constant can be found from equation (6.3). The equilibrium constant can then be used to determine the theoretical conversion, since the equilibrium constant corresponding to reaction equation (2.21) is

$$K = \frac{(F_{H_2,eq})^3 \cdot F_{N_2,eq}}{(F_{NH_3,eq})^2}$$
(F.11)

By setting up a table

$$\begin{tabular}{|c|c|c|c|c|c|} \hline & NH_3 & H_2 & N_2 \\ \hline Start & F_0 & 0 & 0 \\ Equilibrium & F_0\mbox{-}2X & 3 \cdot F_0 \cdot X & F_0 \cdot X \\ \hline \end{tabular}$$

the fraction converted can be theoretically determined by inserting the equilibrium expressions for the three partial pressures into equation (F.11). For different temperatures the equilibrium constant and the fractions converted can be seen in table 6.1.

#### Maple Calculations **F.1**

The mathematical program Maple used for calculating the equilibrium constants at different temperatures:

DeltaG:=DeltaH-Tact\*DeltaS; >

$$\begin{aligned} DeltaG &:= 92220. + 8.31541 \int_{298}^{Tact} 5.871 - .00418100000 T + \frac{66100.000}{T^2} \, dT \\ - Tact \left( 199.06 + 8.31541 \int_{298}^{Tact} \frac{5.871 - .00418100000 T + \frac{66100.000}{T^2}}{T} \, dT \right) \end{aligned}$$

> K:= exp(-DeltaG/(R\*Tact));

$$K := e^{\left(-.1202586523 \left(92220.+8.31541 \int_{298}^{T_{act}} 5.871-.00418100000 T + \frac{66100.000}{T^2} dT + \frac{661000$$

> Keq:=unapply( K, Tact);

$$Keq := Tact \rightarrow e^{\left(-.1202586523 \left(92220.+8.31541 \int_{298}^{Tact} 5.871 - .004181000000 T + \frac{66100.000}{T^2} dT\right)\right)}$$

$$\left. - Tact \left( 199.06 + 8.31541 \int_{298}^{Tact} \frac{5.871 - .00418100000 T + \frac{66100.000}{T^2}}{T} \, dT \right) \right) / Tact \right)$$

29.27527514
> evalf(Keq(543));

68.92635639

 $.1713578850\,10^{-5}$ 

- > evalf(Keq(583));
- 324.9230935
  > evalf(Keq(603));
  657.2384834
- > evalf(Keq(623));
- > evalf(Keq(643));
  - 2383.240111

1275.427919

> evalf(Keq(663));

- > evalf(Keq(683));
- 7522.813285
- > evalf(Keq(703));
  12777.07117
- > evalf(Keq(723));
- 21125.29642
  > evalf(Keq(743));
  - 34070.64152
- 53698.19568
- > evalf(Keq(783));
- 82843.49298
  > evalf(Keq(803));
- 125292.4596
- > evalf(Keq(843));

> evalf(Keq(763));

271430.6193

4301.910408

> evalf(Keq(943));

 $.1436137333\,10^7$ 

- > oms(743):=solve(34070.6=(1.36\*10^(-6)\*X)^4/(1.36\*10^(-6)-2\*X\*1.36\*10^ > (-6))^2,X);
  - $oms(743) := -.271444457810^9, .4999999991, .500000009, .271444456810^9$
- > oms(843):=solve(271430=(1.36\*10^(-6)\*X)^4/(1.36\*10^(-6)-2\*X\*1.36\*10^(
  > -6))^2,X);

 $oms(843) := -.766160946510^9, .4999999997, .5000000003, .766160945510^9$ 

- > oms(943):=solve(1.4\*10^7=(1.36\*10^(-6)\*X)^4/(1.36\*10^(-6)-2\*X\*1.36\*10 > ^(-6))^2,X);
- > (-0)) 2,,,,,
- $oms(943) := -.550243733410^{10}, .5000000000, .5000000000, .550243733310^{10}$
- > omsLavFlow:=solve(271430=(2.67\*10^(-7)\*X)^4/(2.67\*10^(-7)-2\*X\*2.67\*10

> ^(-7))^2,X);

 $omsLavFlow:=-.3902542647\,10^{10},\,.49999999999,\,.5000000001,\,.3902542646\,10^{10}$ 

### Appendix G

## Calculation for the Micro System Characterization

To characterize the micro system, the reciprocate Peclet number is used. A reciprocal Peclet number going towards 0 indicates plug flow behavior, while if the reciprocate Peclet number goes towards infinity the system behaves as a tank reactor.

#### G.1 Space Velocity

The space velocity is defined as the reciprocal residence time

$$SV = \frac{v_0}{\mathcal{V}_{eff}} \tag{7.1}$$

A part of the reactor volume is filled with porous catalyst, so to find the effective reactor volume, the dependency of the space velocity on the porosity is found.

The total volume of the porous catalyst can be found as

$$\varepsilon' = \frac{V_{free \ cat}}{V_{total \ cat}}$$

$$(7.2)$$

$$V_{total\ cat} = \frac{V_{free\ cat}}{\varepsilon'} = \frac{V_{total\ cat} - V_{solid\ cat}}{\varepsilon'} = \frac{V_{solid\ cat}}{1 - \varepsilon'}$$
(G.1)

where  $V_{solid cat}$  is the volume of the solid in the porous catalyst, which can be found as

$$V_{solid\ cat} = \frac{m_{catalyst}}{\rho_{solid\ catalyst}} \tag{G.2}$$

where m is the mass of the solid catalyst and  $\rho$  is the density of the solid catalyst. Inserting equation (G.2) in equation (G.1) gives

$$V_{total\ cat} = \frac{m_{catalyst}}{\rho_{solid\ catalyst}} \cdot \frac{1}{1 - \varepsilon'}$$
(G.3)

and the space velocity can thus be found as a function of the porosity

$$SV = \frac{v_0}{V_{total} - V_{total \ cat}} = \frac{v_0}{V_{eff}}$$
$$= \frac{v_0}{V_{total} - \frac{m_{catalyst}}{\rho_{solid \ catalyst}} \cdot \frac{1}{1 - \varepsilon'}}$$
(G.4)

#### G.1.1 Calculations for the Space Velocity

The total reactor volume of a microreactor with one wide chamber is

$$V_{total} = 1.5 \cdot 10^{-2} m \cdot 1.5 \cdot 10^{-3} m \cdot 200 \cdot 10^{-6} mm = 4.5 \cdot 10^{-9} m^3 = 0.0045 cm^3$$

When the Ru experiments are used to illustrate the space velocity as a function of the porosity, the mass of the solid catalyst is 1.923 mg. To simplify the calculations only the support material is used as the solid catalyst mass. 99.6% Aluminum-oxide has a density of 3.87 g/ml [42], giving a catalyst solid volume of

$$V_{solid cat} = \frac{1.33mg \cdot 10^{-3}g/mg}{3.87g/ml} = 0.00034ml$$

The resulting equation for the space velocity as a function of the porosity with the inlet flow as 0.4 ml/min ammonia with 0.45 ml/min argon is

$$SV = \frac{0.85ml/min}{0.0045ml - \frac{1.33mg \cdot 10^{-3}mg/g}{3.87g/ml} \cdot (\frac{1}{1 - \varepsilon'})}$$

#### G.2 Peclet Number

For equation (7.5) to be used for determining the Peclet, the flow must be laminar. To investigate if the flow is laminar, the Reynolds number can be found [43]

$$N_{Re} = \frac{\mathrm{u}\mathrm{D}_{H}\rho}{\mu} \tag{7.6}$$

where u is the linear velocity,  $D_H$  is the hydraulic diameter of the reactor,  $\rho$  is the density of the fluid, and  $\mu$  is the viscosity.

The hydraulic diameter is defined as [43]

$$D_H \equiv 4 \cdot \frac{S}{L_p} = 4 \cdot \frac{h_{eff} \cdot w}{2(h_{eff} + w)}$$
(G.5)

where S is the cross section area of the reactor and  $L_p$  is the length of the circumference; w is the width of the reactor and  $h_{eff}$  is the height of the of the effective reactor volume.

In the following calculations any roughness on the catalyst surface is neglected meaning that it is assumed that the catalyst surface is completely smooth. The width of the effective volume will not change when catalyst is added, and w is therefore constant. To find the cross section area and thereby also the height of the effective volume, a correspondence between the ratios of two known volumes and their cross section areas is determined

$$\mathbf{h}_{eff} = \frac{\mathbf{A}_{eff}}{\mathbf{w}} \tag{G.7}$$

giving both the height and the cross section area of the effective volume.

From the effective cross section area the linear velocity u can be determined as

$$\mathbf{u} = \frac{v_{total}}{\mathbf{A}_{eff}} \tag{G.8}$$

When the ammonia-argon inlet flow is assumed to be an ideal gas the density of each of the compounds can be determined by the ideal gas law (E.7) as

$$\rho_A = \frac{\mathbf{m}_A}{\mathbf{V}} = \frac{\mathbf{M}_A \cdot \mathbf{p}_A}{\mathbf{R} \cdot \mathbf{T}} \tag{G.9}$$

where  $M_A$  is the molar mass of compound A,  $p_A$  is the partial pressure of compound A, R is the gas constant, and T is the temperature.

The partial pressures of the two compounds can be found from the inlet flow as

$$p_A = 1 \operatorname{atm} \cdot \frac{v_A}{v_{total}} \tag{G.10}$$

where  $v_A$  is the inlet volumetric flow of compound A and  $v_{total}$  is the inlet total volumetric flow.

The density of the mixture can be found using the inlet flows of the two compounds

$$\rho_{total} = \frac{\rho_{ammonia} \cdot v_{0,ammonia} + \rho_{argon} \cdot v_{0,argon}}{v_{0,ammonia} + v_{0,argon}}$$
(G.11)

Finally the viscosity of the inlet flow can be found using the critical pressures and temperatures of ammonia and argon. These are given by Smith et al.[41] as
Table G.1: The critical temperature and pressure of ammonia and argon

	Critical Temperature	Critical Pressure	Critical pressure	Molar mass
	(K)	(bar)	(atm)	(g/mol)
Ammonia	405.7	112.80	111.33	17.031
Argon	150.9	48.98	48.34	39.95

The mixture critical properties is found as "pseudocritical" properties defined by Bird et al. [44] as

Mixture critical temperature : 
$$T'_c = \sum_{A=1}^N x_A T_{cA}$$
 (G.12)

Mixture critical pressure : 
$$p'_c = \sum_{A=1}^N x_A p_{cA}$$
 (G.13)

Mixture critical viscosity : 
$$\mu'_c = \sum_{A=1}^N x_A \mu_{cA}$$
 (G.14)

where  $x_A$  is the molar fraction of compound A,  $T_{cA}$  is the critical temperature of compound A,  $p_{cA}$  is the critical pressure of compound A, and  $\mu_{cA}$  is the critical viscosity of compound A.  $\mu_c$  for each of the compounds can be found as [44]

$$\mu_c = 7.7 M^{1/2} p_c^{2/3} T_c^{-1/6} \tag{G.15}$$

where M is the molar mass with unit g/mol,  $p_c$  is the critical pressure in atm, and  $T_c$  is the critical temperature in K. This gives a value for  $\mu_c$  with unit  $\mu$ poise.

The reduced temperature and pressure are then found as [41, 44]

$$T_r = \frac{T}{T'_c} \tag{G.16}$$

$$p_r = \frac{p}{p'_c} \tag{G.17}$$

where  $T_r$  is the reduced temperature, T is the operating temperature,  $p_r$  is the reduced pressure, and p is the operating pressure. The reduced viscosity,  $\mu_r$ , is found in figure 1.3-1 in Bird et al. [44] and the actual viscosity is then found as [41, 44]

$$\mu = \mu_r \cdot \mu'_c \tag{G.18}$$

## G.2.1 Calculating of the Reynolds Number

To determine the hydraulic diameter, the effective volume must be found. When the porosity is 0.5 and the flow 0.4 ml/min ammonia with 0.45 ml/min argon, the catalytic volume can be found using equation (G.3)

$$V_{total\ cat} = \frac{1.9 \cdot 10^{-3}g}{3.87g/ml} \cdot \frac{1}{1 - 0.5} = 9.82 \cdot 10^{-4}ml$$

giving an effective volume of 0.0045ml - 0.00092ml = 0.00352 ml, and an effective cross section area of (equation (G.6)) for L = 1.5 cm

$$\begin{aligned} \mathbf{A}_{eff} &= \frac{0.0045 cm^3}{1.5 cm} \frac{0.00352 cm^3}{0.0045 cm^3} \\ &= 0.00235 cm^2 \end{aligned}$$

and thereby an effective height of (equation (G.7))

$$\mathbf{h}_{eff} = \frac{0.00235 cm^2}{0.15 cm} = 0.0156 cm$$

This gives a hydraulic diameter of (equation (G.5))

$$D_H = 4 \cdot \frac{0.0157cm \cdot 0.15cm}{2(0.0157cm + 0.15cm)}$$
$$= 0.0283cm = 2.8 \cdot 10^{-4}m$$

From the effective cross section area, the linear velocity u can be found using equation (G.8)

$$u = \frac{0.85cm^3/min}{0.00235cm^2} \\ = 362.4cm/min = 0.060m/s$$

The partial pressures of ammonia and argon in the inlet flow can be determined by the mol fraction of each of the two compounds using equation (G.10)

From the ideal gas law the densities of respectively ammonia and argon is found using equation (G.9)

The density of the mixture can be found using the inlet flows of the two compounds, equation (G.11)

$$\rho_{total} = \frac{0.327kg/m^3 \cdot 0.4 \cdot 10^{-6}m^3 + 0.866kg/m^3 \cdot 0.45 \cdot 10^{-6}m^3}{0.85 \cdot 10^{-6}m^3/ml}$$
  
= 0.612kg/m<sup>3</sup>

Finally the viscosity of the inlet gas mixture of ammonia and argon is found. The critical viscosities for the two compounds is found using equation (G.15) and the critical values in table G.1

ammonia : 
$$\mu_c = 7.7 \cdot 17.031^{1/2} \cdot 111.33^{2/3} \cdot 405.7^{-1/6}$$
  
= 270.3 $\mu$ poise = 2.70  $\cdot 10^{-5} kg/(m \cdot s)$   
argon :  $\mu_c = 7.7 \cdot 39.95^{1/2} \cdot 48.34^{2/3} \cdot 150.9^{-1/6}$   
= 279.9 $\mu$ poise = 2.80  $\cdot 10^{-5} kg/(m \cdot s)$ 

The mol fractions are determined from the partial pressures found above

ammonia : 
$$x = \frac{0.47atm}{1atm} = 0.47$$
  
argon :  $x = \frac{0.53atm}{1atm} = 0.53$ 

the critical properties can now be found using equations (G.12) and (G.13)

Critical mixture temperature : 
$$T'_c = 0.47 \cdot 405.7K + 0.53 \cdot 150.9K$$
  
= 270.8K  
Critical mixture pressure :  $p'_c = 0.47 \cdot 111.33atm + 0.53 \cdot 48.34atm$   
= 78.0atm  
Critical mixture viscosity :  $\mu'_c 0.47 \cdot 2.70 \cdot 10^{-5} kg/(m \cdot s) + 0.53 \cdot 2.80 \cdot 10^{-5} kg/(m \cdot s)$   
= 2.75  $\cdot 10^{-5} kg/(m \cdot s)$ 

The reduced temperature and pressure are found using equations (G.16) and (G.17)

ammonia : 
$$T_r = \frac{298K}{270.7} = 1.10$$
  
argon :  $p_r = \frac{1atm}{77.9atm} = 0.013$ 

Figure 1.3-1 in Bird et al. [44] gives a reduced viscosity of 0.53 in the low density limit. This corresponds to at viscosity of (equation(G.18))

$$\mu = \mu_r \cdot \mu_c = 0.53 \cdot 2.75 \cdot 10^{-5} kg/(m \cdot s) = 1.46 \cdot 10^{-5} kg/(m \cdot s)$$

The Reynolds number can now be determined using equation (7.6)

$$N_{Re} = \frac{0.06m/s \cdot 2.8 \cdot 10^{-4}m \cdot 0.612kg/m^3}{1.45 \cdot 10^{-5}kg/(m \cdot s)} = 0.71$$

The Reynolds number is < 2100 which shows that the flow is laminar.

## G.2.2 Calculations for the Peclet Number

The 0.85 ml/min flow is laminar, and the Peclet number can thus be determined using equation (7.4).

It is not possible to find the diffusion coefficient of ammonia in argon. Therefor the diffusion coefficient for ammonia in air is used, giving  $D_{AB}=0.836 \text{ ft}^2/\text{h} = 2.16 \cdot 10^{-5} \text{ m}^2/\text{s}$  at 0°C and 1 atm [43]. The value is assumed to be independent of temperature in the temperature range in question.

Since the reactor is not a pipe, it has no radius. Therefore the hydraulic diameter is used to determine the radial distance:

$$R = \frac{D_{H}}{2}$$

$$\downarrow$$

$$R^{2} = \frac{D_{H}^{2}}{4}$$

$$= \frac{(2.8 \cdot 10^{-4}m)^{2}}{4} = 1.96 \cdot 10^{-8}m^{2}$$

This gives an Aris-Taylor approximation of (equation (7.5))

$$D_a = 2.16 \cdot 10^{-5} m^2 / s + \frac{(0.060 m/s)^2 \cdot 1.96 \cdot 10^{-8} m^2}{48 \cdot 2.16 \cdot 10^{-5} m^2 / s}$$
  
= 2.17 \cdot 10^{-5} m^2 / s

and a Peclet number of (equation (7.4))

$$N_{Pe} = \frac{0.060m/s \cdot 0.015m}{2.17 \cdot 10 - 5m^2/s}$$
  
= 41.5

this gives a reciprocal Peclet number going toward zero (here 0.024) indicating that the system behaves as a plug flow reactor for the low flows.