Low temperature oxidation of ammonia over platinum and iridium catalysts

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Low Temperature Oxidation of Ammonia over Platinum and Iridium Catalysts

A.C.M. van den Broek
Low Temperature Oxidation of Ammonia over Platinum and Iridium Catalysts

PROEFSCHRIFT

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Introduction

General

The study of the selective catalytic oxidation of ammonia with oxygen to nitrogen and water is an important issue because it could be a solution to pollution by ammonia. The main problem of ammonia is that it is a strong fertilizer, therefore it can change the natural equilibrium in the environment. Ammonia emissions are also linked to acid rain production. Furthermore, ammonia can be health damaging and has an irritating smell. Ammonia emissions are caused by various sources like: the SCR process; soda production; nitric acid production; or agricultural sources [1]. The reaction conditions (like temperature, concentration of reactants, phase, and flow rates) of the catalytic conversion depend on the process that causes the ammonia emission [2]. Furthermore, both direct and indirect gas phase processes can be applied. In the direct gas phase processes the ammonia concentration is low (< 0.1 vol%) and the oxygen and water concentrations are high (20 vol%) [3]. In the indirect gas phase processes ammonia is first adsorbed (usually in water) and in a subsequent process desorbed. In that case the ammonia concentration can be as high as 4 vol% [2]. It is also possible to selectively oxidize ammonia to nitrogen in the liquid phase. At low temperatures (< 800 K) nitrogen is the main product of the reaction on most catalysts (Eq. 1). The reaction is highly exothermic with a reaction enthalpy (ΔH) of -633 kJ.mol⁻¹.

\[
2 \text{NH}_3 + 1\frac{1}{2} \text{O}_2 \rightarrow \text{N}_2 + 3 \text{H}_2\text{O}
\]  

(1)
However, the formation of nitrous oxide is often seen as a byproduct at these temperatures (Eq. 2). This reaction is also highly exothermic with a $\Delta H$ of -551 kJ.mol$^{-1}$.

$$2 \text{NH}_3 + 2 \text{O}_2 \rightarrow \text{N}_2\text{O} + 3 \text{H}_2\text{O}$$ (2)

At higher temperatures (>800 K) nitric oxide is the main product (Eq. 3). This reaction is also exothermic with a $\Delta H$ of -453 kJ.mol$^{-1}$.

$$2 \text{NH}_3 + 2\frac{1}{2} \text{O}_2 \rightarrow 2 \text{NO} + 3 \text{H}_2\text{O}$$ (3)

At even higher temperatures (>1473 K) the production of nitrogen (Eq. 1) is the main reaction.

Most research has been done into the reaction that selectively produces nitric oxide (Eq. 3), since nitric oxide is an intermediate for the production of nitric acid. In this process the nitric oxide is further oxidized to nitrogen dioxide (Eq. 4) and subsequently reacted with water to form nitric acid (Eq. 5).

$$2 \text{NO} + \text{O}_2 \rightarrow 2 \text{NO}_2$$ (4)

$$3 \text{NO}_2 + \text{H}_2\text{O} \rightarrow 2 \text{HNO}_3 + \text{NO}$$ (5)

The production of nitric oxide takes place over a platinum/rhodium gauze in a high flow of ammonia gas and air at a temperature of ~1200 K and pressures between $10^5$ and $10^6$ Pa [4]. The nitric acid production process is widely applied on a large scale.

**Low temperature ammonia oxidation**

Most studies on ammonia oxidation focus on the high temperature (>800 K) process that selectively produces NO, because of the industrial importance. Therefore relatively few studies were done on low temperature (<800 K) ammonia oxidation. Most research on low temperature ammonia oxidation done before 1980 was either academic or spin off from high temperature work. In recent years, however, the low temperature reaction is becoming more important because of the environmental aspect. Now various catalysts of different types have been tested for the low temperature ammonia oxidation reaction: biological catalysts [5], metal oxide catalysts [6, 7], ion-exchanged zeolites [7, 8, 9] and metallic catalysts [1, 7, 8, 10].

Biological catalysts, using the nitrosomonas and nitrobacter bacteria, work at the very low temperature of 313 K and can be very selective to nitrogen [5]; the reaction mechanism is
complex and involves various enzymes containing iron and copper ions as active sites [11]. However, biological catalysts can work only in the liquid phase (water) with low concentrations of ammonia and require a relatively large reactor [12].

Metal oxide catalyst are often used as a catalyst for ammonia oxidation. In a general survey by Il'chenko [7], various simple oxides were tested and the following decreasing activity order for gas phase ammonia oxidation at 503 K was found:

\[
\text{MnO}_2 > \text{Co}_3\text{O}_4 > \text{CuO} > \text{CaO}_2 > \text{NiO} > \text{Bi}_2\text{O}_3 > \text{Fe}_2\text{O}_3 > \text{V}_2\text{O}_5 > \text{TiO}_2 > \text{CdO} > \text{PbO} > \text{ZnO} > \text{SnO}_2 > \text{ZrO}_2 > \text{MoO}_3 > \text{WO}_3.
\]

The selectivity to nitrogen at 503 K decreased from 100 to 50 %, following the order:

\[
\text{V}_2\text{O}_5 = \text{ZnO} = \text{WO}_3 = \text{MoO}_3 > \text{CeO}_2 > \text{TiO}_2 > \text{CuO} > \text{CdO} > \text{SnO}_2 > \text{Fe}_2\text{O}_3 > \text{Co}_3\text{O}_4 > \text{MnO}_2 > \text{NiO} > \text{CaO}_2.
\]

In this sequence of metal oxides, the selectivity to nitrous oxide at 503 K increased from 0 % to 50 %. No other products were found at this temperature. To make a catalyst with a high activity and a high selectivity various mixed metal oxide catalysts were developed. Catalyst systems like MoO_3/SiO_2 [13], Cu/Mn mixed oxide [14], V_2O_5/TiO_2 [6, 15, 16], or CuO/Alumina [17], are active catalysts for gas phase ammonia oxidation at temperatures above 423 K and show a high selectivity to nitrogen.

Metal ions exchanged in zeolites [6, 7, 8, 9] also show a high selectivity to nitrogen in the gas phase oxidation of ammonia. In the survey of Il'chenko [7] also various types of metal ions exchanged in zeolite Y were tested. The following decreasing activity sequence was found:

\[
\text{CuY} > \text{CrY} > \text{AgY} > \text{CoY} > \text{FeY} > \text{NiY} = \text{MnY}.
\]

The selectivity to nitrogen was high (> 95%) in all cases, except for AgY and CrY. More recently metal ions exchanged in ZSM-5 are preferred as a catalyst for low temperature gas phase ammonia oxidation. Mostly used is CuZSM-5 [9], because it is also very efficient in the SCR reaction. However also other metal ions exchanged in ZSM-5 are reported to be effective catalysts, for example Pd, Rh, Pt, and Co [8].
In the studies of Il'chenko [7, 10] also various metal wires and chips were probed in the gas phase ammonia oxidation. The following decreasing activity order at 573 K was found:

$$\text{Pt} > \text{Pd} > \text{Cu} > \text{Ag} > \text{Ni} > \text{Au} > \text{Fe} > \text{W} > \text{Ti}. $$

The selectivity to nitrogen was found to follow the opposite order: so it decreases with increasing activity. At temperatures below 473 K the activity of palladium was reported to be higher than that of platinum. Takao [18] studied various metals supported on TiO$_2$ as catalysts for the low temperature gas phase ammonia oxidation. In that study the following decreasing order in activity was found: Pt $>$ Ir $>$ Au. The Ir/TiO$_2$ catalyst was found to be more selective to nitrogen than Pt/TiO$_2$. In a recent study by Vaabel et al. [19], a Pd/C catalyst was found to be active for the gas phase ammonia oxidation reaction at temperatures below 403 K. Unfortunately nitrogen oxides were not determined in this study, so it was not possible to calculate the selectivity to nitrogen. A recent study of Armor et al. [8] showed a decreasing activity order of Pt $>$ Pd $>$ Rh for zeolite ZSM-5 supported metallic catalysts at 473 K. The selectivity to nitrogen was found to have the opposite order.

When the various types of catalysts are compared it appears that the metallic catalysts are the most active. In the comprehensive survey of Il'chenko [7], the activity of metallic catalysts at low temperature was reported to be 200 to $10^7$ times higher than that of simple oxides. In the more recent study of Armor et al. [8] the activity of Pt, Pd and Rh metallic catalysts was compared with that of V$_2$O$_5$/TiO$_2$. It was concluded that the activity of the precious metal catalysts is at least 100 times higher than that of the metal oxide catalyst.

**Reaction mechanism of low temperature ammonia oxidation on platinum**

The vast majority of scientific work on ammonia oxidation is done on platinum catalysts. Therefore, in this review of reaction mechanisms of ammonia oxidation only the various theories that were developed for this system are discussed. Furthermore, only theories that refer to low temperature ($T < 800$ K) ammonia oxidation are included.

*Research before 1960*

As a spin-off from the high temperature work on platinum gauzes, reaction mechanisms for the production of N$_2$ and N$_2$O at low temperature were also formulated. Since few analytical equipment was available only catalyst performance in reaction could be measured. Reaction mechanisms had to be postulated by the lack of experimental evidence of intermediate
species. Three different general reaction mechanisms were proposed: the nitroxyl, hydroxylamine, and imide mechanism. The nitroxyl (HNO) mechanism was proposed by Andrusow [20]. The first step of this mechanism is the formation of a nitroxyl species (Eq. 6).

\[ \text{NH}_3 + \text{O} \rightarrow \text{HNO} + \text{H}_2\text{O} \]  

Later an extension of this mechanism was formulated by Bodenstein [21, 22] in which the first step of the reaction (Eq. 7) is the formation of hydroxylamine (NH$_2$OH). This hydroxylamine is converted to nitroxyl in a next reaction step (Eq. 8).

\[ \begin{align*} 
\text{NH}_3 + \text{O} & \rightarrow \text{NH}_2\text{OH} \\
\text{NH}_2\text{OH} + \text{O} & \rightarrow \text{HNO} + \text{H}_2\text{O} 
\end{align*} \]

A mechanism in which the first step (Eq. 9) yields imide (NH) was postulated by Raschig [23] and later adapted by Zawadzki [24]. The imide can subsequently react to form nitroxyl (Eq. 10) or hydrazine (Eq. 11).

\[ \begin{align*} 
\text{NH}_3 + \text{O} & \rightarrow \text{NH} + \text{H}_2\text{O} \\
\text{NH} + \text{O} & \rightarrow \text{HNO} \\
\text{NH} + \text{NH}_3 & \rightarrow \text{N}_2\text{H}_4 
\end{align*} \]

The production of N$_2$O at low temperature was postulated by various authors to occur either through an NH$_4$NO$_3$ (Eqs. 12 - 13) intermediate [25] or through direct reaction of nitroxyl species (Eq. 14) [26].

\[ \begin{align*} 
\text{HNO} + \text{O}_2 & \rightarrow \text{HNO}_3 \\
\text{HNO}_3 + \text{NH}_3 & \rightarrow \text{NH}_4\text{NO}_3 & \rightarrow \text{N}_2\text{O} + 2\text{H}_2\text{O} \\
\text{HNO} + \text{HNO} & \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} 
\end{align*} \]

The production of N$_2$ at low temperature was postulated by various authors to occur either through an NH$_4$NO$_2$ (Eqs. 15 - 16) intermediate [25, 27] or through a reaction of ammonia with the nitroxyl species forming a N$_2$H$_2$ species which is subsequently oxidized (Eqs. 17 - 18) [28].

\[ \begin{align*} 
\text{HNO} + \frac{1}{2}\text{O}_2 & \rightarrow \text{HNO}_2 \\
\text{HNO}_2 + \text{NH}_3 & \rightarrow \text{NH}_4\text{NO}_2 & \rightarrow \text{N}_2 + 2\text{H}_2\text{O} 
\end{align*} \]
Development of new techniques and theories

With the development of mass-spectrometry old reaction mechanisms could be disproved and new reaction mechanisms were developed. The experiments were done at a low pressure (< 100 Pa). Fogel et al. [29] proposed a mechanism in which ammonia is oxidized directly by O or O₂ on the surface to NO and water (Eq. 19-21) based on studies using secondary ion emission mass spectrometry. The formation of nitrogen is a result of a reaction of NO with NH₃ (Eq. 22). The low pressure kinetic steady state reaction studies on platinum wire of Pignet and Schmidt [30] supported this theory.

\[
\begin{align*}
\text{NH}_3 + \text{O}_2 & \longrightarrow \text{NO} + \text{H}_2\text{O} + \text{H} & (19) \\
\text{NH}_3 + \text{O} & \longrightarrow \text{NO} + \text{H}_2 + \text{H} & (20) \\
2\text{H} + \text{O} & \longrightarrow \text{H}_2\text{O} & (21) \\
\text{NH}_3 + \text{NO} & \longrightarrow \text{N}_2 + \text{H}_2\text{O} + \text{H} & (22)
\end{align*}
\]

In a series of molecular beam mass spectrometry experiments on a platinum filament Nutt and Kapur [31, 32] find a very similar reaction mechanism. The only difference with the Fogel mechanism is that they find that ammonia adsorbs dissociatively (Eq. 23) and the so formed NH₂ reacts with O₂ to NO (Eq. 24) or with NO to nitrogen (Eq. 25). In none of the low pressure (< 100 Pa) studies nitrous oxide was detected, so the theories do not account for its formation.

\[
\begin{align*}
\text{NH}_3 & \longrightarrow \text{NH}_2 + \text{H} & (23) \\
\text{NH}_2 + \text{O}_2 & \longrightarrow \text{NO} + \text{H}_2\text{O} & (24) \\
\text{NH}_2 + \text{NO} & \longrightarrow \text{N}_2 + \text{H}_2\text{O} & (25)
\end{align*}
\]

At the same time an extensive study of the kinetics of low temperature ammonia oxidation on platinum under atmospheric pressure by Il'chenko [7] yielded an adapted version of the imide reaction mechanism. It was found that the reaction mechanism at temperatures below 503 K started with the formation of an imide (Eq. 9), which could subsequently react form a nitroxyl (Eq. 10). Similar to earlier proposals, nitrous oxide was found to be formed through a reaction of HNO with HNO (Eq. 14). However, the reaction forming nitrogen was proposed to proceed though a reaction of NH with HNO (Eq. 26).

\[
\begin{align*}
\text{HNO} + \text{NH} & \longrightarrow \text{N}_2 + \text{H}_2\text{O} & (26)
\end{align*}
\]
The kinetic studies of Ostermaier et al. [33] on alumina supported platinum catalysts at atmospheric pressure yielded a theory that is a mixture of the theory of Nutt and Kapur, Fogel, the imide theory, and own ideas. They fit their kinetic data with dissociative adsorption of both oxygen and ammonia (Eq. 27 - 28). The so formed NH₂ and O can subsequently react to NO (Eq. 29). The NO subsequently reacts with NH₂ to produce nitrogen (Eq. 25) or with H to form HNO (Eq. 30). The production of N₂O is thought to occur through reaction of HNO with HNO (Eq. 14).

\[
\begin{align*}
\text{NH}_3 & \rightarrow \text{NH}_2 + \text{H} & (27) \\
\text{O}_2 & \rightarrow 2 \text{O} & (28) \\
\text{NH}_2 + 2 \text{O} & \rightarrow \text{NO} + \text{H}_2\text{O} & (29) \\
\text{H} + \text{NO} & \rightarrow \text{HNO} & (30)
\end{align*}
\]

Infrared spectroscopic studies on ammonia oxidation were done by Morrow and Cody [34] on platinum on silica and by Matyshak [35, 36] on disks of various metals. The study of Morrow and Cody showed that on metallic platinum on silica NHO species are formed when a small dose of oxygen was dosed on an ammonia precovered catalyst. On oxidized platinum on silica bridging NH species were formed in a similar experiment. The studies of Matyshak revealed that on platinum NH₂ intermediates are present on the surface and N₂O gas is formed in the reaction system. On the basis of studies of various metals and metal oxides Matyshak constructed a reaction mechanism that generally agrees with that of Nutt and Kapur (Eq. 23 - 25).

**Surface Science**

New insights in the reaction mechanism of ammonia oxidation were obtained from surface science experiments. In these experiments single crystals of platinum were used as a catalyst under high vacuum conditions (pressure < 10⁻⁶ Pa). Gland and Korchak [37] studied the ammonia oxidation reaction on a stepped platinum single crystal surface with steady state reaction studies, Auger spectroscopy, and temperature programmed desorption (TPD). They found that nitrogen was the dominant species formed at low temperature and that NO was the dominant species at high temperature. Like in the other low pressure studies, no N₂O was detected in the experiments. Furthermore it was found that the surface of the catalysts was covered with nitrogen containing compounds when there was an excess of ammonia in the reaction mixture; under these conditions the product was nitrogen. In contrast, the surface was covered with oxygen when there was an excess of oxygen in the reaction mixture; under these conditions the product was NO. More recently the ammonia oxidation was studied by Mieher en Ho [38] on the Pt(111) surface with TPD, temperature programmed reaction spectroscopy.
(TPRS), electron energy loss spectroscopy (EELS), and low energy electron diffraction (LEED). Under low temperature reaction conditions (273 - 473 K) they find that ammonia adsorbs molecularly on the surface (Eq. 31), whereas oxygen adsorbs dissociatively (Eq. 32).

\[
\begin{align*}
\text{NH}_3 & \rightarrow \text{NH}_3^\text{a} \\
\text{O}_2 & \rightarrow 2 \text{O}_\text{a}
\end{align*}
\] (31) (32)

Subsequently the adsorbed \( \text{NH}_3 \) molecule is stripped by reaction with adsorbed oxygen (Eqs. 33 - 35) or adsorbed \( \text{OH} \) (Eqs. 36 - 38) producing eventually N atoms and \( \text{OH} \) or water molecules adsorbed on the surface.

\[
\begin{align*}
\text{NH}_3^\text{a} + \text{O}_\text{a} & \rightarrow \text{NH}_2^\text{a} + \text{OH}_\text{a} \\
\text{NH}_2^\text{a} + \text{O}_\text{a} & \rightarrow \text{NH} + \text{OH}_\text{a} \\
\text{NH}_2 + \text{O}_\text{a} & \rightarrow \text{N}_\text{a} + \text{OH}_\text{a} \\
\text{NH}_2^\text{a} + \text{OH}_\text{a} & \rightarrow \text{NH}_2 + \text{H}_2\text{O}_\text{a} \\
\text{NH}_2 + \text{OH}_\text{a} & \rightarrow \text{NH} + \text{H}_2\text{O}_\text{a} \\
\text{NH}_2 + \text{OH}_\text{a} & \rightarrow \text{N}_\text{a} + \text{H}_2\text{O}_\text{a}
\end{align*}
\] (33) (34) (35) (36) (37) (38)

The formation of water was found to occur through reaction of \( \text{OH} \) with \( \text{NH} \) (Eqs. 36 - 38) or through reaction of \( \text{OH} \) with \( \text{OH} \) (Eq. 39).

\[
\begin{align*}
2\text{OH}_\text{a} & \rightarrow \text{H}_2\text{O}_\text{a} + \text{O}_\text{a}
\end{align*}
\] (39)

The formation of nitrogen was found to occur mostly through recombinative desorption of adsorbed nitrogen atoms (Eq. 40). Possibly the reaction of \( \text{NH} \) with \( \text{N} \) (Eq. 41) or \( \text{NH} \) (Eq. 42) could also contribute to the formation of nitrogen.

\[
\begin{align*}
2\text{N}_\text{a} & \rightarrow \text{N}_2 \text{(g)} \\
\text{N}_\text{a} + \text{NH}_\text{a} & \rightarrow \text{N}_2 \text{(g)} + \text{H}_\text{a} \\
2\text{NH}_\text{a} & \rightarrow \text{N}_2 \text{(g)} + 2\text{H}_\text{a}
\end{align*}
\] (40) (41) (42)

Also from a temperature of 300 K the production of NO was observed. The reaction forming NO was found to mainly be the reaction of adsorbed \( \text{N} \) with \( \text{O} \) (Eq. 43). A minor path for the production of NO was the reaction of \( \text{NH} \) with \( \text{O} \) (Eq. 44). These paths were proposed earlier for the high temperature formation of NO [39]. The produced NO was found to desorb already
at a temperature of 316 K when the ammonia coverage was high; at lower coverage NO desorbed at a temperature of 486 K.

\[
\begin{align*}
N_{\text{a}} + O_{\text{a}} & \rightarrow NO_{\text{a}} \tag{43} \\
NH_{\text{a}} + O_{\text{a}} & \rightarrow NO_{\text{a}} + H_{\text{a}} \tag{44}
\end{align*}
\]

Another recent surface science study on ammonia oxidation was done by Bradley, Hopkinson, and King [40] on the Pt(100) surface using TPD and TPRS. It was found that this surface is more reactive than the Pt(111) surface. The mechanism they propose is similar to the mechanism of Mieher and Ho. However the production of nitrogen and NO was found to occur through other paths. The NO was proposed to be produced by a reaction of NH and O (Eq. 45) different from the reaction proposed by Mieher and Ho (Eq. 44), because in this case no adsorbed H is formed.

\[
NH_{\text{a}} + 2 O_{\text{a}} \rightarrow NO_{\text{a}} + OH_{\text{a}} \tag{45}
\]

The production of nitrogen was proposed to occur through recombinative desorption of N adsorbed on the surface (Eq. 40), like in the Mieher and Ho mechanism, however in this study the production of N was attributed to both reaction of NH with O (Eq. 35) and the dissociation of NO (Eq. 46).

\[
NO_{\text{a}} \rightarrow N_{\text{a}} + O_{\text{a}} \tag{46}
\]

It was concluded that the route to the production of nitrogen (via \(N_{\text{a}}\)) proceeds through the dissociation of NO (Eq. 46) at temperatures above 350 K, whereas the alternative route (Eq. 35) predominates at lower temperatures. In the low temperature regime it was found that the desorption of nitrogen was enhanced by a higher oxygen coverage of the surface. The same coverage dependence was found in a study of nitrogen desorption from a clean platinum surface [41]. In the high temperature regime a higher oxygen coverage favors the reaction to NO.

**Electrochemistry**

In electrochemical studies two reaction mechanism can be distinguished for low temperature liquid phase ammonia oxidation. Both mechanisms start with the stepwise stripping of the ammonia molecule by OH\(_{\text{a}}\), similar to the mechanism of Mieher en Ho (Eqs. 36-38). The most widely adapted mechanism in electrochemistry [42, 43] also agrees with Mieher and Ho that the formation of nitrogen occurs through recombinative desorption of adsorbed N atoms...
(Eq. 40). In the alternative mechanism [44, 45] the formation of nitrogen occurs through a hydrazine-like \((N_2H_{(x+y)})\) intermediate (Eqs. 47-48), in which both \(x\) and \(y\) can be 1 or 2. This route is similar to the nitrogen formation in the imide mechanism (Eqs. 11 and 18). However, in the new mechanism both NH and NH\(_2\) intermediates can react to form the hydrazine-like intermediate.

\[
\begin{align*}
\text{NH}_x + \text{NH}_y & \rightarrow \text{N}_2\text{H}_{(x+y)} & (47) \\
\text{N}_2\text{H}_{(x+y)} + (x+y) \text{OH}^- & \rightarrow \text{N}_2(g) + (x+y) \text{H}_2\text{O} + (x+y) \text{e} & (48)
\end{align*}
\]

**Computational chemistry**

Recently a density functional study has been done by Fahmi and van Santen [46] on ammonia oxidation on a Pt\(_x\) cluster. It was found that ammonia only dissociates when oxygen is present on the surface. The reaction mechanism was found to generally follow the Mieher and Ho mechanism. The only exception to that mechanism is that the activation of \(\text{NH}_2\) by \(\text{OH}\) (Eqs. 36-38) was not found to occur, since these steps are endothermic. Furthermore, it was established that water can poison the ammonia oxidation reaction, since water is more acidic than ammonia.

**Other aspects of low temperature ammonia oxidation on platinum**

**Time on Stream behavior**

Platinum catalysts show a considerable loss of activity as a function of Time On Stream (TOS) in the low temperature ammonia oxidation reaction. This was established in both atmospheric pressure gas phase experiments [33, 47, 48, 49] as well as in liquid phase electrochemical experiments [44, 45]. The loss of activity of the platinum catalysts was attributed to oxidation of the platinum surface [33] or to inhibition of the surface with nitrogen containing intermediates [44, 45]. In a computational chemistry study [46] water is mentioned as a poison for the reaction, therefore \(\text{OH}\) is a potential inhibiting species.

**Metal particle size effect**

In atmospheric pressure gas phase experiments it was further established [33, 47, 48, 49] that large (15.5 nm) metal particles are more active in the low temperature oxidation of ammonia than small (2 nm) metal particles. This particle size effect was found to be enhanced by the loss of activity at the start of the reaction. Therefore smaller metal particles become even less active because they showed a stronger initial loss of activity than larger metal particles.
Introduction

Similar metal particle size effect have been observed for various reactions and metals, for example recently in NO reduction over a platinum on alumina catalyst [50] or for butane hydrogenolysis over a iridium on zeolite catalyst [51].

This study

In this thesis research into two main subjects is described: the preparation of small platinum particles in zeolite HZSM-5 (chapter 2) and the low temperature gas phase oxidation of ammonia over platinum and iridium catalysts (chapters 4 and 5). The gas phase oxidation of ammonia over a [Pt(NH$_3$)$_4$]$^{2+}$ complex in zeolite HZSM-5 connects these two subjects (chapter 3). The main goal of this study is to establish whether platinum and iridium catalysts can be active and selective catalysts for the low temperature oxidation of ammonia to nitrogen.

In the second chapter of this thesis the preparation of small platinum particles in zeolite ZSM-5 is described. Since in this preparation a [Pt(NH$_3$)$_4$]$^{2+}$ complex is oxidized, this process has some resemblance with the oxidation of ammonia. It was found that water combined with acid sites enables the oxidation of part of the [Pt(NH$_3$)$_4$]$^{2+}$ complex already at a low temperature (490 K). Therefore in chapter 3 it was examined whether it was possible to apply this effect to gas phase ammonia oxidation over a catalyst that consists of [Pt(NH$_3$)$_4$]$^{2+}$ in zeolite HZSM-5. It was found that indeed a catalytic reaction was possible with this complex at a temperature of 473 K. Furthermore it was found that the selective reaction to nitrogen is enhanced by water. In order to gain some insight in the reaction mechanism also some infrared experiments were done. In chapter 4 studies of the low temperature gas phase ammonia oxidation reaction are described using platinum and iridium catalysts. The metal particle size of the catalysts was varied in order to examine the particle size effect. It was found that for both metals a particle size effect exists. Furthermore it was found that the iridium catalysts were more active than the platinum catalysts. Also the TOS behavior was studied by measuring the activity of the catalyst as a function of time on stream. It was found that the platinum catalysts slowly lost activity directly from the start of the reaction and more rapidly after some time on stream. Whereas the iridium catalysts were found to first become more active and after some time on stream lose activity. The change in activity occurred at the time of the breakthrough of ammonia for both metals. Therefore, it was concluded that the adsorption of ammonia on the γ-alumina support was the cause of the change in activity. From the measurement of kinetics it was established that the catalyst surface in steady state is covered with reaction intermediates. Water was found to decrease the activity of the catalysts for both metals: platinum catalysts were found to be more sensitive to water than iridium catalysts. In chapter 5 experiments are described to study the surface of the catalysts after
being used in the low temperature oxidation of ammonia. Metal sponge catalysts were used in order to avoid any influence of a catalyst carrier. With combined TPD and TPR measurement on used catalysts it was established that the surface of both platinum and iridium catalysts at steady state is mainly covered with adsorbed NH and OH and some NH₂. This result was confirmed by XPS. The reaction mechanism proceeds through a stepwise dehydrogenation of the ammonia molecule. It was concluded that the rate determining step is the dehydrogenation of adsorbed NH with adsorbed OH to adsorbed N and water. The initial loss of activity is therefore caused by covering of the catalyst surface with adsorbed NH and OH.

References

Preparation of Highly Dispersed Platinum Particles in HZSM-5 Zeolite: A Study of the Pretreatment Process of $[\text{Pt(NH}_3\text{)}_4]^{2+}$ *

Abstract

The pretreatment of $[\text{Pt(NH}_3\text{)}_4]^{2+}$, ion exchanged into zeolite HZSM-5, was studied using temperature programmed techniques and diffuse reflectance UV/VIS spectroscopy. The pretreatment is an important part of the preparation of bifunctional Pt/HZSM-5 catalysts, which are active in the hydroisomerization of alkanes. Pretreatment in a helium atmosphere leads to autoreduction and the conversion of part of the ammonia ligands into hydrogen and nitrogen. Pretreatment in an oxygen containing atmosphere leads to the oxidation of the ammonia ligands into nitrogen, nitrous oxide, and water. Temperature programmed pretreatment with oxygen gives rise to three reaction-rate maximums if the sample is not dried, and the conclusion is that $[\text{Pt(NH}_3\text{)}_4(\text{H}_2\text{O})]^2+$ is formed as an intermediate in the first step. The complex is activated for this first step by an acid site of the zeolite. If temperature programmed pretreatment with oxygen is carried out on a previously dried sample, oxidation of the ligands is a two-step process: three of the ammonia ligands are oxidized in one rapid step and the last ligand is oxidized at a higher temperature. Careful pretreatment in an oxygen containing atmosphere of $[\text{Pt(NH}_3\text{)}_4]$HZSM-5 leads to the formation of the pale green PtHZSM-5 in which platinum is present as $\text{Pt}^{2+}$ coordinated to the zeolite framework. Small platinum particles are formed by subsequent reduction of these platinum ions in flowing hydrogen.

Introduction

The preparation of platinum particles in zeolites is a task which has to be carried out with care; this fact has been recognized since the early days of Pt-zeolite catalysis [1, 2, 3]. The preparation can be divided into three steps: introduction of the platinum, pretreatment (or calcination, when conducted in an oxygen containing atmosphere), and reduction.

The preferred way of introducing platinum into the zeolite is to exchange Na⁺ or H⁺ ions for positively charged platinum complexes (mostly \([\text{Pt(NH}_3\text{)}_4]^{2+}\)) [4]. Much research was done to establish the best conditions for this ion exchange (temperature, with or without competition of ammonium, concentrations, etc.); it was found that a low concentration of \([\text{Pt(NH}_3\text{)}_4]^{2+}\) at room temperature is a good condition for the exchange [5].

The processes that occur during pretreatment of \([\text{Pt(NH}_3\text{)}_4]^{2+}\) or \([\text{Pd(NH}_3\text{)}_4]^{2+}\) in zeolites were examined in many studies, because they can be of great influence on the location and size of the metal particles formed in the subsequent reduction. The studies in which both Pt and Pd were examined showed that both metals behave similar in the pretreatment process [2, 5, 6]. The differences between the metals that were reported are: the greater tendency to autoreduction of \([\text{Pt(NH}_3\text{)}_4]^{2+}\) in zeolites [5]; and the lower stability of \([\text{Pd(NH}_3\text{)}_4]^{2+}\) in zeolite X [6]. Therefore, also studies are discussed here that concern \([\text{Pd(NH}_3\text{)}_4]^{2+}\) exchanged in zeolites; these studies [7, 8, 9] are more detailed about the pretreatment process than the studies concerning \([\text{Pt(NH}_3\text{)}_4]^{2+}\) exchanged in zeolites [1, 3, 4, 10, 11, 12]. Reagan et al. [2] studied the pretreatment of both \([\text{Pt(NH}_3\text{)}_4]^{2+}\) and \([\text{Pd(NH}_3\text{)}_4]^{2+}\) in zeolite NaY using Thermo Gravimetric Analysis (TGA). They concluded that the overall reaction in helium or air is:

\[
\begin{align*}
3 [\text{Pt(NH}_3\text{)}_4]^{2+} & \rightarrow 3 \text{Pt}^0 + 6 \text{NH}_3 + 6 \text{H}^+ && (1)
\end{align*}
\]

In Eq. (1) the platinum ions are reduced by the ammonia ligands; processes like this are called autoreduction [5, 13]. Only minor differences were observed in pretreatment behavior between platinum and palladium. Exner et al. [6] studied the pretreatment of \([\text{Pt(NH}_3\text{)}_4]^{2+}\) and \([\text{Pd(NH}_3\text{)}_4]^{2+}\) in zeolite NaX using Temperature Programmed Mass Spectrometry (TPMS), Differential Thermal Analysis (DTA), and Derivative Thermogravimetry (DTG). They concluded that, during the temperature program, several internal reactions take place in a vacuum. At temperatures below 473 K, some ligands are expelled:

\[
[\text{Pt(NH}_3\text{)}_4]^{2+} \rightarrow [\text{Pt(NH}_3\text{)}_4]^{2+} + (4-x) \text{NH}_3 && (2)
\]
Pretreatment Process of $[\text{Pt(NH}_3\text{)}_4]^{2+}$ in HZSM-5

At temperatures above 473 K, an autoreduction reaction takes place:

\[
[\text{Pt(NH}_3\text{)}_4]^{2+} \rightarrow [\text{PtNH}]^0 + 2\text{H}^+ + (x-1) \text{NH}_3 \quad (3a)
\]

\[
2[\text{PtNH}]^0 \rightarrow 2\text{Pt}^0 + \text{N}_2 + \text{H}_2 \quad (3b)
\]

The reactions in Eqs. (3a) and (3b) occur simultaneously. Brønsted acid sites (Z is zeolite, Z-OH is a Brønsted acid site) react with the liberated ammonia:

\[
\text{Z-OH} + \text{NH}_3 \rightarrow \text{Z-ONH}_4 \quad (4)
\]

At temperatures above 573 K, the reaction in Eq. (4) is reversed:

\[
\text{Z-ONH}_4 \rightarrow \text{Z-OH} + \text{NH}_3 \quad (5)
\]

At temperatures above 723 K, the platinum particles decompose the liberated ammonia into nitrogen and hydrogen. In this atmosphere (containing hydrogen and ammonia), mobile neutral complexes like $[\text{Pt(NH}_3\text{)}_2\text{(H)}_2]^0$ [1] can be formed; these complexes can diffuse rapidly in the zeolite, forming large platinum particles [2]. The products of the pretreatment in oxygen were: water, ammonia, and nitrogen; nitrogen oxides were not found in the study of Exner et al. [6]. Homeyer and Sachtler [7] studied the pretreatment of $[\text{Pd(NH}_3\text{)}_4]^{2+}$ in zeolite NaY using TPMS. In this study was concluded that the pretreatment of $[\text{Pd(NH}_3\text{)}_4]^{2+}$ is a stepwise process: two of the ammonia ligands are oxidized at 543 K; another ammonia ligand is oxidized rapidly at 613 K; and the last ammonia ligand is oxidized at 673 K. The oxidation of the first two ammonia ligands yields $[\text{Pd(NH}_3\text{)}_2]^2+$ coordinated to the zeolite lattice in the supercage. The rapid oxidation of the third ammonia ligand is an evidence for the migration of $[\text{Pd(NH}_3\text{)}_3]^2+$ into a sodalite cage. The oxidation of the last ammonia ligand occurs in the sodalite cage forming $\text{Pd}^{2+}$ coordinated to the sodalite cage oxygen atoms. Oxidation of the ammonia ligands was found to yield nitrogen and water. A complementary study [9] using DR-UV/VIS confirmed these conclusions and furthermore it was concluded that the final $\text{Pd}^{2+}$ ion is coordinated to four oxygen atoms in square planar symmetry. Sauvage et al. [8] recently studied the pretreatment and reduction of $[\text{Pd(NH}_3\text{)}_4]^{2+}$ in zeolites Y and X using TPMS, TPO, and DR-UV/VIS/NIR. In this study it was concluded that in the stepwise pretreatment some ammonia ligands are desorbed as ammonia gas, while others are oxidized to nitrogen and nitrous oxide; the ratio of oxidized to desorbed ligands depended on the zeolite and the zeolite counterion. Another conclusion was that, before the final product $\text{Pd}^{2+}$ coordinated to the zeolite lattice is formed, partly deamminated complexes are formed with general formula: $[\text{Pd(NH}_3\text{)}_4(A)]^{2+}$ coordinated to the zeolite framework, where A is either $\text{H}_2\text{O}$ or $\text{OH}$. Sauvage
et al. [8] comment that no conclusion about the symmetry of the final Pd$^{2+}$ coordination could be made from the UV/VIS spectrum: both C$_{3v}$ [14] and D$_{4h}$ [9] symmetry were proposed in literature. Several studies report that bare Pt$^{2+}$ ions are the final product of the pretreatment of [Pt(NH$_3$)$_4$]$^{2+}$, if carried out in a fast stream of air or oxygen with a very slow heating rate (< 1 K/min) [4, 10, 11, 12]; however also PtO is reported as the final product of the pretreatment [15].

Reduction of the platinum ions is necessary to gain an active catalyst. The reduction of Pt$^{2+}$ (or Pd$^{2+}$) leads to the formation of two protons which participate in the metal-zeolite interaction [10, 16], stabilizing small metal particles.

In the literature cited above samples have been examined which contain a high metal loading (from 5 wt% [8] up to 80 wt% [6]) and are based on the sodium form of the zeolite. However, the bifunctional catalyst that is normally used in the hydroisomerization of alkanes contains much less active metal (0.5-1 wt%) and is based on the acid form of the zeolite. In this study, therefore, samples were examined that are suitable as bifunctional catalysts. The pretreatment of [Pt(NH$_3$)$_4$]$^{2+}$ in HZSM-5 was studied using Temperature Programmed Mass Spectrometry (TPMS), Temperature Programmed Oxidation (TPO) and diffuse reflectance UV/VIS spectroscopy. The results may provide a basis for the empirical procedures for the pretreatment of [Pt(NH$_3$)$_4$]$^{2+}$ in zeolites, and may make improved pretreatment procedures possible. Hydrogen chemisorption measurements were used to determine the number of platinum surface atoms present, formed after pretreatment and reduction, and hence from the known amount of platinum present, to estimate the particle size. High resolution electron microscopy (HREM) measurements were done to check the determined particle size.

Methods

Sample Preparation

A batch of 10 g of NaZSM-5 (Exxon, AT281/78962, Si/Al ≈ 40) was calcined up to a temperature of 823 K in order to remove the template. HZSM-5 was prepared from the calcined NaZSM-5 by triple exchange with 1 M NH$_4$NO$_3$ followed by calcination in dry air up to 773 K. Pt(NH$_3$)$_4$HZSM-5 was prepared by ion exchange, following literature methods [7]. A dilute solution of [Pt(NH$_3$)$_4$](OH)$_2$ (Strem Chemicals, lot nr. 132413-S4) was added dropwise to a stirred HZSM-5 slurry (200 cm$^3$ doubly deionized water per g zeolite); after 24 hours of stirring at room temperature, the slurry was filtered and washed twice with 100 cm$^3$ doubly deionized water. During the exchange, the pH of the solution was found to be 7. UV/VIS measurements of the filtrate showed that the ion exchange was complete.
platinum loading of the sample was 0.50 wt%. A sample of 0.5 wt% [Pt(NH₃)₄]NaZSM-5 was prepared from NaZSM-5 using the same procedure.

**TPMS procedure**

The TPMS data were obtained in a fixed bed flow reactor system, containing approximately 0.5 g of catalyst. Up to 15 mass numbers could be measured using a computer interfaced quadrupole mass spectrometer (Balzers QMG 420) downstream of the catalyst. The TPMS data were measured in a helium or an oxygen/helium flow (2.4 vol% oxygen or 4 vol% oxygen) of 20 cm³/min (STP), while the temperature was increased from 301 to 873 K with a heating rate of 5 K/min. The Standard Temperature and Pressure (STP) were a temperature of 273 K and a pressure of 10⁵ Pa.

**TPO procedure**

The TPO data were obtained in a fixed bed flow apparatus similar to that typically used for temperature programmed reduction, containing approximately 0.3 g of catalyst; the oxygen consumption was measured by a TCD device. TPO experiments were measured in a 4 vol% oxygen/helium flow of 5 cm³/min (STP); the temperature was increased from 293 to 773 K with various heating rates.

**Diffuse-reflectance UV/VIS**

The diffuse reflectance UV/VIS spectra were obtained in a Hitachi 150-20 double beam spectrophotometer equipped with a 60 mm diameter integrating sphere device coated with BaSO₄. The reflectance was measured with Ca(OH)₂ in a quartz cuvette as a reference. The reflectance of HZSM-5 was also measured as a blank sample. Because zeolites are known to show absorption below 400 nm [17, 18] it is necessary to correct for this influence. Therefore, the Kubelka-Munk function [9, 19] was calculated from the measured reflectance of which the reflectance of the blank material was subtracted. A sample of approximately 2 gram of the [Pt(NH₃)₄]²⁺ exchanged HZSM-5 was placed in a small reactor; thereafter, the temperature was ramped with a heating rate of 0.5 K/min to a specified temperature in an oxygen/nitrogen (20/80) flow and held at that temperature for 2 hours. After cooling down in a nitrogen atmosphere the sample was transferred under a nitrogen atmosphere into a quartz cuvette, after which the UV/VIS spectrum was measured. Thereafter the sample was transferred back into the reactor and the pretreatment was started again to the next temperature. After the final pretreatment to 723 K, the sample was contacted with moist air and spectra were measured after several times of exposure.
Chapter 2

Pretreatment and reduction
A sample of 3 g of the [Pt(NH$_3$)$_4$]$^{2+}$ exchanged HZSM-5 was pretreated and reduced in a separate apparatus. Pretreatment was done under an oxygen/nitrogen (20/80) flow of 120 cm$^3$/min/g (STP), while the temperature was ramped from room temperature to 723 K with a rate of 0.5 K/min. After two hours at 723 K, the sample was cooled down in a flow of nitrogen. Subsequently, the sample was reduced in a hydrogen flow of 90 cm$^3$/min/g (STP), while the temperature was ramped from room temperature to 673 K with a rate of 5 K/min.

Hydrogen chemisorption measurements
Hydrogen chemisorption was measured at 298 K using a conventional glass apparatus, following the procedure of Kip et al. [20]. Before measuring hydrogen chemisorption the pretreated and reduced catalyst was rereduced in a flow of hydrogen at 523 K for 1 h, and subsequently evacuated (10$^{-2}$ Pa) for 1 h at the same temperature in order to remove chemisorbed hydrogen. Thereafter a measured amount of hydrogen (P = 100 kPa at room temperature) was admitted to the sample which was kept at 523 K. Hydrogen chemisorption equilibrium was reached quickly (< 5 min), because of the elevated temperature. After adsorption, the sample was allowed to cool to room temperature and was allowed to stabilize for at least 1 h. The hydrogen desorption isotherm was measured by lowering the pressure stepwise and determining the amount of hydrogen that was desorbed from the sample for each step. The H/Pt ratio was determined by extrapolation of the linear high pressure part (20 kPa < P < 80 kPa) of the isotherm to zero pressure. As a blank experiment hydrogen chemisorption was measured on a sample of HZSM-5, that was pretreated in the same way as the catalyst.

Electron microscopy measurements
High resolution transmission electron microscopy (HREM) measurements were done on a sample of carefully pretreated and reduced [Pt(NH$_3$)$_4$]HZSM-5 with a Philips CM30-T electron microscope.
Results

**TPMS**

In the first experiment, a [Pt(NH$_3$)$_4$]$_2$HZSM-5 sample was heated in a helium flow. The signals for water were significant over a temperature range from room temperature up to 723 K. Figure 1 is a response versus temperature plot, showing the results for hydrogen (mass 2), nitrogen (mass 28), and NH$_2$ (mass 16), the latter from fragmentation of ammonia. The plot reveals that there is: a sharp peak in the nitrogen signal at a temperature of 605 K, and a broad peak in the nitrogen signal from 605 up to 725 K; whereas only a small signal for hydrogen is observed in this temperature region. Another feature that can be observed is that the release of ammonia ligands from the platinum complex occurs at high temperature (> 725 K); part of the released ammonia is converted to nitrogen and hydrogen.

![Figure 1: TPMS of 0.5 wt% [Pt(NH$_3$)$_4$]$^{2+}$ in HZSM-5 in a helium atmosphere (Shown are: ammonia (NH$_2$ (mass 16) was used as a marker for ammonia), nitrogen (mass 28), and hydrogen (mass 2)).](image-url)
In the second experiment, a [Pt(NH₃)₄]HZSM-5 sample was heated in a 2.4 vol% oxygen in helium flow. The signals for nitrogen (mass 28) and nitrous oxide (mass 44) were almost equal over the entire temperature range. Ammonia, nitrogen monoxide, or nitrogen dioxide were not found. Figure 2 is a response versus temperature plot, showing the results for oxygen (mass 32), nitrogen (mass 28), and water (mass 18). In the plot it can be clearly seen that the consumption of oxygen is mirrored in the production of nitrogen; although it is evident that the oxygen baseline is influenced by the large amount of water in the mass spectrometer. There are three peaks in the signal for nitrogen: at 490, 570, and 600 K. The oxygen concentration decreases to very low values in the sharp peak at 570 K. Quantitative analysis of the nitrogen signal reveals that the area of the sharp peak at 570 K is twice the area of the peak at 490 K. Also evident is the large release of water from the zeolite up to high temperatures.

In the third experiment, a [Pt(NH₃)₄]HZSM-5 sample was dried by flowing dry helium over the sample overnight at room temperature, after which the sample was heated in a 4.0 vol% oxygen in helium flow. A higher concentration of oxygen was used in this experiment to avoid the concentration falling to the low level of the second experiment. The signals of nitrogen (mass 28) and nitrous oxide (mass 44) were almost equal over the entire temperature range. Ammonia, nitrogen monoxide, or nitrogen dioxide were not found, similar to the results of the second experiment. Figure 3 is a response versus temperature plot, giving the results for oxygen (mass 32), nitrogen (mass 28), and water (mass 18). The consumption of oxygen is mirrored in the production of nitrogen, as in the second experiment; although also in this experiment it is evident that the oxygen baseline is influenced by the amount of water in the mass spectrometer. Only two peaks can be seen in the signal for nitrogen: at 580, and 615 K. The release of water by the zeolite is much smaller than in the second experiment; the water concentration in the flow is low at a much lower temperature. Water is formed in the reaction of oxygen with ammonia, besides nitrogen and nitrous oxide: this is evidenced by the second peak in the water signal. This peak occurs at a slightly higher temperature than the peak of the formation of nitrogen and nitrous oxide; this is due to a strong adsorption of water in the zeolite.
Pretreatment Process of $[\text{Pt(NH}_3\text{)}_4]^{2+}$ in HZSM-5

**Figure 2:** TPMS of 0.5 wt% $[\text{Pt(NH}_3\text{)}_4]^{2+}$ in HZSM-5 in a 2.4 vol% oxygen/helium atmosphere (Shown are: oxygen (mass 32), nitrogen (mass 28), and water (mass 18)).

**Figure 3:** TPMS of dried 0.5 wt% $[\text{Pt(NH}_3\text{)}_4]^{2+}$ in HZSM-5 in a 4 vol% oxygen/helium atmosphere (Shown are: oxygen (mass 32), nitrogen (mass 28), and water (mass 28)).
The second experiment was repeated with a [Pt(NH$_3$)$_4$]NaZSM-5 sample instead of a [Pt(NH$_3$)$_4$]HZSM-5 sample. The signals of nitrogen (mass 28) and nitrous oxide (mass 44) were almost equal over the entire temperature range. Ammonia, nitrogen monoxide, or nitrogen dioxide were not found, similar to the results of the previous experiments. Figure 4 is a response versus temperature plot, giving the results for oxygen (mass 32), nitrogen (mass 28), and water (mass 18). Again, it can be seen that the consumption of oxygen is mirrored in the production of nitrogen. Also a large signal for water is observed over the entire temperature range. Only one clear peak can be seen in the signal for nitrogen: at 560 K. This peak appears to be double and shows some high temperature tail. The most marked difference with the second experiment (Figure 2) is the disappearance of the low temperature peak in the nitrogen signal.
TPO

A series of four TPO experiments were done, with various heating rates (5, 4, 2, and 1 K/min). Figure 5 shows oxygen concentration versus temperature for each heating rate. Since the samples are not dried before the experiment, these results should be comparable with the results of the second TPMS experiment. However, only two peaks were measured in the two experiments with the lowest heating rate; three peaks are found in the other two experiments. The low temperature peak is too small and too broad to be detected in the former case. As can be seen in Figure 5, the peak position in the TPO depends on the heating rate applied: the peaks shift to a lower temperature with decreasing heating rate. Quantitative analysis shows that the area under the large peak is in all cases approximately twice the area under the high temperature peak.

Figure 5: TPO of 0.5 wt% [Pt(NH₃)₄]²⁺ in HZSM-5 with various heating rates: 1 K/min (a), 2 K/min (b), 4 K/min (c), and 5 K/min (d).
**Diffuse-reflectance UV/VIS**

The results of a series of UV/VIS experiments made after pretreatment at a successively higher temperature are shown in Figure 6. Only the start of one large peak with a maximum below 200 nm could be detected after pretreatment to 293 K. A similar spectrum was measured after pretreatment to a temperature of 393 K. After pretreatment to a temperature of 523 K (Figure 6 b) the large band appears to have shifted to lower wavelength, and a small band can be observed at a wavelength of 250 nm; this small band was also observed after pretreatment to higher temperatures. Starting after pretreatment to a temperature of 548 K a band at a wavelength of 640 nm was detected (Figure 6 c-f). The intensity of this peak increases with increasing pretreatment temperature; furthermore the band becomes less broad after pretreatment to a temperature of 723 K. Starting after a pretreatment to a temperature of 573 K, a band at a wavelength of 440 nm was detected (Figure 6 d-f), also increasing in intensity with increasing pretreatment temperature. The large peak with a maximum at a wavelength below 200 nm also appears to increase in intensity with increasing pretreatment temperature. Because of the absorption in the visible region, the sample has got a light green color of the sample after pretreatment at 723 K. The same color change was reported before in literature for Pt$^{3+}$ in zeolite Y [11].

![Figure 6: UV/VIS spectra of 0.5 wt% [Pt(NH$_3$)$_4$]$^{2+}$ in HZSM-5, after pretreatment at a temperature of: 293 K (a), 523 K, (b), 548 K (c), 573 K (d), 623 K (e), and 723 K (f).](image-url)
The green color fades after prolonged exposure to ambient air; this has been examined by measuring UV/VIS spectra of a sample of the $[\text{Pt(NH}_3\text{)}_4]^2+$, pretreated to 723 K, after exposure of air for a certain time (Figure 7). After exposure to moist air the intensity of the peaks at 250, 440, and 640 nm decrease with time (Figure 7 b-e). Eventually, all three peaks disappear from the spectrum (Figure 7 e); only the start of a large band with a maximum below 200 nm can still be observed in the DR-UV/VIS spectrum.

Figure 7: UV/VIS spectra of 0.5 wt% $[\text{Pt(NH}_3\text{)}_4]^2+$ in HZSM-5, after pretreatment to 723 K (a), and subsequent exposure to ambient air for: 1 hour (b), 3 hours (c), 21 hours (d), and 4 days (e).
Pretreatment and hydrogen chemisorption

During careful pretreatment, pale green PtHZSM-5 is formed from white ion exchanged [Pt(NH$_3$)$_4$]HZSM-5. During reduction the color changes from green to gray. Hydrogen chemisorption experiments on the reduced Pt/HZSM-5 sample show that small platinum particles are present; the H/Pt ratio measured is 2.0 ($\pm$ 0.1). The values measured with this hydrogen chemisorption method usually are slightly higher than those obtained by hydrogen chemisorption at room temperature [20]. The HZSM-5 sample was found to chemisorb no detectable amount of hydrogen within experimental error. From the calibration made by Kip et al. [20] and extended by Vaarkamp et al. [21] it can be determined that a H/Pt value of 2.0 indicates a particle size of 2.5 to 5 Å. A representative HREM micrograph of a sample of Pt/HZSM-5 is shown in Figure 8. Most particles that can be seen on the micrograph are approximately 1 nm in size. On the surface of the zeolite crystal some larger particles can be seen. It is possible that smaller particles are missed, since the limits of the microscope are approached.

Figure 8: HREM micrograph of Pt/HZSM-5.
Discussion

Pretreatment in helium

Pretreatment in a helium atmosphere leads to autoreduction, as can be derived from the TPMS results shown in Figure 1. At temperatures between 575 and 725 K the nitrogen signal is much larger than the hydrogen signal, whereas at temperatures higher than 725 K the nitrogen and hydrogen are almost equal. The result obtained between 575 and 725 K contradicts with the results of Exner et al. [6], where nitrogen and hydrogen are observed simultaneously (Eq. 3b). However, the theory of Reagan et al. [2] (Eq. 1) can describe our results, if we consider that in HZSM-5 all ammonia will be adsorbed on the Brønsted acid sites (Eq. 4). Therefore, the total reaction will be:

\[
3 \text{[Pt(NH}_3\text{)}_4]^{2+} + 4 \text{Z-OH} + 6 \text{Z-O}^\cdot \rightarrow 3 \text{Pt}^0 + \text{N}_2 + 10 \text{Z-ONH}_4
\]  \hspace{1cm} (6)

In Eq. 6 the only gaseous product that would be observed is nitrogen, as was measured in the experiment at temperatures between 575 and 725 K. Therefore, we can conclude that autoreduction takes place in a helium atmosphere. At temperatures above 725 K, ammonia will desorb from the Brønsted acid sites (Eq. 5): this desorption is observed in the experiments, as can be seen in Figure 1. At these temperatures part of the released ammonia is converted into nitrogen and H\(_2\); this reaction is catalyzed by the autoreduced platinum particles:

\[
2 \text{NH}_3 \xrightarrow{\text{Pt}} \text{N}_2 + 3 \text{H}_2
\]  \hspace{1cm} (7)

The occurrence of this reaction is evidenced by the results of the first experiment (Figure 1). From the data presented in this study, no conclusions regarding the occurrence of neutral complexes like [Pt(NH\(_3\))\(_2\)(H)\(_2\)]\(^0\) can be made.

Pretreatment in oxygen/helium

The oxidation of the ammonia ligands produces: nitrogen, nitrous oxide, and water. In all TPMS experiments, no response was observed for nitrogen monoxide or nitrogen dioxide. Therefore, the reaction stoichiometry for the oxidation of ammonia ligands in this system must be:

\[
4 \text{NH}_3 + 3\frac{1}{2} \text{O}_2 \rightarrow \text{N}_2 + \text{N}_2\text{O} + 6 \text{H}_2\text{O}
\]  \hspace{1cm} (8)
This result differs from the results of literature studies [6, 7] of the pretreatment of Pt or Pd tetramines: in these studies no nitrogen oxides were reported. However, it must be noted that only nitrogen monoxide and nitrogen dioxide were followed by Homeyer and Sachtler [7], whereas it is not clear which masses were followed by Exner et al. [6]. Only in the study of Sauvage et al. [8] nitrous oxide was reported as a product of the oxidation of ammonia ligands. Another difference with literature studies [2, 6, 8] is that these show a desorption of ammonia in the pretreatment of Pt or Pd tetramines, even in an oxygen containing atmosphere. In our study no desorption of ammonia could be measured when there was oxygen present. This is probably caused by the much lower metal loading used in this study (0.5 wt% Pt) opposed to the metal loading used in literature (from 5 wt% Pd [8] up to more than 10 wt% Pd or Pt [2, 6]). Because of the higher metal loading a (local) shortage of oxygen can arise during the pretreatment, which suppresses the oxidation of NH₃. In this study, however, the metal loading is so low that similar shortages of oxygen can not occur. That shortages of oxygen do not occur in our experiments is evidenced by the results of the second TPMS experiment, in which the oxygen concentration decreases to a very low value in the sharp peak at 570 K. Therefore, a shortage of oxygen could be expected in the zeolite channels. This lack of oxygen would lead to the autoreduction mechanism. If autoreduction takes place more nitrogen than nitrous oxide should be formed, according to Eqs. (6) and (8). However, the nitrogen and nitrous oxide signals are also equal in this part of the TPMS plot, therefore there is no indication that this mechanism is occurring. Apparently, there is no shortage of oxygen in the zeolite channels during pretreatment.

The UV/VIS spectra presented in Figure 6 provide information about the pretreatment process. From literature [22] it is known that the spectrum of the square planar complex [Pt(NH₃)₄]²⁺ in solution has a strong absorption maximum at a wavelength of 198 nm with a small shoulder at 218 nm, both of which are caused by 5d → 6 p transitions; this large peak is accompanied by two other small shoulders, caused by ligand field (d-d) transitions, at the wavelengths 233 nm and 288 nm. The start of the large peak that can be seen in Figure 6 a, therefore probably is the start of the large 5d → 6 p transition of [Pt(NH₃)₄]²⁺; the shoulders are apparently too weak to be detected. In literature these small shoulders were detected on the strong absorption in the spectrum of samples of [Pt(NH₃)₄]²⁺ adsorbed on silica [23], alumina [24], and zeolite X [25]. The fact that the metal loading in our experiment was much lower (0.5 wt%) than the ones used in literature (2.5 to 3.0 wt%) must be the explanation for the absence of the shoulders in our study. Therefore, we conclude that [Pt(NH₃)₄]²⁺ has not changed upon exchange into the zeolite. The shift of the large peak and the appearance of the band at 250 nm after pretreatment to 523 K can be attributed to a small distortion of square planar symmetry caused by a stronger ionic interaction of [Pt(NH₃)₄]²⁺ with the zeolite negative charge; the increased interaction is caused by the loss of the solvating effect of water.
Pretreatment Process of [Pt(NH₃)₄]²⁺ in HZSM-5

as the zeolite becomes drier. The two peaks at a wavelength of 440 nm and 640 nm are interpreted as the d-d-transitions shifted and increased in intensity from 233 and 288 nm in [Pt(NH₃)₄]²⁺; the exchange of the ammonia ligands with the oxygen atoms of the zeolite can explain this shift, because the oxygen atoms of the zeolite are known to be much weaker ligands than ammonia [9]. Because of the shift to larger wavelength, the interference of the zeolite signal becomes less important and the peak can be detected easier. We assume that the symmetry of the complex remains square planar, because this is the most common symmetry for Pt(II)L₄ complexes; the spectrum measured after pretreatment to 723 K is in agreement with this assumption. Before the final coordination of Pt²⁺ to the zeolite lattice is established, apparently another species exists evidenced by the broad nature of the peak at 640 nm after pretreatment to a temperature of 573 to 623 K. This species could be a partly deamminated complex with the general formula [Pt(NH₃)₃(A)y]²⁺ (with A either H₂O or OH), similar to the one proposed for palladium [8]. This species has disappeared after pretreatment to a temperature of 723 K: the peak at 640 nm has become narrower. The visual result of the shift is the light green color of the sample. A similar shift and increase in intensity was reported to occur in the pretreatment of [Pd(NH₃)₄]²⁺ in zeolite X or Y [8, 9, 14]. The shift in the case of platinum (approx. 19,500 cm⁻¹) is larger than the shift in the case of palladium (approx. 12,700 cm⁻¹), which can be expected for a third row transition metal as opposed to a second row transition metal [26]. Even though the assumption of square planar symmetry (D₄h) holds, the possibility of coordination with three zeolite oxygen atoms in a C₃ᵥ symmetry cannot be excluded from our DR-UV/VIS results; this is similar to case of Pd²⁺ in zeolite X or Y [8]. Also in the case of palladium in zeolites NaY and H-mordenite [7, 27] a color change was observed (from white to pink).

The disappearance of the bands at 250, 440, and 640 nm after exposure of Pt²⁺ in zeolite HZSM-5 to moist air (Figure 7) can be attributed to the formation of [Pt(H₂O)₄]²⁺ solvated in the pores of the zeolite; the spectrum of [Pt(H₂O)₄]²⁺ in solution shows a high intensity peak at wavelengths shorter than 210 nm and three small bands at wavelengths of 273, 319, and 389 nm [28]. Similarly to the spectrum of [Pt(NH₃)₄]²⁺ in zeolite HZSM-5 (Figure 6a) these small bands are likely not to be detected, because of the low platinum loading used in this study. The same reaction was reported to occur on Pd²⁺ in zeolites Y and 5A, forming [Pd(H₂O)₄]²⁺ in the zeolite pores [29].

There is a remarkable difference in the TPMS results for the dried and the non dried sample. The non dried sample gives rise to three nitrogen/nitrous oxide peaks with a mutual ratio of 1:2:1 (combining the ratios found in the TPMS and TPO experiments). The dried sample gives rise to only two nitrogen/nitrous oxide peaks: the peak at 490 K is disappeared. This low temperature peak also disappears when a NaZSM-5 sample is used instead of a HZSM-5 sample. Therefore it can be concluded that the existence of this peak is caused by the
presence of water in combination with acid sites. We propose that, in the non dried case, an
ammonia ligand is exchanged for a water ligand, which is a normal reaction for platinum
tetrammine complexes [26]; the released ammonia ligand is oxidized:

\[
4 \text{[Pt(NH}_3]_4^{2+} + \frac{3}{2} \text{O}_2 + 4 \text{H}_2\text{O} \rightarrow 4 \text{[Pt(NH}_3](H}_2\text{O)}^{2+} + \text{N}_2 + \text{N}_2\text{O} + 6 \text{H}_2\text{O}
\] (9)

Apparently the acid site activates the complex for this reaction, since it is not observed in the
experiment with [Pt(NH\textsubscript{3})\textsubscript{4}]\textsuperscript{2+} exchanged in NaZSM-5. In the dried case this reaction will
occur to a much lower extent, because there is much less water present. In the non dried case,
the next step in the pretreatment is that two of the three ammonia ligands are oxidized rapidly
and possibly more water ligands are added (due to the oxidation of ammonia water is formed):

\[
2 \text{[Pt(NH}_3]_4(H}_2\text{O)}^{2+} + \frac{3}{2} \text{O}_2 + x \text{H}_2\text{O} \rightarrow 2 \text{[Pt(NH}_3](H}_2\text{O)}_{(x+y)}^{2+} + \text{N}_2 + \text{N}_2\text{O} + 6 \text{H}_2\text{O}
\] (10)

This reaction takes place at a temperature of 570 K. The last ammonia ligand is lost and,
again, possibly more water is added:

\[
4 \text{[Pt(NH}_3](H}_2\text{O)}_{(x+y)}^{2+} + \frac{3}{2} \text{O}_2 + y \text{H}_2\text{O} \rightarrow 4 \text{[Pt(H}_2\text{O)}_{(x+y)}^{2+} + \text{N}_2 + \text{N}_2\text{O} + 6 \text{H}_2\text{O}
\] (11)

This reaction takes place at a temperature of 600 K. From the results of the DR-UV/VIS
measurements it was concluded that after pretreatment to 723 K bare Pt\textsuperscript{2+} ions are formed;
therefore the water ligands must be lost finally:

\[
\text{[Pt(H}_2\text{O)}_{(x+y)}^{2+} \rightarrow \text{Pt}^{2+} + (1+x+y) \text{H}_2\text{O}
\] (12)

In the dried case, the first reaction step is that three ammonia ligands are oxidized in one rapid
step. Since the ammonia oxidation gives rise to a high water concentration (see Figure 3), this
can lead to the addition of some water ligands:

\[
4 \text{[Pt(NH}_3]_4^{2+} + 10\frac{1}{2} \text{O}_2 + x \text{H}_2\text{O} \rightarrow 4 \text{[Pt(NH}_3](H}_2\text{O)}^{2+} + 3 \text{N}_2 + 3 \text{N}_2\text{O} + 18 \text{H}_2\text{O}
\] (13)

This reaction takes place at a temperature of 580 K. From the DR-UV/VIS results no
conclusions could be made regarding the presence of water ligands; however it is clear that
ligands are present up to a pretreatment temperature of 623 K. When the last ammonia ligand
is lost still a high concentration of water is present, so again water ligands can be added to the
complex:
Pretreatment Process of [Pt(NH$_3$)$_4$]$^{2+}$ in HZSM-5

4 [Pt(NH$_3$)$_3$(H$_2$O)$_y$]$^{2+}$ + 3½ O$_2$ + y H$_2$O $\rightarrow$ [Pt(H$_2$O)$_{l(y+y)}$]$^{2+}$ + N$_2$ + N$_2$O + 6 H$_2$O  \hspace{1cm} (14)

This reaction takes place at a temperature of 615 K. From the DR-UV/VIS can be concluded that ligands are present up to a pretreatment temperature of 623 K; however after pretreatment to 723 K all ligands are lost and bare Pt$^{2+}$ is formed, therefore the water ligands are finally lost:

[Pt(H$_2$O)$_{l(x+y)}$]$^{2+}$ $\rightarrow$ Pt$^{2+}$ + (x+y) H$_2$O \hspace{1cm} (15)

The observed influence of water might afford a new interpretation of the results of Homeyer and Sachtler [7]. In that study a pattern was observed in the nitrogen signal which is similar to the pattern observed in the non dried case of this study. Furthermore, the authors reported that a large amount of water was released by the zeolite. Therefore, it can be concluded that the intermediate observed by Homeyer and Sachtler is [Pd(NH$_3$)$_3$(H$_2$O)$_2$]$^{2+}$ instead of [Pd(NH$_3$)$_3$]$^{2+}$ coordinated to the zeolite lattice. This conclusion is supported by the knowledge that palladium complexes are, like platinum complexes, capable of ligand exchange with water [26]. Another comment concerns the sharp peak observed in both studies. Our data cannot be explained in terms of this sharp peak being evidence for the migration of [Pd(NH$_3$)$_3$]$^{2+}$ into the sodalite cage, because no such cages are present in HZSM-5. Instead, a different, more general, interaction must be responsible for the sharpness of this peak: apparently the [Pt(NH$_3$)$_3$(H$_2$O)$_y$]$^{2+}$ or [Pd(NH$_3$)$_3$(H$_2$O)$_y$]$^{2+}$ species are stabilized well by any zeolite framework.

Our results support the empirical knowledge that has been developed during the last 20 years for the pretreatment of [Pt(NH$_3$)$_4$]$^{2+}$ in zeolites in the formation of Pt/zeolite catalysts: a high oxygen containing flow and a low heating rate are necessary to gain small platinum particles in zeolites. The oxygen is necessary to prevent autoreduction, while the high flow rate and the low heating rate provide for the removal of water.

Pretreatment and hydrogen chemisorption

As was discussed above, the green color of pretreated Pt(NH$_3$)$_4$HZSM-5 is an indication for the presence of Pt$^{2+}$ coordinated to the zeolite lattice. This is in contrast to studies on [Pt(NH$_3$)$_4$]$^{2+}$ in zeolite Y, in which PtO was found after pretreatment [15], leading to a gray/black color. This can be attributed to the high metal loading used in these studies and also to the use of zeolite Y. Apparently, autoreduction of [Pt(NH$_3$)$_4$]$^{2+}$ is much more difficult to avoid with these conditions: this gives rise to the formation of Pt metal particles, which are oxidized to PtO or PtO$_2$ particles [5]. Some studies report a green/grey color [11]: this is
probably caused by the presence of a mixture of Pt\textsuperscript{2+} and PtO. The green color changes to gray during reduction of the Pt\textsuperscript{2+} ions, indicating the formation of metallic platinum. Very small platinum particles (2.5 - 5 Å) are formed during this process, according to hydrogen chemisorption measurements. Also HREM shows very small platinum particles inside the zeolite crystal and some larger particles on the crystal surface.

Conclusions

Pretreatment of \([\text{Pt}(\text{NH}_3)_4]^{2+}\) ion exchanged into zeolite HZSM-5 in a helium atmosphere leads to autoreduction; part of the ammonia ligands are converted into nitrogen and hydrogen. Pretreatment in an oxygen containing atmosphere causes the ammonia ligands to be oxidized into: nitrogen, nitrous oxide, and water. If the sample is not dried, temperature programmed oxidation of the ligands occurs in three steps. In this case \([\text{Pt}(\text{NH}_3)_4(\text{H}_2\text{O})]^2+\) is formed as an intermediate in the first step. The complex is activated for this first step by an acid site of the zeolite. If the sample is dried, temperature programmed oxidation of the ligands occurs in two steps; \([\text{Pt}(\text{NH}_3)_3(\text{H}_2\text{O})]^2+\) can not be formed, because not enough water is present. The reaction forming \([\text{Pt}(\text{NH}_3)(\text{H}_2\text{O}))^2+\) is fast, in both cases. In the last step \([\text{Pt}(\text{H}_2\text{O})_x]^2+\) is formed, which is dehydrated to bare Pt\textsuperscript{2+} at higher temperatures. If pretreatment is carried out in a high flow of an oxygen containing atmosphere with a low heating rate, Pt\textsuperscript{2+} coordinated to oxygen atoms of the zeolite is formed; these platinum ions can be recognized by the characteristic green color. Reduction of these platinum ions leads to the formation of very small platinum particles.

References

Pretreatment Process of [Pt(NH$_3$)$_4$]$^{2+}$ in HZSM-5

Water Promoted Ammonia Oxidation by a Platinum Amine Complex in Zeolite HZSM-5 Catalyst

Abstract

In this study it was found that [Pt(NH₃)₄]HZSM-5 is an active catalyst for the gas phase selective oxidation of ammonia at low temperature. Furthermore it was established that, in contrast with other catalysts, the catalyst becomes more active in the presence of water. Furthermore, the selectivity to nitrogen was found to increase when water is present. Water probably takes part in the reaction that leads to the production of nitrogen. An infrared spectroscopy study revealed that acid sites of the zeolite are involved in the reaction. Furthermore it was found that ammonium and hydride are formed by reaction of the [Pt(NH₃)₄]²⁺ with water or oxygen. The hydride signal disappeared when ammonia was added to the catalyst. Unfortunately it was not possible to elucidate the reaction mechanism from the infrared measurements.

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Introduction

Selective oxidation of ammonia with oxygen to nitrogen and water could be a solution to pollution by ammonia, caused by various ammonia emissions like: the SCR process; soda production; or agricultural sources [1]. Usually the concentration of ammonia in the gas phase emission is low (< 1 vol%), therefore the process should use a catalyst that is active at a low concentration [1] or the ammonia should be concentrated by adsorption in water and subsequent desorption [2]. Various catalysts of different types have been tested for the ammonia oxidation reaction; biological catalysts [3], metal oxide catalysts [4, 5], ion-exchanged zeolites [4, 5, 6] and metallic catalysts [5, 7, 8]. The most active catalysts at low temperature are the precious metal (Pt, Pd, Ir) catalysts [5, 7, 8]. At low temperature (< 800 K) the product of the reaction is nitrogen, as shown in Eq. 1.

\[
2 \text{NH}_3 + \frac{1}{2} \text{O}_2 \rightarrow \text{N}_2 + 3 \text{H}_2\text{O} \quad (1)
\]

The formation of nitrous oxide is often seen as a byproduct, following Eq. 2.

\[
2 \text{NH}_3 + 2 \text{O}_2 \rightarrow \text{N}_2\text{O} + 3 \text{H}_2\text{O} \quad (2)
\]

Since nitrous oxide is an unacceptable environmental emission, an effective catalyst should have a high selectivity towards nitrogen [9]. A recent study [9] showed that ion-exchanged [Pt(NH₃)₄]²⁺, RhCl₃, and Pd(NO₃)₂ in zeolite NaZSM-5 are active in the gas phase ammonia oxidation at temperatures from 473 K. Although reduction of the metal-ions increased the activity the unreduced complexes were also active. The activity of these catalyst was found to be suppressed by the addition of water. In a recent study [10] on the decomposition of [Pt(NH₃)₄]²⁺ ion-exchanged in zeolite HZSM-5, it was shown that the partial decomposition of this complex in a 2.4 vol% oxygen in helium flow is already possible at a temperature around 490 K. However, it was found that at that temperature this reaction is only possible in the presence of water. This suggests that water might be expected to have a positive effect if [Pt(NH₃)₄]²⁺ in zeolite HZSM-5 is used as a catalyst in the gas phase oxidation of ammonia at a temperature of 473 K. This would be remarkable since water usually decreases the activity of catalysts [8, 9]. Therefore, in this study the activity of [Pt(NH₃)₄]²⁺ in zeolite HZSM-5 was studied in the gas phase oxidation of ammonia at 473 K. The reaction was carried out both with a gas mixture containing added water and a reaction mixture which was dry.
Water Promoted Oxidation of Ammonia by [Pt(NH$_3$)$_4$]HZSM-5

Methods

Sample preparation
A batch of 10 g of NaZSM-5 (Exxon, AT281/78962, Si/Al \(\approx 40\)) was calcined up to a temperature of 823 K in order to remove the template. HZSM-5 was prepared from the calcined NaZSM-5 by triple exchange with 1 M NH$_4$NO$_3$ followed by calcination in dry air up to 773 K. [Pt(NH$_3$)$_4$]HZSM-5 was prepared by ion exchange, following literature methods [10, 11]. A dilute solution of [Pt(NH$_3$)$_4$](OH)$_2$ (Strem Chemicals, lot nr. 132413-S4) was added dropwise to a stirred HZSM-5 slurry (200 cm$^3$ doubly deionized water per g zeolite); after 24 hours of stirring at room temperature, the slurry was filtered and washed twice with 100 cm$^3$ doubly deionized water. During the exchange, the pH of the solution was found to be 7. A UV/VIS measurement of the filtrate showed that the ion exchange was complete. Samples were prepared with a platinum loading of 0.5 wt%, 2.0 wt% and 3.5 wt% (maximum exchange, all H$^+$ exchanged for [Pt(NH$_3$)$_4$]$^{2+}$). In the reaction setup particles were used with a particle size between 125 and 425 µm; samples of the catalyst were pelletized, crushed, and sieved to acquire the appropriate particle size.

Measurement of catalytic activity
Catalytic tests were done in a fixed bed reaction setup equipped with a gas chromatograph (ATI UNICAM 610, spec 2790) and a quadrupole mass spectrometer (Balzers QMG-420) for on-line analysis of the reactants and products. The gas chromatograph was could analyze ammonia, oxygen, water, nitrogen, and nitrous oxide quantitatively. The quadrupole mass spectrometer was used for the detection of ammonia, oxygen, water, nitrogen, and nitrous oxide quantitatively and for detection of the presence of nitrogen monoxide and nitrogen dioxide. In order to measure accurately, the mass spectrometer was calibrated for each experiment with the gas chromatograph using the reaction mixture. A quartz tube with an internal diameter of 4 mm was used as the reactor. An amount of 150 mg of a (0.5 wt% Pt) [Pt(NH$_3$)$_4$]HZSM-5 catalyst was used in the reactor (GHSV \(\approx 6000\)). A reaction mixture consisting of 1.3 vol% of ammonia and 1.0 vol% of oxygen in helium was used as a standard reaction mixture; if water was added a concentration of 1.7 vol% was used. The total flow was 30.7 cm$^3$/min (STP) for all experiments.

Infrared experiments
Infrared experiments were done on a Bruker IFS 113v FTIR spectrometer, equipped with a heated vacuum cell. The spectra were recorded by adding at least 500 scans at a resolution of 4 cm$^{-1}$, using a DTGS detector. Samples of 30 mg [Pt(NH$_3$)$_4$]ZSM-5 were pressed to form self-supporting disks. Experiments were done on samples with a platinum loading of 0.5 wt%,
2.0 wt\%, and 3.5 wt\%. The sample was dried in the setup in a vacuum during 8 hours at 473 K after heating to 473 K at 0.5 K/min.

Results

In Figure 1 the concentration of nitrous oxide is shown as a function of time on stream for the oxidation of ammonia over a 0.5 wt\% [Pt(NH$_3$)$_4$]ZSM-5 sample with and without water in the reaction mixture. From Figure 1 it can be clearly seen that at the start of the reaction nitrous oxide is produced, but the production rate drops rapidly after 0.1 hours on stream. This drop in activity occurs at the moment that ammonia is first measured (breakthrough of ammonia). Furthermore it is obvious that in the first 0.1 hours of the reaction slightly more nitrous oxide is produced in the dry case than in the case with water in the reaction mixture. After the drop in production rate, however, it appears that the production rate of nitrous oxide is larger in the case when water is present in the reaction mixture than in the dry case. However due to the noise at this low concentration the difference is not significant.

![Figure 1: Concentration of nitrous oxide in the oxidation of ammonia over [Pt(NH$_3$)$_4$]ZSM-5 at 473 K, reaction mixture: water, 0 vol\% dotted line; 1.7 vol\% full line; ammonia 1.3 vol\%; oxygen 1.0 vol\%; GHSV 6000.](image)
In Figure 2 the concentration of nitrogen is shown as a function of time on stream for the oxidation of ammonia over a \([\text{Pt(NH}_3\text{)}_4]\text{HZSM-5}\) sample with and without water in the reaction mixture. From Figure 2 it can be clearly seen that at the start of the experiment not much nitrogen is produced, but the production rate increases rapidly after the breakthrough of ammonia at 0.1 hours on stream. Furthermore, it appears that the production rate is much larger when there is water in the reaction mixture: after the rapid increase the reaction rate increases gradually when there is water in the reaction mixture, whereas it decreases rapidly when the reaction mixture is dry. Also it must be noted that in the first 0.1 hours on stream the production of nitrogen can be seen immediately when water is present, whereas the production nitrogen starts after some time when there is no water in the reaction mixture.

The Turn Over Frequency (TOF) that can be derived from the combined production of nitrogen and nitrous oxide at two hours on stream is calculated to be 2.2 mole of ammonia converted per mole of \([\text{Pt(NH}_3\text{)}_4]\) per hour in the case with water and 0.7 mole of ammonia converted per mole of \([\text{Pt(NH}_3\text{)}_4]\) per hour in the dry case.

Figure 2: Concentration of nitrogen in the oxidation of ammonia over \([\text{Pt(NH}_3\text{)}_4]\text{HZSM-5}\) at 473 K, reaction mixture: water, 0 vol% dotted line; 1.7 vol% full line; ammonia 1.3 vol%; oxygen 1.0 vol%; GHSV 6000.
Figure 3: Infrared spectra measured at 473 K of [Pt(NH$_3$)$_4$]ZSM-5, dried overnight (a), after exposure to water and oxygen (b), and after subsequent exposure to ammonia (c).

All infrared experiments shown in this study were done on a [Pt(NH$_3$)$_4$]ZSM-5 sample containing 2.0 wt% platinum. The experiments using 0.5 wt% samples showed too small signals. The experiments using 3.5 wt% samples showed no differences in the spectra after different treatments. In Figure 3 the results are shown of infrared experiments simulating the ammonia oxidation. The dried catalyst (spectrum a) shows peaks for ammonia (1345 cm$^{-1}$), ammonium (1455 cm$^{-1}$), and overtones of the zeolite framework peaks (1640, 1875, and 1995 cm$^{-1}$). Spectrum b was measured after admission of water, oxygen, or water and oxygen to the dried sample. The ammonia peak clearly decreases and the ammonium peak increases. Furthermore a new peak is developed at 2120 cm$^{-1}$. An exchange experiment with deuterium showed that this peak can be attributed to a hydride. Spectrum c was measured after subsequent admission of ammonia to the sample. The ammonia peak has increased back to its original height, the ammonium peak has also increased, and the hydride peak has disappeared from the spectrum.
In order to interpret the infrared data of Figure 3, it is necessary to obtain information on the infrared data of NO adsorbed on a Pt amine complex and its reactivity towards oxygen and water. Therefore, in Figure 4 the result of an experiment is shown in which a $[\text{Pt(NH}_3\text{)}_4]\text{ZSM-5}$ sample was dried (spectrum a) and thereafter exposed to nitrogen monoxide (spectrum b). As can be seen the ammonia peak almost disappears and new peaks have developed at 1910 and 2160 cm$^{-1}$. The peak at 1910 cm$^{-1}$ is attributed to coordinated nitrogen monoxide and the small peak at 2160 cm$^{-1}$ to an impurity in the nitrogen monoxide gas cylinder (probably CO). When the sample was subsequently exposed to oxygen, no difference was found in the spectrum. However, when the sample was subsequently exposed to water spectrum c was measured. The nitrogen monoxide peak almost completely disappeared and the hydride peak developed. Spectrum d was obtained when the sample was subsequently exposed to ammonia. The nitrogen monoxide and hydride peak disappeared, and the ammonium and ammonia peak developed. However it is obvious that the ammonia peak in this case is smaller than in the starting material. This is agreement with the observation that the sample became black after any experiment in which the sample was exposed to nitrogen monoxide and subsequently to ammonia. Apparently part of the platinum ions is reduced to platinum metal during these experiments.
Discussion

From the results of the experiments two periods in the reaction can be seen: before and after the breakthrough of ammonia gas. Since the experiment was performed with and without water four different reaction states can be distinguished as shown in Table 1.

Table 1: Products in various reaction states.

<table>
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<th>Before breakthrough of NH₃</th>
<th>After breakthrough of NH₃</th>
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<tbody>
<tr>
<td>Without H₂O</td>
<td>N₂O, no N₂</td>
<td>some N₂, no N₂O</td>
</tr>
<tr>
<td>With H₂O</td>
<td>N₂O, some N₂</td>
<td>N₂, no N₂O</td>
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</table>

The reaction of ammonia with oxygen over [Pt(NH₃)₄]²⁺ in zeolite HZSM-5 is sensitive to the ammonia concentration at the catalyst. Since ammonia is adsorbed by the acid sites of the zeolite, at the start of the reaction the ammonia concentration is low and the acid sites are available; but after some time the zeolite acid sites are fully covered with ammonia and the ammonia concentration at the [Pt(NH₃)₄]²⁺ site will be the same as in the gas phase. In Table 1 it can be clearly seen that before the breakthrough of ammonia the product of the reaction is mostly nitrous oxide, whereas the favored product is nitrogen after the breakthrough of ammonia. Therefore, the reaction forming nitrous oxide must be either enabled by the acid sites or suppressed by ammonia gas. In contrast, the reaction forming nitrogen must be either enabled by ammonium sites or ammonia gas or suppressed by the acid sites. Furthermore it can be seen in Table 1 that the presence of water also influences the reaction selectivity. Addition of water only influences the reaction producing nitrogen: more nitrogen is produced when water is present. Possibly nitrogen can be produced only by a reaction involving water. That there is some production of nitrogen without water in the reaction mixture does not necessarily disagree with this theory. Water should be present in this case as well since it was produced by the oxidation reaction. That the initial production of nitrogen is zero in the experiment without water in the reaction mixture supports this theory: the production of nitrogen can only start after some water is available. Also the small peak observed in the dry case at the moment of ammonia breakthrough agrees with this view: because of the higher ammonia concentration water is released by the zeolite. Once the reaction producing nitrogen is running it could produce the water to sustain itself.

The reaction could possibly proceed through a mechanism similar to that of the oxidation of coordinated ammonia on Ru amine complexes [12, 13] in a basic solution and the reaction of nitrogen monoxide with Ru and Os amine complexes [14, 15, 16]. This would
involve the formation of a complex with a nitrosyl and a hydride ligand. This nitrosyl ligand could be oxidized further by oxygen to form a nitrate ligand. Subsequently, the nitrate ligand can react with an ammonia and the hydride to form ammonium nitrate which decomposes to nitrous oxide and water. Alternatively, the nitrosyl ligand could react with water to form a nitrite ligand. Similar to the nitrate, the nitrite ligand can react with an ammonia and the hydride to form ammonium nitrite which decomposes to nitrogen and water. A reaction mechanism involving the reactions described above would explain the unusual behavior of this catalyst towards water. The explanation of the behavior of the catalyst before and after the breakthrough of ammonia would be that the complex can be activated to form a nitrosyl complex by either the extraction of an ammonia ligand by an acid site or the exchange of an ammonia ligand with water. The nitrosyl complex formed by action of an acid site would eventually yield nitrous oxide. This complex can not be formed anymore after the breakthrough of ammonia since then there are no acid sites available anymore. The nitrosyl complex formed by the action of water would eventually yield nitrogen. This complex can still be formed after breakthrough of ammonia and the rate forming nitrogen will be higher, since the ammonia concentration is raised and more active sites are available for this path since the other reaction path is not reactive anymore. Although this reaction mechanism can explain the results observed in this study there is no direct evidence for the occurrence of the intermediates yet. However, platinum(II) amine complexes with a hydride ligand [17] or nitrosyl, nitrite, or nitrate ligands [18] are known in literature.

In order to examine whether the above mentioned mechanism is valid for this reaction infrared experiments were done. By means of the infrared experiments it was found that when all acid site were exchanged for [Pt(NH₃)₄]⁺ (the 3.5 wt% Pt sample) there was no activity towards oxygen or water. This indicates that the acid sites of the zeolite participate in the reaction. The same conclusion was reached in another study on basis of the stability of [Pt(NH₃)₄]⁺ in NaZSM-5 to in an oxygen containing environment at low temperature [19]. The infrared experiments shown in Figure 4 reveal that the in situ formed Pt-NO complex in zeolite HZSM-5 reacts readily with water to form a hydride. Also it appears that this Pt-NO complex doesn’t react with oxygen. In the experiments shown in Figure 3 it was found that when [Pt(NH₃)₄]HZSM5 was reacted with water or oxygen ammonium and hydride were formed. The formation of ammonium is an indication of the role of the acid sites: apparently ammonia is transferred from the complex to the acid site (Eq. 3).

\[
\text{[Pt(NH₃)₄]⁺ + HZ} \rightarrow \text{[Pt(NH₃)₃]²⁺ + NH₄Z} \quad (3)
\]

This [Pt(NH₃)₄]²⁺ complex will obviously be more reactive than the original [Pt(NH₃)₄]⁺ complex. Therefore it can be concluded that the acid sites activate the [Pt(NH₃)₄]²⁺ complex.
In Figure 3 it appeared that the activated complex reacts with oxygen or water to form a hydride complex. Since, besides the hydride peak, no signal for nitrosyl, nitrite or nitrate can be seen it is not clear whether the reaction proceeded to the products or that a different reaction path is active. Therefore, a definite answer to the question whether the proposed reaction mechanism is valid cannot be given on the basis of these infrared experiments.

Part of the nitrogen and nitrous oxide that is observed in the reaction experiments will be produced from the decomposition of the [Pt(NH₃)₄]²⁺ complex. It is not possible from the experiments described in this study to discriminate between the products of the decomposition of [Pt(NH₃)₄]²⁺ and the reaction of ammonia with oxygen. During 2 hours on stream a total turnover of 4.5 mole of ammonia per mole of [Pt(NH₃)₄]²⁺ (experiment with water) and 1.5 mole of ammonia per mole of [Pt(NH₃)₄]²⁺ (experiment without water) was measured. It is known that only one of the four amine ligands of the [Pt(NH₃)₄]²⁺ complex is decomposed at 473 K when water is present and none when water is absent [10]. Therefore, the catalytic turnover during the experiment are calculated to be 3.5 mole of ammonia per mole of [Pt(NH₃)₄]²⁺ (experiment with water) and 1.5 mole of ammonia per mole of [Pt(NH₃)₄]²⁺ (experiment without water). The slow increase in production of nitrogen in time (0.1 - 2.0 hours on stream) that can be observed in Figure 2 indicates that the formation of the active species is being completed during this time. However, only experiments with labeled molecules can provide information about the part of the products that can be attributed to the catalytic reaction at a certain time on stream.

In order to compare the activity of the [Pt(NH₃)₄]²⁺ in HZSM-5 catalyst with the metallic catalyst the activity of a reduced Pt/HZSM-5 catalyst has to be known. Since this platinum catalysts are known to show light-off behavior around 473 K [19], the activity can not be determined directly. Therefore the comparison has to be made with an activity that is determined at somewhat deviating conditions (ammonia concentration 2.0 vol%, oxygen concentration 1.5 vol%, no water, 50 cm³/min (STP) flow) is known to be 0.91 mole of ammonia converted per mole of surface Pt per hour at 443 K [8]. Using the activation energy of 72 kJ/mole which was determined for this catalyst, the activity at 473 K without light-off is expected to be approximately 3.1 mole of ammonia converted per mole of surface Pt per hour. Since the activity of metallic catalysts is known to decrease under the influence of water [8, 9] it appears that the activity of the [Pt(NH₃)₄]²⁺ in HZSM-5 catalyst is similar (2.2 mole of ammonia converted per mole of [Pt(NH₃)₄]²⁺ per hour) to that of the metallic catalyst. For practical purposes, however, it must be noted that a strong particle size effect gives rise to an enhanced activity of catalyst that contain larger metal particles [8, 19].
Conclusions

In this study it was found that [Pt(NH₃)₄]HZSM-5 is an active catalyst for the oxidation of ammonia at low temperature (473 K) that, in contrast with other catalysts, becomes more active in the presence of water. Furthermore, the selectivity to nitrogen was found to increase when water is present. At the start of the reaction nitrous oxide was found to be the main product. However, nitrogen became the main product after the breakthrough of ammonia; the nitrous oxide production decreased. It appears that water enables the reaction path to nitrogen, since the reaction rate for this path was much higher if water was present in the reaction mixture. Probably water takes part in the reaction that leads to the production of nitrogen. Unfortunately the reaction mechanism could not be elucidated with infrared experiments that simulated the ammonia oxidation reaction. The activity of this catalyst is approximately the same as the activity of small metallic platinum particles in zeolite HZSM-5.

References

8. Chapter 4 of this thesis
Platinum and Iridium Catalysts for the Low Temperature Oxidation of Ammonia *

Abstract

The low temperature gas phase oxidation of ammonia over supported and unsupported platinum and iridium catalysts was studied. Catalysts with different sizes of metal particles were compared in activity and kinetic measurements. It was found for both metals that the activity depended on the particle size of the metal: larger particles were found to be more active than smaller metal particles. The initial activity of platinum and iridium was similar. However, a low steady state activity was found for the platinum catalysts; this is due to inhibition of the surface with reaction intermediates. In contrast a high steady state activity was found for the iridium catalysts; these catalysts first become more active and than become less active, also resulting in a catalyst that is inhibited by reaction intermediates. The activity of the iridium catalysts was found to be suppressed by oxygen. In the steady state, iridium catalysts were about 10 times more active for the ammonia oxidation reaction than platinum catalysts. Water decreased the activity of the catalysts for both metals: platinum catalysts were found to be more sensitive to water than iridium catalysts.

Chapter 4

Introduction

Low temperature selective oxidation of ammonia with oxygen to nitrogen and water could be a solution to several ammonia spills [1]. Metallic catalysts are often used for this reaction because they combine a high activity and selectivity to nitrogen at a low reaction temperature (< 473 K) [1, 2, 3, 4, 5]. An extensive study by Il'chenko [5, 6] on various metal wires showed that the activity for gas phase ammonia oxidation at 573 K decreases in the following order: Pt > Pd > Cu > Ag > Ni > Au > Fe > W > Ti. The selectivity to nitrogen was found to follow the opposite order. At temperatures below 473 K the activity of palladium was reported to be higher than that of platinum. Takao et al. [7] studied various metals supported on TiO₂ as a catalyst for gas phase ammonia oxidation; the following order in activity was found: Pt > Ir > Au. However, Ir/TiO₂ was found to be more selective to nitrogen than Pt/TiO₂. Recently, in a study by Vaabel et al. [8] a Pd/C catalyst was found to be active for gas phase ammonia oxidation at temperatures below 403 K. Unfortunately nitrogen oxides were not determined in this study, so it was not possible to calculate the selectivity to nitrogen. In a recent patent of Topsøe [9], sulfated supported Pt/Cu catalysts showed a high selectivity to nitrogen in gas phase ammonia oxidation at temperatures around 573 K. Armor et al. [4] recently compared palladium, rhodium, and platinum catalysts supported on zeolite ZSM-5 and alumina. An activity sequence of Pt > Pd > Rh was found for the gas phase oxidation of ammonia at temperatures of 473 - 623 K; the selectivity to nitrogen was highest for the Rh and Pd catalysts. It was found that reduced metal catalysts are more active than calcined catalysts. It was also shown that the noble metal catalysts were less sensitive to water in the reaction mixture than V₂O₅/TiO₂ catalysts. The metal that is studied in most detail is platinum, since this metal (alloyed with Rh) is also used in the high temperature ammonia oxidation to nitrogen monoxide [10, 11]. Previous studies on gas phase ammonia oxidation on platinum by Ostermaier et al. [12, 13, 14] showed that Pt/γ-alumina catalysts are very active at a low temperature, but the catalysts lose most of their activity rapidly after the start of the reaction. This effect was attributed to oxidation of the platinum surface [14]. Also Ostermaier et al. found that there is a strong particle size effect for this catalyst: large (15.5 nm) platinum particles are more active than small (2 nm) platinum particles [13, 14]. Furthermore, the Pt/γ-alumina catalyst showed light-off behavior at a temperature of approximately 473 K [12, 13, 14].

In this study platinum and iridium catalysts with various metal particle sizes were prepared and tested in the low temperature gas phase ammonia oxidation. To examine the processes that form the working catalyst, the activity of the catalyst was measured as a function of Time On Stream (TOS). These experiments were repeated with various reactant
concentrations and with water in the reactant mixture to examine their influence on the activity and selectivity of the catalyst. To examine the particle size effect, catalysts with different particle sizes were tested under steady state reaction conditions. Reaction orders and activation energies were determined from the results of these experiments.

**Methods**

*Sample preparation*

All supported metal catalysts contained 0.5 wt% of the metal on the support. The Pt/HZSM-5 sample was prepared by ion-exchange of \([Pt(NH_3)_4(OH)]_2\) in HZSM-5 zeolite. Thereafter the sample was calcined at a temperature of 723 K and reduced at a temperature of 673 K yielding small platinum particles in the zeolite pores, as described earlier [15]. The γ-alumina supported platinum and iridium catalysts were prepared by incipient wetness impregnation of dried γ-alumina with a solution of \(H_2PtCl_6\) or \(IrCl_3\cdot3H_2O\), respectively. The impregnated samples were dried in air at a temperature of 373 K for at least 12 hours. Batches of the γ-alumina supported catalysts were sintered by treatment in flowing air at a temperature of 923 K for 16 hours. The platinum and iridium sponge samples were acquired from Johnson Matthey. The sponge samples were of >99.9 % purity. The size of the sponges was between 250 and 350 μm for the platinum sample and < 841 μm for the iridium sample. In the reaction setup particles were used with a particle size between 125 and 425 μm; if necessary, samples of the catalyst were pelletized, crushed, and sieved to acquire the appropriate particle size. All catalysts were reduced in the reaction setup by heating the sample in a hydrogen flow from 298 K up to a temperature of 573 K.

*Electron microscopy measurements*

High resolution transmission electron microscopy (HREM) measurements were done on a Philips CM30-T electron microscope. HREM was used to study the supported metal catalysts. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) measurements were done on a Jeol 840 electron microscope. SEM and EDS were used to study the metal sponge catalysts.

*Krypton BET measurements*

Krypton BET measurements were done on a Micromeritics ASAP 2000 set-up at the Laboratory of Chemical Technology of Eindhoven University of Technology, using a standard procedure without any pretreatment of the sample. The BET measurements were done on the metal sponge samples to determine the surface area of the metal. Krypton was
used as an adsorbent because of the low surface area of the metal sponge samples. The average metal particle size was determined from the surface area, assuming cubic closest packed symmetry for both metals.

**Hydrogen chemisorption measurements**

Hydrogen chemisorption was done on the supported metal samples, to determine the metal surface area. Hydrogen chemisorption was measured at 298 K using a conventional glass apparatus, following the procedure of Kip et al. [16]. Before measuring hydrogen chemisorption the catalyst was reduced in a flow of hydrogen at 573 K for 1 h, and subsequently evacuated (10⁻² Pa) for 1 h at the same temperature to remove any chemisorbed hydrogen. Thereafter a measured amount of hydrogen (P = 100 kPa at room temperature) was admitted to the sample. Hydrogen chemisorption equilibrium was reached quickly (< 5 min), because of the elevated temperature. After cooling to 298 K, the hydrogen desorption isotherm was measured by lowering the pressure stepwise and determining the amount of hydrogen that was desorbed from the sample for each step. The H/M ratio was determined by extrapolation of the linear high pressure part (20 kPa < P < 80 kPa) of the isotherm to zero pressure. The average metal particle size was determined from the H/M ratio assuming a half sphere shape for the particles.

**Measurement of catalytic activity**

Catalytic tests were done in a fixed bed reaction setup equipped with a gas chromatograph (ATI UNICAM 610, spec 2790) and a quadrupole mass spectrometer (Balzers QMG-420) for on-line analysis of the reactants and products. The gas chromatograph was could analyze ammonia, oxygen, water, nitrogen, and nitrous oxide quantitatively. The quadrupole mass spectrometer was used to check the results of the gas chromatograph and for the detection of nitrogen monoxide and nitrogen dioxide. The reactor was assumed to be differential at low conversion, using calculated estimations of diffusion and heat transfer. To keep the conversion below 10 %, the amount of catalyst in the reactor was different for the various catalysts. For some experiments it was necessary to dilute the catalyst with inert material in order to satisfy plug flow requirements. In this case the catalyst was diluted with γ-alumina particles of the same particle size as the catalyst. It was determined experimentally that γ-alumina is not active for the ammonia oxidation at the conditions used in this study. Depending on the catalyst load, a quartz tube with an internal diameter of 4 or 8 mm was used as the reactor. Typical amounts of catalyst were 1.4 g for the 8 mm reactor (GHSV ≈ 1000) and 200 mg for the 4 mm reactor (GHSV ≈ 7000). A standard reaction mixture was used in most cases, consisting of 2.0 vol% of ammonia and 1.5 vol% of oxygen in helium with a total flow of 48.8 cm³/min (STP). In experiments in which water could be added, the standard
Pt and Ir Catalysts in Low Temperature Oxidation of NH₃

The mixture contained 1.7 vol% ammonia, 1.2 vol% oxygen and (if added) 0.9 vol% water in helium with a total flow of 58.8 cm³/min (STP). Reaction rates (expressed per ammonia converted per hour, \( R_{\text{NH}_3} \)) were calculated from the concentration of nitrogen (\( C_{\text{N}_2} \)) and nitrous oxide (\( C_{\text{N}_2\text{O}} \)) and the total flow (\( F \)), following Eq. 1. By using production rates instead of conversion for this calculation it was assured that the calculated rate represents reaction and not adsorption of the reactant. It was checked that under steady state conditions the mass balance was complete. The Turn Over Frequency (TOF) was calculated from the reaction rate (\( R_{\text{NH}_3} \)) divided by the metal surface of the catalyst (\( A_M \)) (Eq. 2). The surface area was determined by hydrogen chemisorption or Krypton BET.

\[
\begin{align*}
R_{\text{NH}_3} &= F(C_{\text{N}_2} + C_{\text{N}_2\text{O}}) \quad \text{(mole NH}_3\text{ per hour)} \\
\text{TOF} &= \frac{R_{\text{NH}_3}}{A_M} \quad \text{(mole NH}_3\text{ per mole metal surface per hour)}
\end{align*}
\]

In the Time On Stream (TOS) experiments a flow with the reactants was switched to a reduced catalyst at time zero. The concentrations of the reactants and products were measured using the mass spectrometer for at least 2 hours on stream. Steady state experiments were done using the gas chromatograph after at least 12 hours on stream. Reaction orders were determined by lowering the concentration of one of the reactants at a fixed concentration of the other reactant. For the platinum catalysts reaction orders were determined at a temperature of 433 K. For the iridium catalysts reaction orders were determined at a temperature of 403 K and also at 473 K. Activation energies were determined by variation of the temperature. For the platinum catalysts in the range 413 - 443 K. For the iridium catalysts in the range 473 - 443 K and 413 - 383 K. Used catalysts were regenerated by reduction in a hydrogen flow at 573 K. The regenerated catalyst showed exactly the same behavior as the fresh catalysts.
Chapter 4

Results

Particle size determination

The results of the various particle size determination techniques are summarized in Table 1. HREM micrographs for samples of Pt/ZSM-5, unsintered Pt/γ-alumina, sintered Pt/γ-alumina, unsintered Ir/γ-alumina, and sintered Ir/γ-alumina, are given in Figures 1 - 5. For the supported metal catalysts, the results of the hydrogen chemisorption measurement agree with the results of the HREM measurements. However, HREM showed that an additional small number of larger particles was present in all samples. In the case of the sintered Ir/γ-alumina sample (Figure 5), most of the metal particles are located in the close vicinity of each other, as opposed to the other supported samples. SEM micrographs for samples of platinum and iridium sponge are shown in Figure 6. For the unsupported catalysts, the particle size determined with krypton BET agrees with the particle size that was determined with SEM. In the SEM micrographs it can be seen that the sponges consist of small non-porous particles that are clustered together in much larger sponge-like structures. From EDS it was found that no large impurities are present in the sponges. In all further calculations the hydrogen chemisorption H/M ratio and the krypton BET surface area are used representing the metal surface area.

Table 1: Metal particle size determination.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>H2 chemisorption</th>
<th>HREM</th>
<th>BET</th>
<th>SEM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H/M size (nm)</td>
<td>size (nm)</td>
<td>area (m²/g)</td>
<td>size (µm)</td>
</tr>
<tr>
<td>Pt/HZSM-5</td>
<td>2.00 &lt; 1.0</td>
<td>&lt;1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt/γ-alumina</td>
<td>0.38 3.6</td>
<td>2.4 - 3.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt/γ-alumina sintered</td>
<td>0.19 7.2</td>
<td>4.0 - 7.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt sponge</td>
<td></td>
<td></td>
<td>0.099 3.0</td>
<td>1.0 - 5.0</td>
</tr>
<tr>
<td>Ir/γ-alumina</td>
<td>1.60 &lt; 1.0</td>
<td>&lt;1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ir/γ-alumina sintered</td>
<td>0.40 3.4</td>
<td>2.5 - 7.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ir sponge</td>
<td>0.567 0.50</td>
<td>0.2 - 3.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a: size of the small non-porous particles.
Figure 1: HREM micrograph of Pt/HZSM-5.

Figure 2: HREM micrograph of unsintered Pt/γ-alumina.
Figure 3: HREM micrograph of sintered Pt/γ-alumina.

Figure 4: HREM micrograph of unsintered Ir/γ-alumina.
Figure 5: HREM micrograph of sintered Ir/γ-alumina.

Figure 6: SEM images of iridium sponge (left) and platinum sponge (right).
Chapter 4

Platinum Catalysts

The results of the Time On Stream (TOS) experiments on the 3.6 nm Pt/alumina catalyst are given in Figure 7 and Figure 8. Plotted is the activity of the catalyst as TOF (mole NH₃ per mole surface platinum sites per hour). The TOF was derived from the production rates of nitrogen and nitrous oxide using Eqs. 1 and 2. The selectivity to nitrogen was constant during the TOS experiment at 90%, the remaining 10% being nitrous oxide. Figure 7 shows the activity of the catalyst as a function of TOS for different oxygen concentrations. Figure 8 shows the activity of the catalyst as a function of TOS for different ammonia concentration levels.

From the results shown in Figure 7 it can be seen that the activity of the catalyst decreases slowly after the start of the experiment and after approximately 0.13 hours the activity of the catalyst decreases rapidly to a relatively stable level. During the slow decrease of activity ammonia could not be detected. However at the time of the rapid decrease in activity ammonia could be measured for the first time, this is the so-called breakthrough of ammonia. Furthermore it can be seen that the oxygen concentration does not appear to influence the TOS behavior of this catalyst. The same result is found in the steady state results; the measured TOF (~ 5.0 per hour, after 12 hours on stream, not shown) is similar for the different oxygen concentrations.

From the results shown in Figure 8 it can be seen that the ammonia concentration strongly influences the activity of the catalyst as a function of TOS. If the ammonia concentration is lowered, the initial activity of the catalyst is lower and the rapid decrease in activity takes place later. Also in this case it was found that the breakthrough of ammonia takes place at the time of the rapid decrease in activity. However, after 0.35 hours on stream the activity of the catalyst is similar for all ammonia concentrations. The same result is found in the steady state results; the measured TOF (~ 5.0 per hour, after 12 hours on stream, not shown) is similar for the different ammonia concentrations.
Figure 7: Activity as a function of Time on Stream (TOS) for 3.6 nm Pt/alumina catalyst at 413 K, variation of oxygen concentration: 
- ◆ = 1.5 vol%; □ = 1.1 vol%; ▲ = 0.8 vol%; ammonia concentration = 2.0 vol%; GHSV = 1000.

Figure 8: Activity as a function of Time on Stream (TOS) for 3.6 nm Pt/alumina catalyst at 413 K, variation of ammonia concentration:
- ◆ = 2.0 vol%; □ = 1.6 vol%; ▲ = 1.2 vol%; ● = 0.8 vol%; oxygen concentration = 1.5 vol%; GHSV = 1000.
Figure 9: Activity as a function of Time on Stream (TOS) for 3.6 nm Pt/γ-alumina catalyst at 413 K, variation of water concentration: • = 0 vol%; ○ = 0.9 vol%; ammonia concentration = 1.7 vol%; oxygen concentration = 1.2 vol%; GHSV = 1200.

Figure 9 shows the activity of the 3.6 nm Pt/γ-alumina catalyst as a function of TOS for a reaction flow with and without added water. The slow decrease in activity after the start of the experiment apparently is not influenced by the addition of water to the reactant stream. In contrast, the rapid decrease in activity appears to occur slightly earlier if water is added to the reaction mixture. Like in the previous experiments, the rapid decrease in activity occurs at the time of the breakthrough of ammonia. The resultant activity (TOF) of the catalyst after one hour on stream is 5.3 per hour for the case when there is no water and only 2.5 per hour in the case when there is water in the reaction mixture. Therefore the addition of water appears to decrease the steady state activity of the 3.6 nm Pt/γ-alumina catalyst.
The results of the steady state activity measurements for the platinum catalysts are given in Table 2. It is clear that with increasing particle size the reaction rate increases strongly. The platinum sponge catalyst shows an activity per surface site that is at least two orders of magnitude higher than the catalyst with the smallest platinum particles. The reaction order in oxygen appears to show a decreasing trend as a function of particle size. However this trend falls within the error margins, therefore it is not significant. The average reaction order in oxygen is 0.4. The reaction order in ammonia does not show a trend. Furthermore, the values are not significantly different. The average reaction order in ammonia is 0.04. The activation energy increases significantly as a function of particle size. The selectivity to nitrogen was 90 % for all supported platinum catalysts and 80 % for the platinum sponge catalyst, which was diluted with γ-alumina. The remaining product was found to be nitrous oxide; no nitrogen monoxide or nitrogen dioxide was detected.

After steady state measurements, a used catalyst could be regenerated by reduction in a hydrogen flow at 573 K. The regenerated catalyst showed exactly the same TOS and steady state reaction behavior as a freshly prepared catalyst. Even after repeated use and regeneration no difference was found in the performance of the catalyst.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Particle size (nm)</th>
<th>Reaction order in O₂</th>
<th>Reaction order in NH₃</th>
<th>Eₐcta (kJ/mole)</th>
<th>TOF (h⁻¹) at 413 K</th>
<th>TOF (h⁻¹) at 443 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/HZSM-5</td>
<td>&lt; 1.0</td>
<td>0.6 ± 0.3</td>
<td>0.1 ± 0.2</td>
<td>72 ± 11</td>
<td>0.22 ± 0.03</td>
<td>0.91 ± 0.03</td>
</tr>
<tr>
<td>Pt/γ-alumina</td>
<td>3.6</td>
<td>0.4 ± 0.1</td>
<td>0.07 ± 0.03</td>
<td>80 ± 8</td>
<td>2.1 ± 0.1</td>
<td>7.9 ± 0.1</td>
</tr>
<tr>
<td>Pt/γ-alumina</td>
<td>7.2</td>
<td>0.3 ± 0.2</td>
<td>0.1 ± 0.1</td>
<td>92 ± 6</td>
<td>3.5 ± 0.3</td>
<td>13.7 ± 0.3</td>
</tr>
<tr>
<td>Pt sponge</td>
<td>3.0·10⁻¹</td>
<td>0.3 ± 0.1</td>
<td>-0.1 ± 0.2</td>
<td>108 ± 3</td>
<td>72 ± 7</td>
<td>605 ± 7</td>
</tr>
</tbody>
</table>

Error margins are 95 % confidence intervals.
Iridium Catalysts

The results of the Time On Stream (TOS) experiments for the 3.4 nm Ir/alumina catalyst are given in Figure 10 and Figure 11. The TOF was derived from the production rates of nitrogen and nitrous oxide using Eqs. 1 and 2. The selectivity to nitrogen was constant during the TOS experiment at 90%, the remaining 10% being nitrous oxide. Figure 10 shows the activity of the catalyst as a function of TOS for different oxygen concentrations. Figure 11 shows the activity of the catalyst as a function of TOS for different ammonia concentration levels.

From the results shown in Figure 10 it can be seen that the 3.4 nm Ir/γ-alumina catalyst becomes more active during the first 0.2 hours on stream, but after that moment the activity decreases. During the increase of activity no ammonia could be detected. Breakthrough of ammonia was found to occur at the time of maximum activity of the catalyst. Lowering the oxygen concentration apparently increases the activity of the catalyst. The maximum activity peak is higher when at a lower oxygen concentration is applied. Furthermore it also occurs at a later TOS. The activity continues to be larger for a lower oxygen concentration after 0.8 hours on stream. Also at steady state the TOF (after 12 hours on stream, not shown) is larger for a lower oxygen concentration; ranging from 4.8 per hour to 6.3 per hour.

From the results in Figure 11 it can be seen that the ammonia concentration also influences the TOS behavior of this catalyst. A lower ammonia concentration causes a slower increase in activity and a lower peak activity. Therefore the maximum activity is reached later when less ammonia is present. Breakthrough of ammonia was found to occur at the time of maximum activity of the catalyst. After 0.8 hours on stream the activity is similar for the different ammonia concentrations. Also at steady state the TOF (~ 4.5 per hour, after 12 hours on stream, not shown) is similar for the different ammonia concentrations.
Figure 10: Activity as a function of Time on Stream (TOS) for 3.4 nm Ir/alumina catalyst at 393 K, variation of oxygen concentration: • = 1.5 vol%; ■ = 1.0 vol%; ▲ = 0.5 vol%; ammonia concentration = 2.0 vol%; GHSV = 1000.

Figure 11: Activity as a function of Time on Stream (TOS) for 3.4 nm Ir/alumina catalyst at 393 K, variation of ammonia concentration: • = 2.0 vol%; ■ = 1.6 vol%; ▲ = 1.2 vol%; ● = 0.8 vol%; oxygen concentration = 1.5 vol%; GHSV = 1000.
Figure 12: Activity as a function of Time on Stream (TOS) for 3.4 nm Ir/γ-alumina catalyst at 393 K, variation of water concentration: ◆ = 0 vol%; ● = 0.9 vol%; ammonia concentration = 1.7 vol%; oxygen concentration = 1.2 vol%; GHSV = 1200.

Figure 12 shows the activity of the 3.4 nm Ir/γ-alumina catalyst as a function of TOS for a reaction flow with and without added water. The increase of activity at the start of the reaction is slightly enhanced if water is added in the reaction mixture. In that case the maximum activity peak is higher and occurs at a earlier TOS. As in the previous experiments the breakthrough of ammonia occurred at the time of maximum activity. The decrease in activity is even stronger than the increase of activity was when water is added in the reaction mixture. Therefore the resultant TOF is lower when water is added to the reaction mixture. After two hours on stream the TOF is 7.7 per hour for the case when there is no water and 6.1 per hour in the case when there is water in the reaction mixture.
Table 3: Activity measurement results for the iridium catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Particle size (nm)</th>
<th>Reaction order in O₂</th>
<th>Reaction order in NH₃</th>
<th>E_act (kJ/mole)</th>
<th>TOF (h⁻¹) at 413 K</th>
<th>TOF (h⁻¹) at 443 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir/γ-alumina</td>
<td>&lt; 1.0</td>
<td>0.1 ± 0.1 a</td>
<td>0.10 ± 0.05 a</td>
<td>85 ± 12 a</td>
<td>0.7 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>Ir/γ-alumina</td>
<td>3.4</td>
<td>0.2 ± 0.2 a</td>
<td>0.06 ± 0.02 a</td>
<td>128 ± 1 a</td>
<td>(42 ± 20) c</td>
<td>520 ± 50</td>
</tr>
<tr>
<td>Ir/γ-alumina</td>
<td>3.4</td>
<td>0.0 ± 0.1 b</td>
<td>0.4 ± 0.1 b</td>
<td>103 ± 8 b</td>
<td>20.2 ± 0.4</td>
<td>(144 ± 20) c</td>
</tr>
<tr>
<td>Ir sponge</td>
<td>5.0·10²</td>
<td>-0.3 ± 0.1 b</td>
<td>0.24 ± 0.05 b</td>
<td>126 ± 3 b</td>
<td>642 ± 9</td>
<td></td>
</tr>
</tbody>
</table>

*a*: order measured at 473 K, E_act determined at 473 - 443 K  
*b*: order measured at 403 K, E_act determined at 413 - 383 K  
*c*: extrapolated from measurements at respectively 473 - 443 K or 413 - 383 K  

Error margins are 95 % confidence intervals.

The results of the steady state activity measurements for the iridium catalysts are given in Table 3. Because of the large difference in activity for these catalysts, the measurements were done in two different temperature ranges. The high temperature range (reaction order 473 K, activity measurements 473 - 443 K) was used for both the γ-alumina supported catalysts. The low temperature range (reaction order 403 K, activity measurements 433 - 383 K) was used for the sintered Ir/γ-alumina and the Ir sponge catalyst. To compare the activity in the different temperature ranges it was necessary to extrapolate some activity results using the activation energy. The activity of the 3.4 nm Ir/γ-alumina catalyst at high temperature was extrapolated to 413 K. Also the activity of the 3.4 nm Ir/γ-alumina catalyst at low temperature was extrapolated to 443 K It appears that larger particles are much more active for the reaction than smaller particles. At high temperature range (473K), the reaction orders in both oxygen and ammonia remain the same within experimental error. In the low temperature regime, both the order in oxygen and the order in ammonia decrease significantly with increasing particle size. The activation energy increases significantly with particle size. Furthermore the activation energy is smaller for the same catalyst (3.4 nm γ-Ir/alumina) when measured in the low temperature regime than in the high temperature regime. The selectivity to nitrogen was between 90 % and 98 % for the iridium catalysts. The selectivity was higher for samples in which the catalyst was diluted with inert material. The remaining product was found to be nitrous oxide; no nitrogen monoxide or nitrogen dioxide was detected.
Discussion

Platinum catalysts

The TOS experiments carried out on the 3.6 nm Pt/γ-alumina catalyst presented in Figure 7 and Figure 8 show that the activity decreases strongly with TOS; the final activity is about 15 times lower than the initial activity. Furthermore, it was found that the TOS behavior consists of two parts: a slower decrease in activity at the beginning of the reaction and a rapid decrease in activity after some time on stream. Also it was noted that at this time the breakthrough of ammonia was measured. Variation of the oxygen concentration (Figure 7) does not influence the observed TOS behavior. Apparently, oxygen does not play an important role in the process. Variation of the ammonia concentration (Figure 8) does influence the TOS behavior: a lower ammonia concentration causes a lower activity at the start and it takes longer to achieve the rapid decrease in activity part. This indicates that adsorption of ammonia is causing the observed rapid decrease in activity. When there is a lower concentration of ammonia in the reactant flow it takes a longer time to adsorb a certain amount of ammonia. In a reference experiment it was established that the γ-alumina carrier is able to adsorb a large quantity of ammonia. Therefore the following sequence of events emerges. At the start of the TOS experiment most ammonia is adsorbed on the alumina carrier. The part that is adsorbed on the platinum surface reacts with adsorbed oxygen to nitrogen and nitrous oxide which are observed as products. The platinum surface is slowly covered with inhibiting reaction intermediates causing the slow decrease in activity observed at the start of the reaction. After a certain amount of ammonia is adsorbed by the γ-alumina carrier it becomes saturated. At this time the ammonia concentration rises sharply and the platinum surface becomes covered rapidly by the inhibiting reaction intermediates causing the rapid decrease in activity. Since both the ammonia and the oxygen concentration have no influence on the resultant activity the inhibiting species must be a reaction intermediate. Furthermore it was found in TPD experiments that are published elsewhere [17] that the inhibited platinum surface has a high coverage of both NH and OH. Variation of the reactant concentrations at steady state provided the reaction orders presented in Table 2: a relatively high order in oxygen and a relatively low order in ammonia were measured with the platinum catalysts. These reaction orders lead to the conclusion that the surface of the steady state catalyst is highly covered. Surface reactions or desorption of products will be the rate determining step leading to low reaction orders. Addition of water to the reaction mixture makes the rapid decrease in activity happen earlier, as shown in Figure 9 for the 3.6 nm Pt/γ-alumina catalyst. Since it is known that water and ammonia adsorb at similar sites on γ-alumina this agrees with the theory described earlier. When water is added to the reaction mixture the γ-alumina carrier is saturated at an earlier time, since ammonia and water adsorb at the same sites. Therefore the breakthrough of
ammonia occurs at an earlier time, causing the rapid decrease of the platinum catalyst. The resultant activity in the experiment when water was added to the reactant flow is lower than the activity in the case when no water was added to the reactant flow. Therefore the platinum surface must be different at steady state reaction when water is added to the flow. Most likely the surface coverage with OH is larger in this case because of a shift in reaction equilibrium, since water is also a product of the reaction.

The effect of platinum particle size becomes clear from the results presented in Table 2: larger particles are more active than smaller particles. This is the same results as that was found before in the literature for platinum catalysts [13, 14]. The value of the activation energy for the platinum sponge catalyst (108 kJ/mole) is comparable to the values (113 kJ/mole) determined in literature for platinum wire [7, 6] and platinum particles of 15.5 nm on γ-alumina [13]. The variation in reaction order and activation energy indicates changes in the relative values of elementary reaction parameters. Larger particles appear to have a lower order in oxygen, indicating a higher surface coverage of oxygen containing intermediates. Unfortunately the experimental error is too large to prove this trend in the oxygen reaction order. The reaction order in ammonia apparently is equal for different particle sizes. However, large particles show a significantly higher activation energy than small particles. In general three possibilities arise from the reaction orders. Firstly, in the case of a relatively high reaction order in oxygen the surface coverage with oxygen containing intermediates will be relatively low, therefore it can be expected that dissociative adsorption of oxygen or a reaction step between adsorbed ammonia and atomic O [18] is the rate determining step. Secondly, in the case of a relatively low order in ammonia the surface coverage with nitrogen containing intermediates will be high; therefore, it can be expected that desorption of nitrogen is the rate determining step. Thirdly, in the case of intermediate reaction orders both nitrogen and oxygen containing intermediates will present on the surface reaction: some intermediate surface reaction can be the rate determining step. The activation energy for the dissociation of oxygen on a platinum (111) surface is known to be 29 kJ/mole [19]. Since the activation energies measured in this study are much higher, it is unlikely that dissociation of oxygen is the rate determining step. The activation energy for the desorption of nitrogen from platinum (111) surface is known to be 105 kJ/mole [20] at low coverage. On Cu the activation energy of oxygen promoted ammonia dissociation is 132 kJ/mole [18]. From the data presented here it is not possible to decide whether nitrogen desorption or the activation of ammonia (or NH₃) by oxygen is the rate determining step. Since the reaction rate is higher for larger platinum particles, a higher oxygen coverage possibly enhances the rate determining step. This is in contrast with the findings of earlier studies [13, 14] in which a higher surface coverage with oxygen was found for smaller particles with ex-situ hydrogen titration; this result gave rise to the conclusion that of poisoning of the catalyst surface with oxygen causes the particle size
effect. If nitrogen desorption is the rate determining step, this higher reaction rate could be explained by an enhanced desorption of nitrogen at a higher oxygen coverage. This was found to be the case for the platinum (111) surface [21]. If activation of ammonia (or NH₃) by oxygen is the rate determining step, however, an increased surface coverage with oxygen will also enhance the reaction rate.

Iridium catalysts

The TOS experiments carried out on the 3.4 nm Ir/γ-alumina catalyst presented in Figure 10 and Figure 11 show that the catalyst first becomes more active and then loses activity. The final activity is approximately equal to the initial activity, the maximum activity is 3 to 10 times larger than the initial activity. Variation of the oxygen concentration (Figure 10) influences the TOS behavior: a lower oxygen concentration causes a higher maximum at a slightly later time on stream. Different oxygen concentrations create different catalysts: apparently the catalyst surface becomes partly inhibited by oxygen during the initiation of the reaction. Furthermore, it was found in TPD experiments that are published elsewhere [17] that the iridium surface has a high coverage with both OH and NH after reaction. Variation of the ammonia concentration (Figure 11) also influences the TOS behavior: a lower ammonia concentration causes a lower rise in activity and the maximum activity is lower and is reached after a longer time on stream. Similar as discussed for platinum also in this case the adsorption of ammonia on γ-alumina can explain these results. At the start of the TOS experiment most ammonia adsorbed on the γ-alumina carrier. The part of the ammonia that adsorbed on the iridium surface reacts with oxygen to form nitrogen and nitrous oxide. In contrast to the platinum case the activity increases with time when an iridium catalyst is applied. Apparently the activity of the iridium catalyst is increased when the empty surface becomes covered with reaction intermediate species. However, when the γ-alumina carrier becomes saturated with ammonia the iridium surface is exposed to a higher concentration of ammonia. As a result the surface composition changes and the activity decreases. This explanation agrees with the data after 12 hours on stream: the activity is similar for all different ammonia concentrations. Different ammonia concentrations create a similar catalyst. Variation of the reactant concentrations at steady state provided the reaction orders presented in Table 3: a relatively low order in oxygen and a relatively low order in ammonia were measured with the 3.4 nm Ir/γ-alumina catalyst at 403 K. These reaction orders support the conclusions of the TOS experiments: the surface of the steady state catalyst is covered with reaction intermediates. Addition of water to the reaction mixture does not appear to influence the TOS behavior much, as shown in Figure 12 for the 3.4 nm Ir/γ-alumina catalyst. The maximum activity is reached earlier in the case when there is water in the mixture. As discussed for platinum, this agrees with the idea of saturation of the γ-alumina carrier with
ammonia and water. When water is added to the reactant flow the \( \gamma \)-alumina surface is saturated at an earlier time and the breakthrough of ammonia occurs at an earlier time leading to the decrease in activity. At steady state the addition of water leads to a less active catalyst. This is probably caused by a shift in the reaction equilibrium because water is a product of the reaction.

For the 3.4 nm Ir/\( \gamma \)-alumina catalyst it is also shown that the temperature at which the reaction is started is important for the resultant steady state catalyst. In Table 3 it can be seen that after a higher temperature start the activity is two to four times larger than after a low temperature start. From the reaction orders and activation energy it can be seen that the surface composition of the catalyst must be different after a start at a different temperature. Since the temperature influences the surface composition of the steady state catalyst it is not possible to directly compare the result for all the different iridium particle sizes. It is of course possible to compare the results for the \(< 1 \) nm Ir/\( \gamma \)-alumina catalyst with the results of the 3.4 nm Ir/\( \gamma \)-alumina catalyst after the high temperature start. Furthermore it is possible to compare the results of the Ir sponge catalyst with the 3.4 Ir/\( \gamma \)-alumina catalyst after the low temperature start. It is obvious that the larger iridium particles are more active than the smaller particles, if the results for the \(< 1 \) nm Ir/\( \gamma \)-alumina catalyst are compared with the results of the 3.4 nm Ir/\( \gamma \)-alumina catalyst after the high temperature start. The small iridium particles show: similar reaction orders in oxygen and ammonia; and a significantly lower activation energy. Possibly poisoning of the surface by oxygen containing intermediates could be the cause for the very low activity of the \(< 1 \) nm Ir/\( \gamma \)-alumina catalyst. Small iridium particles are oxidized very easily, yielding an almost complete loss of activity. Again, it is obvious that the larger iridium particles are more active than the smaller particles, if the results for the Ir sponge catalyst are compared with the results of the 3.4 nm Ir/\( \gamma \)-alumina catalyst after the low temperature start. The iridium sponge catalyst shows: a lower reaction order in oxygen and ammonia; and a higher activation energy. Apparently, the larger iridium particles can obtain a higher total surface coverage leading to a larger activity.

Comparison of Platinum and Iridium catalysts
If we compare the activity of platinum and iridium catalysts in the steady state, it is obvious that for the conditions studied the iridium catalysts are about 10 times more active in the low temperature oxidation of ammonia than platinum catalysts. The only exception is the case of very small particles: where the activities are approximately equal for both metals. The difference between the catalysts is caused by processes during the start of the reaction. At the start of the reaction the activities of both metals are comparable. The activity of the platinum catalyst decreases to an activity about 15 times lower than the initial activity. Whereas the activity of the iridium catalyst increases to about 10 times the initial activity and than
Chapter 4

decreases to about the initial activity. Both metals show a strong particle size effect: large metal particles are more active than small metal particles. Finally, for both metals water decreased the activity of the catalyst, but the catalyst remained active. Platinum was found to be more sensitive to water than iridium. The result that iridium is more active than platinum disagrees with the results of Takao [7]. However, it was also found that the metal particle size influences the activity largely. Since the particle size was not determined in Takao's study [7] it can be argued that a larger metal particle size in this case caused the larger activity of the platinum catalyst.

For application purposes the highest activity per gram of metal is an interesting parameter. It appears that for the catalysts used in this study the optimum metal particle size in this respect is around 3.5 nm for both metals. It was found that in our reaction conditions iridium catalysts are preferred over the much applied platinum catalysts, especially if the oxygen concentration is low. Iridium catalysts are more active and more resistant to water than the platinum analogues. However, if higher concentrations of oxygen will be applied it is possible that the activity of the iridium catalyst is diminished. Another important parameter is the selectivity to nitrogen. The iridium catalysts show a higher selectivity to nitrogen than the platinum catalysts in the case when the sample was diluted with γ-alumina.

Conclusions

This study of the low temperature oxidation of ammonia over platinum and iridium metal catalysts showed that the iridium catalysts have a 10 times higher activity than the platinum catalysts in the conditions used. The initial activity is similar for platinum and iridium. However, a low steady state activity is found for the platinum catalysts; this is due to inhibition of the surface with reaction intermediates. In contrast a high steady state activity is found for the iridium catalysts; these catalysts first become more activate and than become less activate, resulting in catalyst that is also inhibited by reaction intermediates. Furthermore, it was shown that for both metals the activity is strongly dependent on the particle size of the metal. Also in the case of iridium catalysts it was shown that the reaction rate depends on the temperature at which the catalyst is used in the reaction: if the reaction is started at a high temperature the catalyst is more active than when the reaction is started at a low temperature. The activity of the iridium catalysts was found to be suppressed by oxygen. Water decreased the activity of the catalysts for both metals: platinum catalysts were found to be more sensitive to water than iridium catalysts.
References

1. Chapter 1 of this thesis.
17. A.C.M. van den Broek, J. van Grondelle, and R.A. van Santen, to be published. (Chapter 5 of this thesis)
Determination of Surface Coverage of Catalysts: Temperature Programmed Experiments on Platinum and Iridium Sponge Catalysts after Low Temperature Ammonia Oxidation*

Abstract

The activity of iridium and platinum sponge catalysts was studied in the low temperature gas phase oxidation of ammonia with oxygen. Under the reaction conditions used, iridium was found to be more active and more selective to nitrogen than platinum. Furthermore it was established from activity measurements that both catalysts loose activity as a function of time on stream due to inhibition of the surface by reaction intermediates. The used catalysts were studied with XPS and temperature programmed techniques. It was found that the surface of the catalysts had a high coverage of NH and OH and some additional NH$_2$. It seems most likely that the reaction mechanism proceeds through a stepwise dehydrogenation of the ammonia molecule. It appears that the last dehydrogenation step (NH by OH to N and water) is the rate determining step. The high selectivity of iridium to nitrogen can be explained by the higher activity of iridium to dissociate NO.

* Submitted for publication: A.C.M. van den Broek, J. van Grondelle, and R.A. van Santen.
Introduction

Low temperature selective oxidation of ammonia with oxygen to nitrogen and water could be a solution to several ammonia spills [1]. Metallic catalysts are often used for this reaction because they combine a high activity and selectivity to nitrogen at a low reaction temperature (< 473 K) [1, 2, 3, 4, 5]. Of the various metals platinum [5, 6, 7] and iridium [6, 7] are found to be the most active catalysts. Furthermore it was established [6, 8, 9] that larger metal particles are more active in the gas phase oxidation of ammonia than smaller metal particles. Also it was found that the platinum catalysts show a considerable loss of activity with time on stream [6, 8, 9, 10, 11, 12]. In contrast the iridium catalysts show a different time on stream behavior: first the activity increases, but after some time the activity decreases. Finally, the activity stabilizes at a reaction rate comparable to the initial rate [6]. As a result iridium catalysts are found to be much more active than platinum catalysts. The loss of activity of the platinum catalysts was attributed to oxidation of the platinum surface [9] or to inhibition of the surface with reaction intermediates [6, 11, 12]. The increase and decrease of activity of the iridium catalysts was attributed to a changing surface composition with reaction intermediates [6].

Information on mechanistic aspects of the ammonia oxidation reaction is available for platinum catalysts from gas phase surface science [13, 14, 15, 16], liquid phase electrochemical [11, 12], and theoretical studies [17]. The reaction mechanism was described in studies on the Pt(100) surface [13] or the Pt(111) surface [15, 16] or platinized platinum electrode [11, 12]. The mechanism starts with the adsorption of the reactants on the surface, following Eq. 3 and Eq. 4.

$$\text{NH}_3 + s \quad \rightarrow \quad \text{NH}_3(a) \quad (3)$$
$$\text{O}_2 + 2* \quad \rightarrow \quad 2 \text{ O}(a) \quad (4)$$

After adsorption the NH$_3$ molecule is stripped by O, as in Eqs. 5 - 7 or by OH, as in Eqs. 8 - 10.

$$\text{NH}_3(a) + \text{O}(a) \quad \rightarrow \quad \text{NH}_2(a) + \text{OH}(a) \quad (5)$$
$$\text{NH}_2(a) + \text{O}(a) \quad \rightarrow \quad \text{NH}(a) + \text{OH}(a) \quad (6)$$
$$\text{NH}(a) + \text{O}(a) \quad \rightarrow \quad \text{N}(a) + \text{OH}(a) \quad (7)$$
Surface Coverage of Pt and Ir Catalyst after Ammonia oxidation

\[ \text{NH}_3(a) + \text{OH}(a) \rightarrow \text{NH}_3(a) + \text{H}_2\text{O}(a) \] (8)
\[ \text{NH}_3(a) + \text{OH}(a) \rightarrow \text{NH}(a) + \text{H}_2\text{O}(a) \] (9)
\[ \text{NH}(a) + \text{OH}(a) \rightarrow \text{N}(a) + \text{H}_2\text{O}(a) \] (10)

Thereafter \( \text{N}_2 \) can be formed \([13, 15]\) according to Eq. 11.

\[ 2 \text{N}(a) \rightarrow \text{N}_2(g) + 2s \] (11)

Or, alternatively \([11, 12]\) from \( \text{NH}_x(a) \) \((x = 1 \text{ or } 2)\) via a \( \text{N}_2\text{H}_x \) \((x = 2 \text{ to } 4)\) as shown in Eq. 12.

\[ \text{NH}_x(a) + \text{NH}_y(a) \rightarrow \text{N}_x\text{H}_{x+y}(a) \] (12a)
\[ \text{N}_x\text{H}_{x+y}(a) + (x+y)\text{OH}(a) \rightarrow \text{N}_2(g) + (x+y)\text{H}_2\text{O} \] (12b)

On the formation of NO at low temperature the literature does not agree. Two reactions are reported, Eq. 13 \([13]\) and Eq. 14 \([15]\).

\[ \text{NH}(a) + 2 \text{O}(a) \rightarrow \text{NO}(a) + \text{OH}(a) + * \] (13)
\[ \text{N}(a) + \text{O}(a) \rightarrow \text{NO}(a) + * \] (14)

The onset of NO desorption from the platinum surface (Eq 15) was observed in various studies starting at a temperature of 300 K \([15]\), 400 K \([13]\), or 550 K \([16]\).

\[ \text{NO}(a) \rightarrow \text{NO}(g) + s \] (15)

Also, on the Pt(100) surface it is possible to dissociate NO at temperatures higher than 350 K \([13]\), as shown in Eq. 16. On the Pt(111) or Pt(110) surface NO dissociation is only possible at higher temperatures \([18]\).

\[ \text{NO}(a) + * \rightarrow \text{N}(a) + \text{O}(a) \] (16)

In this study platinum and iridium sponge catalysts were tested in the low temperature \((< 373 \text{ K})\) gas phase ammonia oxidation reaction. In order to determine the cause of the time on stream behavior, used catalysts were studied with XPS and temperature programmed experiments.
Methods

Sample preparation
The platinum and iridium sponge samples were acquired from Johnson Matthey. The sponge samples were of > 99.9 % purity. The size of the sponges was between 250 and 350 μm for the platinum sample and < 841 μm for the iridium sample. In the reaction setup particles were used with a particle size between 125 and 425 μm; if necessary, samples of the catalyst were pelletized, crushed, and sieved to acquire the appropriate particle size. All catalysts were reduced in the reaction setup by heating the sample in a hydrogen flow from 298 K up to a temperature of 573 K.

Electron microscopy measurements
Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) measurements were done on a Jeol 840 electron microscope. Both reduced as well as used platinum and iridium sponge samples were measured.

Krypton BET measurements
Krypton BET measurements were done on a Micromeritics ASAP 2000 set-up, using a standard procedure without any pretreatment of the sample. Krypton was used as an adsorbent because of the low surface area of the metal sponge samples. The average metal particle size was determined from the surface area, assuming cubic closest packed symmetry for both metals.

Experimental setup
Catalytic and temperature programmed tests were done in a fixed bed reaction setup equipped with a gas chromatograph (ATI UNICAM 610, spec 2790) and a quadrupole mass spectrometer (Balzers QMG-420) for on-line analysis of the reactants and products. The gas chromatograph could analyze NH₃, O₂, H₂O, N₂, and N₂O quantitatively. The mass spectrometer was used to check the results of the gas chromatograph and for the detection of NO and NO₂. A quartz tube with an internal diameter of 4 mm was used as the reactor.

Steady state catalytic tests
For the steady state catalytic tests the reactor was filled with the metal sponge (12.2 mg for Ir, 92.8 mg for Pt) diluted with about 130 mg of γ-alumina. The reactor was assumed to be differential at low conversion, using calculated estimations of diffusion and heat transfer. The catalyst was diluted with γ-alumina in order to satisfy plug flow requirements. It was
Surface Coverage of Pt and Ir Catalyst after Ammonia oxidation

determined experimentally that γ-alumina is not active for oxidation of ammonia at the conditions used in this study. Catalytic tests were done with a reaction mixture consisting of 2.0 vol% of ammonia and 1.5 vol% of oxygen in helium with a total flow of 48.8 cm³/min (STP). The reaction temperature was adjusted to keep conversion below 10%. Reaction rates (expressed as moles of ammonia converted per hour, \(R_{\text{NH}_3}\)) were calculated from the concentrations of nitrogen (\(C_{N_2}\)) and nitrous oxide (\(C_{N_2O}\)) following Eq. 17. By using production rates instead of conversion for this calculation it was assured that the calculated rate represents reaction and not adsorption of the reactant. It was checked that under steady state conditions the mass balance was complete. The Turn Over Frequency (TOF) was calculated from the reaction rate \(R_{\text{NH}_3}\) divided by the metal surface of the catalyst \(A_M\) (Eq. 18). The surface area was determined by hydrogen chemisorption or Krypton BET.

\[
R_{\text{NH}_3} = F(C_{N_2} + C_{N_2O}) \quad \text{(mole NH}_3\text{ per hour)}
\]

\[
TOF = \frac{R_{\text{NH}_3}}{A_M} \quad \text{(mole NH}_3\text{ per mole metal surface per hour)}
\]

Steady state experiments were done using the gas chromatograph after at least 12 hours on stream. Reaction orders were determined by lowering the concentration of one of the reactants at a fixed concentration of the other reactant. For the platinum catalysts reaction orders were determined at a temperature of 433 K. For the iridium catalysts reaction orders were determined at a temperature of 403 K. Activation energies were determined by variation of the temperature. For the platinum catalysts in the range 413 - 443 K. For the iridium catalysts in the range 413 - 383 K. Used catalysts were regenerated by reduction in a hydrogen flow at 573 K. The regenerated catalyst showed exactly the same behavior as the fresh catalysts.

Time On Stream (TOS) experiments

For the TOS and the temperature programmed experiments a sample of 1.0 g of pure sponge was used as the catalytic bed. In the Time On Stream (TOS) experiments a flow with the reactants was switched to a reduced catalyst at time zero. The concentrations of the reactants and products were measured using the mass spectrometer for at least 2 hours on stream. A flow consisting of 2.0 vol% of ammonia and 1.5 vol% of oxygen in helium with a total flow of 48.8 cm³/min (STP) was used. The experiment was done at a temperature of 323 K for the iridium sponge catalyst and at 373 K for the platinum sponge catalyst.
XPS experiments

XPS experiments were done on a V.G. Scientific XP spectrometer, Al Kα photon radiation was used. The measurements were corrected for charging by using the Ir 4f signal at 60.9 eV or the Pt 4f signal at 71.2 eV as a reference. XP spectra were taken of freshly reduced platinum and iridium sponge samples as well as of samples that were used in a TOS experiment. The samples were taken out of the reactor and transported in air to be fitted on an iron stub carrying an indium foil. Because of interference of an InO₂ layer on the indium foil it was not possible to get a clear O 1s signal for oxygen on platinum or iridium.

Temperature Programmed Experiments

Two different experiments were done to examine the adsorbed species on the catalyst: Temperature Programmed Desorption (TPD) followed by Reduction; and Temperature Programmed Reduction.

![Scheme 1: Outline of the TPD and Reduction experiment.](image)

The experimental sequence for the TPD and Reduction experiment is shown in Scheme 1. First a TOS experiment is done with the catalyst for two hours. Then the catalyst was flushed with a helium flow of 10.2 cm³/min (STP) for 1 hour at the reaction temperature. Subsequently, in the TPD experiment, the temperature was raised with 10 K per minute to a temperature of 773 K. After 30 minutes at 773 K, the Reduction experiment was carried out by switching the helium flow to a 20 vol% H₂ in helium mixture, with a flow rate of 10.2 cm³/min (STP). After 1 hour at 773 K the temperature was lowered to the reaction temperature and the flow was switched back to pure helium. The catalyst was found to be regenerated by the TPD and Reduction experiment and was used in the next experiment.
The experimental sequence for the TPD and Reduction experiment is shown in Scheme 2. First a TOS experiment is done with the catalyst for two hours. Then the catalyst was flushed with a helium flow of 10.2 cm³/min (STP) for 1 hour at the reaction temperature. Subsequently, the Temperature Programmed Reduction (TPR) experiment was started. The reactor flow was switched to a 20 vol% H₂ in helium mixture with a flow rate of 10.2 cm³/min (STP). First the temperature is kept at the reaction temperature, this is the isothermal part of the TPR. After 1 hour the temperature programmed part of the TPR was started, in which the temperature was raised with 10 K per minute to 773 K. After 30 minutes at 773 K the temperature was lowered to the reaction temperature and the flow was switched to pure helium. Like in the TPD and Reduction experiment, the catalyst was found to be regenerated by the TPR experiment and was used in the next experiment.

Both the TPD and Reduction experiment and the TPR experiment were repeated using D₂ instead of H₂. The experiments with H₂ made it possible to distinguish between NH₃ and H₂O (mass 17 and 18). The results of the D₂ experiments gave information about the occurrence of the various deuterated forms: ND₃ and D₂O (mass 20), ND₂H and HDO (mass 19), NDH₂ and H₂O (mass 18), and NH₃ (mass 17). However, in the calculation of concentrations from these data the experimental error was enhanced largely by interference of fragmentation ions of the different deuterated species. As a consequence it was not possible to distinguish between the various deuterated species.
Chapter 5

Results

Particle size determination
The results of the particle size determination are given in Table 1. The particle size determined with krypton BET agrees with the particle size that was determined with SEM. From the SEM pictures that are shown in Figure 1, it can be deduced that the sponges consist of small non-porous particles that are clustered together in much larger sponge-like structures. From EDS it was found that no significant impurities were present in the sponges.

Table 1: Metal particle size determination.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET</th>
<th>SEM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>area (m²/g)</td>
<td>size (μm)</td>
</tr>
<tr>
<td>Ir sponge</td>
<td>0.567</td>
<td>0.50</td>
</tr>
<tr>
<td>Pt sponge</td>
<td>0.099</td>
<td>3.0</td>
</tr>
</tbody>
</table>

a: size of the small non porous particles.

Figure 1: SEM images of iridium sponge (left) and platinum sponge (right).

Steady state catalytic tests
The results of the steady state catalytic tests are summarized in Table 2. The iridium catalyst was found to be more active than the platinum catalyst. Furthermore the selectivity to nitrogen was also higher for the iridium catalyst. The reaction orders that were determined are all low, the order in O₂ is lower for iridium than for platinum, whereas the order in NH₃ is higher for iridium than for platinum. The activation energy was found to be somewhat higher for the iridium catalyst.
As can be seen in Figure 2 and Figure 3, both iridium and platinum catalysts showed severe loss of activity after the catalyst was exposed to the reaction mixture. The resultant steady state activity was similar for both catalysts, but it must be noted that the iridium catalyst was tested at 323 K, whereas the platinum catalyst was tested at 373 K. Similar to the case of supported iridium catalysts [6], the iridium sponge catalyst first becomes more active at the start of the reaction and becomes less active. Figure 2 clearly shows that maximum activity was reached in 20 seconds, thereafter the activity decreased to 10 % of the maximum activity in 60 seconds. Finally after 1200 seconds (not shown) the activity is stable at 2 % of the maximum activity. The selectivity to N₂ is 100 % at the start of the reaction, dropping to 95 % during some TOS, the remainder being N₂O. The platinum sponge catalyst is also found to become more active and subsequently become less active. This is in contrast to the supported case [6] in which it was found that platinum catalysts loose activity directly from the start of the reaction. As shown in Figure 3, the activity increases during the first 12 seconds on stream, then it decreases. The activity decreased to 10 % of the initial activity in just 60 seconds. After 1200 seconds on stream (not shown) the activity is stable at 2 % of the initial activity. As can be clearly seen in Figure 3, immediately at the start of the reaction mostly N₂O is produced; the production decreasing rapidly after 8 seconds on stream. Thereafter an large increase in N₂ production is seen, the production rapidly decreasing after 12 seconds on stream. At steady state the selectivity to N₂ is constant at 75 %, the remainder being N₂O.
Figure 2: Initiation of reaction with a stoichiometric reaction mixture with an iridium sponge catalyst, △ = N₂, ○ = N₂O; ammonia concentration = 2.0 vol%; oxygen concentration = 1.5 vol%; GHSV = 3000.

Figure 3: Initiation of reaction with a stoichiometric reaction mixture with a platinum sponge catalyst, △ = N₂, ○ = N₂O; ammonia concentration = 2.0 vol%; oxygen concentration = 1.5 vol%; GHSV = 3000.
**XPS experiments**

The XP spectra around the binding energy of N 1s of both reduced and used iridium sponge are shown in the top part of Figure 4. The broad N 1s peak centered around 399 eV can only be observed in the used sample. From literature [19, 20] it is known that N 1s signal of NH$_x$ (x = 0 - 3) has a binding energy below 400 eV, whereas the N 1s signal of NO$_x$, N$_2$H$_x$, and NH$_4^+$ have a binding energy above 400 eV. Therefore, the measured N 1s signal must be due to an adsorbed NH$_x$ (x = 0 - 2) species, excluding NH$_3$ since it would already be desorbed at the temperature used in this experiment. The broad nature of the peak suggests that a mixture of the various NH$_x$ (x = 0 - 2) species are present on the surface of the used iridium catalyst.

![Figure 4: XP-spectra for N 1s of a used (a) or reduced (b) sample for iridium sponge (top) and platinum sponge (bottom).](image-url)
The XP spectra around the binding energy of N 1s of both reduced and used platinum sponge are shown in the bottom part of Figure 4. The N 1s peak centered around 398 eV can only be observed in the used sample. Similarly as in the case of iridium discussed above, this peak must be caused by adsorbed NH₅ (x = 0 - 2) species. Furthermore it is known from a study of NO adsorption on Pt(100) and Pt(310) [18] that NOads and Nads give rise to N 1s peaks at 401 eV and 399.5 eV respectively. Another study [21] showed that on Pt(111) NH₃ and NH₅ (x = 1 or 2) show N 1s peaks at 399.8 eV and 397.5 eV respectively. Comparing the results of both metals in Figure 4 it appears that N 1s signal observed in the platinum case is less broad and at a lower binding energy than that of the iridium case. Therefore, it is most likely that NH₅ (x = 1 or 2) species cause the N 1s signal that is observed in the XP-spectrum of the used platinum sample.

*Temperature programmed experiments on iridium sponge*

The result of the TPD experiment on iridium sponge is shown in Figure 5 and summarized in Table 3. In Figure 5, the desorption of N₂ and H₂O can be seen clearly together with smaller amounts of N₂O and NH₃. The peaks of N₂ and N₂O are relatively sharp and are centered around a temperature of 410 K, whereas NH₃ and H₂O show broad peaks centered around a temperature of 430 K. This difference is probably caused by a stronger adsorption of NH₃ and H₂O in the reaction system. The peaks of N₂ and NH₃ also appear to have two shoulders at 450 K and 510 K respectively. In the subsequent reduction with H₂, also listed in Table 3, only small amounts of H₂O, N₂ and NH₃ were observed. In the D₂ reduction (not shown) no signal for mass 20 (D₂O or ND₃) was detected. The results of the TPR experiment with H₂ are shown in Figure 6 (isothermal part) and Figure 7 (temperature programmed part). In the isothermal part of the TPR experiment the immediate formation of N₂, followed by the subsequent production of NH₃ and H₂O can be clearly seen. In the temperature programmed part NH₃ and H₂O are observed in two peaks at 410 K and 480 K. The first peak consist of mainly H₂O, whereas the latter is observed in both H₂O and NH₃. In the TPR experiment with D₂ (not shown) no signal for mass 20 (D₂O or ND₃) was detected.
Figure 5: TPD experiment on iridium sponge after reaction at 323 K, ▲ = N₂, ■ = H₂O, ○ = N₂O, + = NH₃.

Table 3: Desorbed species per surface site in the TPD and Reduction experiments for iridium sponge, variation of reactant concentration.

<table>
<thead>
<tr>
<th>Reactant concentration</th>
<th>NH₃</th>
<th>O₂</th>
<th>Desorbed species per surface site</th>
<th>TPD</th>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>N₂</td>
<td>N₂O</td>
<td>NH₃</td>
</tr>
<tr>
<td>2.0</td>
<td>0.8</td>
<td>0.128ᵃ</td>
<td>0.010ᵃ</td>
<td>0.025ᵃ</td>
<td>0.24ᵇ</td>
</tr>
<tr>
<td>2.0</td>
<td>1.5</td>
<td>0.122ᵃ</td>
<td>0.011ᵃ</td>
<td>0.021ᵃ</td>
<td>0.24ᵇ</td>
</tr>
<tr>
<td>1.0</td>
<td>1.5</td>
<td>0.104ᵃ</td>
<td>0.011ᵃ</td>
<td>0.019ᵃ</td>
<td>0.23ᵇ</td>
</tr>
</tbody>
</table>

ᵃ: 95 % confidence interval is ± 0.003, for N₂, N₂O, and NH₃.
ᵇ: 95 % confidence interval is ± 0.01, for H₂O.
Figure 6: Isothermal part of TPR experiment on iridium sponge after reaction at 323 K, $\Delta = \text{N}_2$, $\blacksquare = \text{H}_2\text{O}$, $\times = \text{NH}_3$.

Figure 7: Temperature programmed part of TPR experiment on iridium sponge after reaction at 323 K, $\Delta = \text{N}_2$, $\blacksquare = \text{H}_2\text{O}$, $\times = \text{NH}_3$. 
The results of the TPD experiment after ammonia oxidation with various reactant concentrations are shown in Figure 8 and also summarized in Table 3. From the results it appears that when the catalyst is exposed to a lower concentration of NH₃, less N₂ and H₂O is formed in the TPD experiment. When the catalyst is exposed to a lower concentration of O₂, the amounts of N₂ and H₂O formed in the TPD are about the same as after exposition to stoichiometric concentrations. However, after exposition to a lower concentration of O₂, the first peak in the TPD is lower and the second peak in the TPD is higher than in the TPD after exposition to stoichiometric concentrations. The subsequent reduction with H₂ is also listed in Table 3. It was found that after ammonia oxidation with a lower amount of O₂, less H₂O and more NH₃ were produced in the reduction. Whereas after ammonia oxidation with a lower amount of NH₃, more H₂O was produced in the reduction. In the D₂ reduction (not shown) no signal for mass 20 (D₂O or ND₃) was detected.
Figure 8: Experiments after reaction of iridium sponge with various reactant concentrations: a. N₂ signal of TPD, b. H₂O signal of TPD, reaction conditions: ▲ = excess NH₃, ■ = stoichiometric, ● = excess O₂.
Temperature programmed experiments on platinum sponge

The result of the TPD experiment on platinum sponge is shown in Figure 9 and summarized in Table 4. In Figure 9, the desorption of N₂, H₂O, N₂O and NH₃ can be seen clearly; all signals show broad peaks. The peaks of N₂ and N₂O are centered around a temperature of 490 K, whereas the NH₃ and H₂O peaks are centered around a temperature of 510 K. Similarly to the case of the iridium experiments, this difference in temperature is probably caused by a stronger adsorption of NH₃ and H₂O in the reaction system. In the subsequent reduction with H₂, also listed in Table 4, a significant amount of H₂O together with small amounts of N₂ and NH₃ were observed. In the D₂ reduction (not shown) no signal for mass 20 (D₂O or ND₃) was detected. The results of the TPR experiment with H₂ are shown in Figure 10 (isothermal part) and Figure 11 (temperature programmed part). In the isothermal part of the TPR experiment only the production of H₂O can be seen. In the temperature programmed part a small amount of NH₃ can be seen at temperatures above 480 K together with a larger amount of H₂O peaking at the same temperature. In the TPR experiment with D₂ (not shown) no signal for mass 20 (D₂O or ND₃) was detected.

Figure 9: TPD experiment on platinum sponge after reaction at 373 K,

\[ \Delta = \text{N}_2, \quad \bullet = \text{H}_2\text{O}, \quad \bigcirc = \text{N}_2\text{O}, \quad + = \text{NH}_3, \]
Table 4: Desorbed species per surface site in the TPD and Reduction experiments for platinum sponge, variation of reactant concentration.

<table>
<thead>
<tr>
<th>Reactant concentration</th>
<th>Desorbed species per surface site</th>
<th>TPD</th>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NH₃</td>
<td>O₂</td>
<td>N₂</td>
</tr>
<tr>
<td>2.0 0.8</td>
<td>0.14&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.05&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>2.0 1.5</td>
<td>0.09&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.03&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.06&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>1.0 1.5</td>
<td>0.15&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.04&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup>: 95% confidence interval is ±0.01, for N₂.
<sup>b</sup>: 95% confidence interval is ±0.02, for N₂O and NH₃.
<sup>c</sup>: 95% confidence interval is ±0.03, for H₂O.

Figure 10: Isothermal part of TPR experiment on platinum sponge after reaction at 373 K, ▲ = N₂, ■ = H₂O, + = NH₃.
The results of the TPD experiment after reaction with various reactant concentrations are shown in Figure 12 and also summarized in Table 4. From the results it appears that when the catalyst is exposed to reactant concentrations other than stoichiometric, more N\textsubscript{2} and H\textsubscript{2}O and less N\textsubscript{2}O and NH\textsubscript{3} are formed. The subsequent reduction with H\textsubscript{2} is also listed in Table 4. It was found that after ammonia oxidation with a lower amount of O\textsubscript{2}, less H\textsubscript{2}O and more NH\textsubscript{3} were produced in the reduction. Whereas after ammonia oxidation with a lower amount of NH\textsubscript{3}, more H\textsubscript{2}O was produced in the reduction. In the D\textsubscript{2} reduction (not shown) no signal for mass 20 (D\textsubscript{2}O or ND\textsubscript{3}) was detected.
Figure 12: Experiments after reaction of platinum sponge with various reactant concentrations: a. N$_2$ signal of TPD, b. H$_2$O signal of TPD, reaction conditions: ▲ = excess NH$_3$, ■ = stoichiometric, ● = excess O$_2$. 
Discussion

Iridium Sponge

In the TOS experiment shown in Figure 2 it appeared that the iridium sponge catalyst becomes less active after an initial increase in activity. In the steady state measurements shown in Table 2 it was found that the reaction orders were low, which is an indication of a highly covered catalyst surface. Therefore it is likely that the loss of activity is caused by intermediate species adsorbed on the catalyst surface.

In order to determine the nature of the surface species on the used catalyst it must be first noted that the catalyst is flushed with helium at the reaction temperature (323 K) before the start of the TPD experiment; therefore any reaction product on the surface will desorb at this stage of the experiment. This is consistent with literature findings on the desorption of molecularly adsorbed N₂ [22], N₂O [22], H₂O [23] on iridium surfaces. Molecularly adsorbed O₂ however can be expected to remain adsorbed on the surface at this temperature [22], whereas molecularly adsorbed NH₃ will desorb [24]. From the results of the XPS study on the used catalyst sample it was concluded that the only N containing species on the surface can be N, NH and NH₂. From the results of the reduction and TPR experiment with deuterium it was found that no ND₃ or D₂O was produced. From this result it can be concluded that there is no O_ads or O₂_ads on the surface, since D₂O would be produced if O_ads or O₂_ads would react with D_ads. Furthermore it can be deduced from this result that there is no N_ads on the surface. In the TPR experiment with H₂ the production of NH₃ is observed. Furthermore, it is known that the hydrogenation of NH₂ is the rate determining step in the production of NH₃ over Rh(111) [25]. Therefore, there should be some ND₃ formed in the TPR experiment if there is N_ads present on the surface. Since no ND₃ is observed it can be concluded that there is no N_ads on the surface. The only surface species on the used iridium sponge catalyst can therefore only be: OH, NH, and NH₂. The composition of the iridium surface after the TOS experiment can now be calculated from the combined results of the TPD and Reduction experiments. The results are shown in Table 5, together with the results for the platinum sponge catalyst. The values for NH and NH₂, however, must be treated with some care. Since the desorption of H₂O and NH₃ is broad it is possible that some signal is missed which would result in a larger value for NH₂ and a lower value for NH. However, obviously there is more NH than NH₂ on the surface.
Chapter 5

Table 5: Calculated surface composition of used catalysts.

<table>
<thead>
<tr>
<th>Reactant concentration</th>
<th>Iridium sponge</th>
<th>Platinum sponge</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NH}_3 )</td>
<td>( \text{O}_2 )</td>
<td>( \Theta \text{NH} )</td>
</tr>
<tr>
<td>2.0</td>
<td>0.8</td>
<td>0.32(^a)</td>
</tr>
<tr>
<td>2.0</td>
<td>1.5</td>
<td>0.29(^a)</td>
</tr>
<tr>
<td>1.0</td>
<td>1.5</td>
<td>0.24(^a)</td>
</tr>
</tbody>
</table>

\( ^a \): 95% confidence interval is ± 0.02, for iridium.

\( ^b \): 95% confidence interval is ± 0.06, for platinum.

The results in Table 3 also show that during the TPD after reaction with a stoichiometric reaction mixture almost all \( \text{NH}_3 \) and \( \text{OH} \) reacts to form products. Only a small amount of \( \text{OH} \) and \( \text{NH}_3 \) remains on the surface and reacts with \( \text{H}_2 \) in the subsequent reduction experiment. Furthermore, the results show that variation of the reactant concentrations varies the surface composition of the used catalyst. Compared to reaction with a stoichiometric reaction mixture, it would be expected that reaction with a lower concentration of oxygen gives rise to a larger amount of \( \text{NH}_3 \) and a smaller amount of \( \text{OH} \) on the surface. This is indeed found in the combined TPD and Reduction experiments. In the TPD experiment more \( \text{N}_2 \) and \( \text{NH}_3 \) and less \( \text{H}_2 \text{O} \) is produced. After the TPD experiment only some \( \text{NH}_3 \) remains on the surface. Therefore, in the subsequent reduction, only some \( \text{NH}_3 \) is produced. Compared to reaction with a stoichiometric reaction mixture, it would be expected that reaction with a lower concentration of ammonia gives rise to a larger amount of \( \text{OH} \) and a smaller amount of \( \text{NH}_3 \) on the surface. This is indeed found in the combined TPD and Reduction experiments. In the TPD experiment less \( \text{N}_2 \), \( \text{NH}_3 \) and \( \text{H}_2 \text{O} \) is produced. After the TPD experiment a larger amount of \( \text{OH} \) and some \( \text{NH}_3 \) remain on the surface. Therefore, in the subsequent reduction, \( \text{H}_2 \text{O} \) together with some \( \text{NH}_3 \) is produced.

Platinum Sponge

In the TOS experiment shown in Figure 3 it appeared that the activity of the platinum sponge catalyst decreases after an initial increase in activity. Furthermore the selectivity to nitrogen and nitrous oxide changes strongly in the initial period. In the steady state measurements shown in Table 2 it was found that the reaction orders were low, which is an indication of a highly covered catalyst surface. Similar to the case of iridium, it is therefore likely that the loss of activity is caused by intermediate species adsorbed on the catalyst surface. Furthermore the change in selectivity is a strong indication of a change in surface coverage;
the reactions forming N\textsubscript{2} and N\textsubscript{2}O are apparently depended on surface coverage in the case of platinum.

Similar to the iridium case discussed above, the catalyst was flushed with helium at the reaction temperature (373 K) before the start of the TPD experiment; therefore any molecularly adsorbed reactant and reaction product on the surface would desorb at this stage of the experiment. This is consistent with literature findings on the desorption of molecularly adsorbed N\textsubscript{2} [26], N\textsubscript{2}O [27], H\textsubscript{2}O [28], O\textsubscript{2} [29] and NH\textsubscript{3} [21, 30] on platinum surfaces. From the results of the XPS study on the used catalyst sample it was concluded that the only N containing species on the surface can be NH and NH\textsubscript{2}•. In the results of the reduction and TPR experiment with deuterium it was found that no ND\textsubscript{3} or D\textsubscript{2}O was produced. As discussed above for the iridium catalyst it can be concluded from this result that there is no O\textsubscript{ads} or N\textsubscript{ads} on the surface. The result that there is no N\textsubscript{ads} on the surface agrees with the result of the XPS experiment. The only surface species on the used platinum sponge catalyst can therefore only be: OH, NH, and NH\textsubscript{2}•. Therefore in contrast with electrochemical studies on platinum [11, 12] it can be excluded in this study that the loss of activity is due to N\textsubscript{ads}. The composition of the platinum surface after the TOS experiment can now be calculated from the combined results of the TPD and Reduction experiments. The results are shown in Table 5, together with the results for the iridium sponge catalyst. As discussed for iridium, the values for NH\textsubscript{ad} and NH\textsubscript{2}• must be treated with some care.

The results in Table 4 also show that during the TPD almost all NH\textsubscript{x} on the surface reacts with OH to form products, whereas some OH remains on the surface. This OH is reduced with H\textsubscript{2} in the subsequent reduction experiment. Furthermore the results show that variation of the reactant concentrations in the reaction leads to different surface compositions. Compared to reaction with a stoichiometric reaction mixture, it would be expected that reaction with a lower concentration of oxygen gives rise to a larger amount of NH\textsubscript{x} and a smaller amount of OH on the surface. This is indeed found in the combined TPD and Reduction experiments. In the TPD experiment, however, a larger amount of H\textsubscript{2}O is produced. This indicates that the reactions forming N\textsubscript{2} and N\textsubscript{2}O are coupled to the reaction forming H\textsubscript{2}O. Because of the larger amount of NH\textsubscript{x} on the surface, besides N\textsubscript{2} and N\textsubscript{2}O also a larger amount of H\textsubscript{2}O is produced in the TPD experiment. After the TPD experiment less OH remains on the surface together with some NH\textsubscript{x}. Therefore, in the subsequent reduction, less H\textsubscript{2}O and even some NH\textsubscript{x} is produced. Compared to reaction with a stoichiometric reaction mixture, it would be expected that reaction with a lower concentration of ammonia gives rise to a larger amount of OH and a smaller amount of NH\textsubscript{x} on the surface. However, this is not found. From the combined TPD and Reduction experiments both a higher NH\textsubscript{x} as well as OH coverage is found. Apparently the surface with a higher OH coverage can contain more NH\textsubscript{x}, while the value of x is lower.
Comparison of Iridium and Platinum Sponges

At steady state, after the initial loss of activity the iridium catalyst showed to be almost 10 times more active than the platinum catalyst. Furthermore the selectivity to nitrogen is significantly enhanced on the iridium catalyst. Therefore iridium is a more suitable catalyst than platinum for the low temperature selective oxidation of ammonia under the conditions used in this study. Since the reaction orders that were found are different for iridium and platinum other reaction conditions may change the difference in performance. Both the used platinum and iridium have a surface covered with NH, NH$_2$ and OH species. It appears that there is somewhat more NH$_2$ and OH on the platinum surface than on the iridium surface. The largest difference in behavior between iridium and platinum can be seen in the TPD experiments: the products desorb from the surface at much lower temperatures in the case of the iridium catalyst.

Time On Stream (TOS) behavior and reaction mechanism

Iridium is known to form stronger interactions with adsorbed species than platinum, for example with oxygen and nitrogen adatoms [31, 32]. Therefore iridium catalysts are more active than platinum catalysts in reactions in which bond braking is rate determining. This is the reason that iridium is more active than platinum in the decomposition of ammonia [33], but not in the decomposition of hydrazine [34, 35]. Iridium catalysts are less active than platinum in reactions in which desorption of the products is the rate determining step. Because of the stronger interaction with the adsorbed oxygen atoms the reaction rate over iridium is lower than that over platinum in the oxidation of hydrogen and carbon monoxide [36]. Since in this study it was found that iridium is much more active than platinum in the low temperature ammonia oxidation reaction it appears that a bond braking step will be the rate determining step in this reaction. Therefore the reaction producing N$_2$ will not proceed through a N$_2$H$_x$ intermediate (Eq. 12). In that case platinum would be expected to be the most active catalyst. It was shown that there is no N$_2$H$_x$ intermediate on the surface. Furthermore no hydrazine is seen as product of the reaction. Therefore the formation of the N$_2$H$_x$ intermediate would have to be the rate determining step. Since this is a N-N bond forming step it would be expected that platinum would be more active than iridium. The other route to form N$_2$ is the associative desorption of N$_{ads}$ (Eq. 11). This reaction is known in surface science to occur at higher temperatures (400 K for Pt [37], 500 K for Ir [32]) than the reaction temperatures used in this study. However, nitrogen is seen as a reaction product. Since there is no N$_{ads}$ found on the surface all N$_{ads}$ that was on the surface must be desorbed during the flushing with helium. Possibly the high surface coverage during reaction makes the desorption of N$_2$ possible at this low temperature. This could also be the explanation of the increasing activity at the start of the
reaction; the desorption of nitrogen is only possible at a high surface coverage. Since the associative desorption of N\(_2\) would be expected to be faster on platinum this step can not be the rate determining step at steady state reaction. Furthermore the surface would be covered with N\(_{ads}\) if this step would be rate determining. Therefore it seems more likely that the stepwise dehydrogenation of NH\(_3\) (Eqs. 5 - 10) is rate determining. In that case iridium would be expected to be more active than platinum, since N-H bonds are broken in these steps. Since the surface of both platinum and iridium is covered with mainly NH and OH it appears that the reactions using this NH are the slowest step (Eq. 7 and 10). Since there is no O on the surface the main reaction therefore is the reaction of NH with OH (Eq. 10). From computational chemistry it is known that this surface reaction is endothermic [17]. Therefore this path will be much slower than the path via the reaction of NH with O (Eq. 7). The loss of activity is therefore caused by inhibition of active sites with NH and OH. The TPD experiments provide evidence for this mechanism. The production of water from hydroxyl groups on platinum or iridium should occur at temperatures below the reaction temperature used in this study [23, 28]. However during the TPD production of water is observed. This water therefore must be produced by the reaction of NH\(_x\) with OH (Eqs. 9 - 10).

The reaction forming N\(_2\)O must proceed via a NO intermediate. Since no NO is seen as a reaction product or on the surface of the used catalyst the reaction forming N\(_2\)O must be fast. The lower production of N\(_2\)O on iridium can be explained by the stronger bonding of reaction intermediates on the iridium surface. There will be less NO formed on iridium and any formed NO will dissociate easier [32], therefore reducing the amount of NO on the iridium surface to react with N to form N\(_2\)O.

Conclusions

In this study it was shown that, under the reaction condition used, iridium is a more active and selective catalyst than platinum for the low temperature (< 373 K) oxidation of ammonia with oxygen to nitrogen. Furthermore it was established that both catalysts loose activity with time on stream due to inhibition of the surface with reaction intermediates. The used catalysts were found to contain a high coverage with NH and OH and some additional NH\(_2\). Since iridium is more active than platinum the reaction mechanism must proceed through a stepwise dehydrogenation of the ammonia molecule. Since most of the nitrogen on the surface is NH it appears that the last dehydrogenation step (NH with OH to N and water) is the rate determining step. The high selectivity of iridium to nitrogen can be explained by the stronger interaction of iridium with reaction intermediates.
References

1. Chapter 1 of this thesis.
6. Chapter 4 of this thesis.
Surface Coverage of Pt and Ir Catalyst after Ammonia oxidation

Summary and Concluding Remarks

This thesis describes research into two main subjects: the preparation of small platinum particles in zeolite HZSM-5 and the low temperature oxidation of ammonia over platinum and iridium catalysts. The oxidation of ammonia over a \( \text{[Pt(NH}_3\text{)}_4\text{]}^{2+} \) complex in zeolite HZSM-5 connects these two subjects.

In the second chapter of this thesis the preparation of small platinum particles in zeolite ZSM-5 is described. The pretreatment of \( \text{[Pt(NH}_3\text{)}_4\text{]}^{2+} \), ion exchanged into zeolite HZSM-5, was studied using temperature programmed techniques and diffuse reflectance UV/VIS spectroscopy. It was found that combination of water and the acid sites of the zeolite enables the oxidation of the complex at low temperature (490 K). Careful pretreatment in an oxygen containing atmosphere of \( \text{[Pt(NH}_3\text{)}_4\text{]} \text{HZSM-5} \) leads to the formation of the pale green \( \text{PtHZSM-5} \) in which platinum is present as \( \text{Pt}^{2+} \) coordinated to the zeolite framework. Small platinum particles are formed by subsequent reduction of these platinum ions in flowing hydrogen.

In chapter 3 it was examined whether it was possible to use \( \text{[Pt(NH}_3\text{)}_4\text{]}^{2+} \) in HZSM-5 as a catalyst in the low temperature (473 K) ammonia oxidation. It was found that indeed a catalytic reaction was possible with this complex. Furthermore it was found that the selectivity to nitrogen and nitrous oxide changed during the reaction. Also it was found that the selective reaction to nitrogen is enhanced by the presence of water in the reaction mixture, where water usually has the opposite effect. Infrared experiments were done to gain some insight in the reaction mechanism. Unfortunately from these experiments no conclusive evidence for a reaction mechanism could be obtained.

In chapter 4 studies of the low temperature ammonia oxidation reaction are described using platinum and iridium catalysts. The metal particle size of the catalysts was varied in order to examine the particle size effect. It was found that for both metals a particle size effect exists: larger metal particles were found to be more active than smaller metal particles. Furthermore it was found that the iridium catalysts were more active than the platinum catalysts. Also the TOS behavior was studied by measuring the activity of the catalyst as a function of time. It was found that the platinum catalysts lost activity directly from the start of
the reaction, whereas the iridium catalysts first became more active and then lost activity. From the measurement of kinetics it was established that the catalyst surface in steady state is covered with reaction intermediates. Water in the feed was found to decrease the activity of the catalysts for both metals: platinum catalysts were found to be more sensitive to water than iridium catalysts.

In chapter 5 experiments are described in which the surface of the platinum and iridium catalysts after reaction was studied. Metal sponges were used as the catalysts in order to avoid the influence of any catalyst carrier. In reactivity experiments it was found that iridium was more active and more selective to nitrogen than platinum. With combined TPD and TPR measurements of the used catalysts it was established that the surface of both platinum and iridium catalysts is covered with mainly NH and OH and some NH₂. This result was confirmed by XPS experiments on the used catalysts. It was found that the reaction mechanism proceeds through a stepwise dehydrogenation of the ammonia molecule. It was concluded that the rate determining step is the dehydrogenation of NH with OH to N and water. The loss of activity is therefore caused by inhibition of the surface with NH and OH. The high selectivity of iridium to nitrogen can be explained by the stronger interaction of iridium with reaction intermediates.

Summarizing, the reaction mechanism that best describes the results found in this study is the following. First the reactants are adsorbed on the surface (Eq. 1 - 2).

\[
\begin{align*}
\text{NH}_3 & \rightarrow \text{NH}_3,a \\
\text{O}_2 & \rightarrow 2\text{O}_a
\end{align*}
\]

(1) (2)

At the start of the reaction the surface is empty apart from the adsorbed reactants and the ammonia molecule is stripped by adsorbed oxygen atoms (Eq. 3 - 5).

\[
\begin{align*}
\text{NH}_3,a + \text{O}_a & \rightarrow \text{NH}_2,a + \text{OH}_a \\
\text{NH}_2,a + \text{O}_a & \rightarrow \text{NH}_a + \text{OH}_a \\
\text{NH}_a + \text{O}_a & \rightarrow \text{N}_a + \text{OH}_a
\end{align*}
\]

(3) (4) (5)

However, the surface becomes increasingly populated with OH as a result of these reactions. As a result stripping of the ammonia molecule has to take place via the thermodynamically unfavorable route by reaction with OH (Eq. 6 - 8).

\[
\begin{align*}
\text{NH}_3,a + \text{OH}_a & \rightarrow \text{NH}_2,a + \text{H}_2\text{O}_a \\
\text{NH}_2,a + \text{OH}_a & \rightarrow \text{NH}_a + \text{H}_2\text{O}_a \\
\text{NH}_a + \text{OH}_a & \rightarrow \text{N}_a + \text{H}_2\text{O}_a
\end{align*}
\]

(6) (7) (8)
The production of nitrogen occurs through the associative desorption reaction (Eq. 9).

\[ 2 \text{N}_2 \rightarrow \text{N}_2 \text{(g)} \]  

(9)

Nitrogen monoxide is produced on the surface by reaction of \( \text{NH}_3 \) with \( \text{O}_2 \) or \( \text{OH}_3 \) (Eqs. 10 - 11).

\[ \text{NH}_3 + 2 \text{O}_2 \rightarrow \text{NO}_2 + \text{OH}_3 \]  

(10)

\[ \text{NH}_3 + 2 \text{OH}_3 \rightarrow \text{NO}_2 + \text{H}_2\text{O}_3 \]  

(11)

However the formed nitrogen monoxide will dissociate (Eq. 12) or react with \( \text{N}_2 \) to nitrous oxide (Eq. 13). In the case of iridium the dissociation of nitrogen monoxide is faster causing the high selectivity to nitrogen. In the case of platinum dissociation of nitrogen monoxide is more difficult and a larger fraction of the \( \text{NO}_2 \) reacts to form nitrous oxide. Since nitrogen monoxide is not seen as a product, desorption of nitrogen monoxide apparently does not occur. Since on a used catalyst nitrogen monoxide is not observed by XPS or temperature programmed experiments, it also does not remain on the surface.

\[ \text{NO}_2 \rightarrow \text{N}_2 + \text{O}_2 \]  

(12)

\[ \text{NO}_2 + \text{N}_2 \rightarrow \text{N}_2\text{O} \text{(g)} \]  

(13)

The above mechanism also explains the time on stream behavior of the platinum and iridium catalysts. At the start of the reaction the surface composition of the catalyst changes. In the case of platinum the reaction forming \( \text{N}_2\text{O} \) (Eq. 13) is preferred over the reaction to \( \text{N}_2 \) (Eq. 9) at the start of the TOS experiment. Most likely the surface is partly covered with \( \text{NO}_2 \) at this time. However after some time the activity to \( \text{N}_2\text{O} \) decreases and the activity to \( \text{N}_2 \) decreases. Now the surface coverage with \( \text{NO}_2 \) will be low, most probably the surface is mainly covered with \( \text{N}_2 \). The production of \( \text{N}_2 \), however, also decreases rapidly. This is caused by the increasing coverage of the surface with \( \text{OH} \) and \( \text{NH}_3 \) as was established by temperature programmed experiments. The high coverage with \( \text{OH} \) makes the reaction path through the unfavorable reaction of \( \text{NH}_3 \) with \( \text{OH} \) (Eq. 6 - 8) necessary. Since almost only \( \text{NH}_3 \) is found on the surface it was concluded that the reaction of \( \text{OH} \) with \( \text{NH}_3 \) is the rate determining step at steady state reaction. In the case of iridium the surface does not become covered by \( \text{NO}_2 \) shortly after the start of the reaction. Instead the surface becomes covered by \( \text{NH}_3 \) and \( \text{OH} \) as a result of the reaction of \( \text{NH}_3 \) with \( \text{O} \) (Eq. 3 - 5). Apparently the reaction is at first enhanced by an increasing surface coverage. However, similar to the platinum case, the reaction rate
 decreases when the unfavorable reaction of NH₅ with OH (Eq. 6 - 8) becomes necessary. In steady state condition the surface is, like in the platinum case, covered by mainly NH and OH. So also in the iridium case the reaction of OH with NH is the rate determining step at steady state reaction.

Concluding this thesis it is interesting to determine how the catalysts that were tested in this study relate to the industrial application. To compare the activity of the catalysts the Weisz window is often used. A catalyst that has an activity within the Weisz window has the proper activity to be used in industry. The Weisz window ranges from 10⁻⁶ to 10⁻⁵ mole.cm⁻³.s⁻¹. The platinum catalysts that were tested in this study show activities between 10⁻⁸ and 10⁻⁷ mole.cm⁻³.s⁻¹ at a temperature 413 K. However it is known that platinum catalyst show a light off at temperature around 473 K. At a temperature higher than 473 K the platinum catalysts will probably have an activity within the Weisz window. The iridium catalysts show a higher activity, the sintered 0.5 wt% Ir/γ-alumina and the iridium sponge catalyst have an activity that lies within the Weisz window at 413 K. However the iridium sponge catalyst will not be very practical, since it is very expensive. The most promising catalyst of this study therefore is the sintered 0.5 wt% Ir/γ-alumina catalyst. Further research is necessary to determine the activity and selectivity of this catalyst in conditions (reactant concentrations, flow, etc.) more close to the industrial application.
Samenvatting en Conclusie

Dit proefschrift is een verslag van onderzoek naar twee verschillende onderwerpen: de bereiding van kleine platina deeltjes in zeoliet HZSM-5 en de lage temperatuur oxidatie van ammoniak over platina en iridium katalysatoren. De oxidatie van ammoniak over een $[\text{Pt(NH}_3\text{)}_4]^2^+$ complex in zeoliet HZSM-5 verbindt deze twee onderwerpen.

In het tweede hoofdstuk van dit proefschrift is de bereiding van kleine platina deeltjes in zeoliet HZSM-5 beschreven. De voorbehandeling van $[\text{Pt(NH}_3\text{)}_4]^2^+$ ion gewisseld in zeoliet HZSM-5 was bestudeerd met temperatuur geprogrammeerde technieken en diffuse reflectie UV/VIS spectroscopie. Gevonden is dat water samen met de zure sites van de zeoliet de oxidatie van het platina complex al mogelijk maken bij een lage temperatuur ($490$ K). Een voorzichtige voorbehandeling van $[\text{Pt(NH}_3\text{)}_4]^2^+$HZSM-5 in een zuurstofhoudende atmosfeer leidt tot de vorming van het licht groene PtHZSM-5 waarin platina aanwezig is als Pt$^{2^+}$ gecoördineerd aan het zeoliet. Door reductie van deze platina ionen in een waterstof flow worden kleine platina metaaldeeltjes gevormd.

In hoofdstuk 3 is onderzocht of het mogelijk was om $[\text{Pt(NH}_3\text{)}_4]^2^+$ in HZSM-5 te gebruiken al een katalysator voor de lage temperatuur ($473$ K) oxidatie van ammoniak. Er is inderdaad gevonden dat een katalytische reaktie mogelijk is met deze katalysator. Bovendien werd gevonden dat de selectiviteit naar stikstof en distikstofoxide veranderde tijdens de reaktie. Ook werd gevonden dat de selectieve reaktie naar stikstof bevorderd wordt door de aanwezigheid van water in het reaktiemengsel, terwijl het effect van water over het algemeen negatief is. Om inzicht te verkrijgen in het reaktiemechanisme zijn infrarood metingen gedaan. Helaas was het niet mogelijk om hiermee een definitief bewijs voor een bepaald reaktiemechanisme te vinden.

In hoofdstuk 4 is een studie naar de lage temperatuur oxidatie van ammoniak over platina en iridium katalysatoren beschreven. De grootte van de metaaldeeltjes was gevarieerd om het deeltjesgrootte effect te kunnen bestuderen. Er is gevonden dat beide metalen een deeltjesgrootte effect vertonen: grotere metaaldeeltjes bleken aktiever te zijn dan kleine metaaldeeltjes. Bovendien is gevonden dat de iridium katalysatoren aktiever waren dan de platina katalysatoren. Het gedrag van de katalysator tijdens de reaktie was ook bestudeerd.
door de activiteit van de katalysator te meten als functie van de tijd. The platina katalysator bleek steeds minder aktief te worden tijdens de reaktie. De iridium katalysatoren bleek echter in het begin steeds aktiever te worden maar na een tijd weer activiteit te verliezen. Uit metingen van kinetiek bleek dat het oppervlak van de katalysator tijdens de reaktie vol zit met intermediaire reaktieprodukten. Toevoeging van water aan het reaktiemengsel gaf een afname van activiteit te zien voor beide metalen. De platina katalysatoren waren wel gevoeliger voor water dan de iridium katalysatoren.

In hoofdstuk 5 is het oppervlak bestudeerd van platina en iridium katalysatoren die gebruikt werden in de ammoniak oxidatie. Om de invloed van drager materialen uit te sluiten zijn metaal sponsen gebruikt als katalysator. In activiteitsmetingen werd gevonden dat iridium een aktievere katalysator is dan platina. Uit gecombineerde temperatuur geprogrammeerde desorptie en reductie experimenten werd geconcludeerd dat het oppervlak van zowel platina als iridium bedekt is met voornamelijk NH en OH en een beetje NH₂. De resultaat werd bevestigd door XPS metingen. Het reaktiemechanisme geschied door een stapsgewijze dehydrogenering van ammoniak. De snelheidsbepalende stap is de dehydrogenering van NH door OH naar N en water. Het verlies van activiteit wordt dus veroorzaakt door het bedekken van het oppervlak door NH en OH. De hoge selectiviteit naar stikstof van de iridium katalysatoren kan worden verklaard door de sterkere interaktie van iridium met intermediaire reaktieprodukten.

Samengevat is het reaktiemechanisme voor de oxidatie van ammoniak door zuurstof over metalen dat de resultaten van deze studie het best beschrijft de volgende. Eerst worden de reactanten op het oppervlak geadsorbeerd (Vgl. 1 - 2).

\[
\begin{align*}
\text{NH}_3 & \quad \rightarrow \quad \text{NH}_3,a \\
\text{O}_2 & \quad \rightarrow \quad 2 \text{O}_a
\end{align*}
\]

Het oppervlak is leeg bij het begin van de reaktie. Alleen de geadsorbeerde reactanten zijn aanwezig op het oppervlak en kunnen met elkaar reageren, het geadsorbeerde ammoniak wordt gedehydrogeneerd door geadsorbeerde zuurstofatomen (Vgl. 3 - 5).

\[
\begin{align*}
\text{NH}_3,a + \text{O}_a & \quad \rightarrow \quad \text{NH}_2,a + \text{OH}_a \\
\text{NH}_2,a + \text{O}_a & \quad \rightarrow \quad \text{NH}_a + \text{OH}_a \\
\text{NH}_a + \text{O}_a & \quad \rightarrow \quad \text{N}_a + \text{OH}_a
\end{align*}
\]

Maar als het oppervlak raakt steeds voller met OH door deze reakties. Daardoor moet de dehydrogenering van ammoniak via de thermodynamisch ongunstige reaktie met OH plaatsvinden (Vgl. 6 - 8).
De productie van stikstof vindt plaats door de associatieve desorptie reaktie (Eq. 9).

\[
\begin{align*}
2 \text{N}_2 & \rightarrow \text{N}_2(\text{g}) \\
\end{align*}
\]  

Stikstofmonoxide wordt gemaakt op het oppervlak door de reaktie van NH\(_a\) met O\(_a\) of OH\(_a\) (Vgl. 10 and 11).

\[
\begin{align*}
\text{NH}_a + 2 \text{O}_a & \rightarrow \text{NO}_a + \text{OH}_a \\
\text{NH}_a + 2 \text{OH}_a & \rightarrow \text{NO}_a + \text{H}_2\text{O}_a \\
\end{align*}
\]  

Maar het zo gevormde stikstofmonoxide kan weer dissociëren (Vgl. 12) of reageren met Na tot distikstofmonoxide (Vgl. 13). Op iridium is de dissociatie van stikstofmonoxide sneller dan de reaktie naar distikstofmonoxide. Dit veroorzaakt de hoge selectiviteit naar stikstof van deze katalysator. Op platina is de dissociatie van stikstofmonoxide moeilijker en er zal een groter deel van het NO\(_a\) reageren naar distikstofmonoxide. De desorptie van stikstofmonoxide komt niet voor, stikstofmonoxide wordt immers niet waargenomen als produkt. Ook is vastgesteld dat het niet op het oppervlak blijkt zitten, het is niet waargenomen in de XPS en de temperatuur geprogrammeerde metingen.

\[
\begin{align*}
\text{NO}_a & \rightarrow \text{N}_a + \text{O}_a \\
\text{NO}_a + \text{Na} & \rightarrow \text{N}_2\text{O} \ (\text{g}) \\
\end{align*}
\]  

Het bovenstaande mechanisme verklaard ook het gedrag van de katalysatoren als functie van tijd. Tijdens de start van de reaktie veranderd de oppervlakte samenstelling van de katalysator. In het geval van platina is eerst de reaktie die distikstofmonoxide vormt (Vgl. 13) aktiever dan de reaktie naar stikstof (Vgl. 9). Waarschijnlijk is het oppervlak op dat moment gedeeltelijk bedekt met NO\(_a\). Maar de activiteit naar distikstofmonoxide wordt na enige tijd minder terwijl de activiteit naar stikstof stijgt. Nu zal de oppervlaktebedekking met NO\(_a\) klein zijn. Waarschijnlijk is het oppervlak nu voornamelijk gevuld met Na. Echter, de produktie van stikstof daalt ook snel hierna. Dit wordt veroorzaakt door de toenemende bedekking van het oppervlak met OH en NH zoals aangetoond was met de temperatuur geprogrammeerde experimenten. De hoge bedekking met OH maakt het reaktie pad via de onvoordelige reaktie
Hoofdstuk 6

van NH met OH (Vgl. 6 - 8) noodzakelijk. Omdat er vrijwel alleen OH en NH op het oppervlak werd gevonden werd geconcludeerd dat de reaktie van NH met OH de snelheidsbepalende stap moet zijn. Het iridium oppervlak raakt niet gevuld met NO na de start van de reaktie. In plaats daarvan raakt het oppervlak gevuld met NH$_x$ en OH door de reaktie van NH$_x$ met O (Vgl. 3 - 5). Blijkbaar wordt de reactiesnelheid in eerste instantie hoger door een toenemende oppervlaktebezetting. Maar, zoals ook in het geval van platina, gaat de reaktiesnelheid dalen zodra de onvoordelige reaktie aan NH$_x$ met OH (Eq. 6 - 8) nodig wordt. In de stabiele toestand is het oppervlak gevuld met voornamelijk NH en OH, zoals ook voor platina gevonden werd. Dus ook in het geval van iridium is de snelheidsbepalende stap tijdens de stabiele toestand de reaktie van OH met NH.

Ter afsluiting van dit proefschrift is het interessant om te bekijken in hoeverre de katalysatoren uit deze studie zouden werken in de industriële toepassing. Om de activiteiten te vergelijken wordt vaak het Weisz window gebruikt. Een katalysator met een activiteit binnen het Weisz window heeft ongeveer de goede activiteit om te worden toegepast als industriële katalysator. Het Weisz window varieert tussen waarden van $10^{-6}$ tot $10^{-5} \text{mol.cm}^{-3} \text{s}^{-1}$. De platina katalysatoren uit deze studie hebben activiteiten tussen $10^{-8}$ en $10^{-7} \text{mol.cm}^{-3} \text{s}^{-1}$ bij een temperatuur van 413 K. Maar het is bekend dat platina katalysatoren ontbranden vertonen bij een temperatuur ronde 473 K. Daarom zullen de platina katalysatoren waarschijnlijk een activiteit binnen het Weisz window vertonen bij temperaturen boven de 473 K. De iridium katalysatoren zijn aktiever dan de platina katalysatoren. De gesinterde 0.5 wt% Ir/γ-alumina en de iridium spons katalysatoren vertonen al activiteiten binnen het Weisz window bij een temperatuur van 413 K. Echter de iridium spons katalysator is niet erg praktisch want het is een erg dure katalysator. De meest veelbelovende katalysator uit deze studie is daarom de gesinterde 0.5 wt% Ir/γ-alumina katalysator. Meer onderzoek is echter nog nodig naar de activiteit en selectiviteit van deze katalysator bij condities (concentratie van reaktanten, flow snelheid, etc.) die dichter bij de industriële toepassing staan.
Dankwoord

Zoals het cliché wil is het werk dat beschreven is in een proefschrift natuurlijk niet het werk van één persoon. Daarom wil ik op deze plaats een aantal mensen persoonlijk bedanken voor hun bijdrage. Op de eerste plaats natuurlijk mijn promotor, Rutger van Santen, die met zijn niet aflatend enthousiasme mij telkens weer op de 'grote lijn' wees. Op meer praktisch gebied komt dan direct Joop van Grondelle, waar ik altijd bij terecht kon met mijn vragen en die mij soms ook weer met beide benen op de grond zette bij te wilde plannen. Verder natuurlijk door de jaren heen alle leden van de metaalgroep voor inhoudelijke en minder inhoudelijke discussies. Van hen wil ik mijn kamergenoten met name bedanken: Piet IJben, Frank de Gauw, Pieter Stobbelaar en Kieran Hodnett. Ook de studenten Martin Waals en Ruben Bajens hebben hun bijdrage geleverd door het uitvoeren van een groot aantal experimenten.

Van buiten de metaalgroep wil ik graag Marco Hendrix van de vakgroep TVM bedanken voor het uitvoeren van de SEM metingen. Ook wil bij deze Particia Kooymen van het Nationale Centrum voor HREM aan de TU Delft bedanken voor het grote aantal HREM metingen die ze heeft uitgevoerd. Jammer genoeg heeft een groot aantal het proefschrift niet gehaald, met name die betrekking hadden op de mysterieuze ‘dip’. Ook de EXAFS metingen van Barbara Mojet van (toen) de Universiteit Utrecht (nu capaciteitsgroepgenoot) hadden betrekking op de ‘dip’ en hebben dit boekje niet gehaald. De op het laatste moment nog uitgevoerde infraroodmetingen van Jos van Wolput zijn wel in het proefschrift gekomen. De TAP experimenten die zijn uitgevoerd in samenwerking met Ton Sommen en Jozef Hoebink hebben helaas ook niet het boekje gehaald. De XPS experimenten van Peter Thüne wel, zij vormen een goed aanvullend bewijs voor de oppervlakte bedekking van de sponzen.

Mijn ouders bedank ik voor de steun en richting die ze mij altijd hebben gegeven. Ik denk dat pappa zeker trots zou zijn geweest als hij dit proefschrift zou kunnen lezen. Ik wil Annemarie graag bedanken voor haar steun en geduld. Vooral tijdens de laatste loodjes was ik niet altijd even ‘aanwezig’. Tenslotte wil ik mijn dochter Hanna bedanken. Niet voor de slapeloze nachten, maar wel voor haar plezier. Daardoor werd ik steeds herinnerd aan wat echt belangrijk is.
Curriculum vitae


In 1993 startte hij met de korte onderzoekersopleiding bij de vakgroep anorganische chemie en katalyse, die hij in 1996 afslotte. Als verlenging van de onderzoekersopleiding werd het onderzoek naar de lage temperatuur oxidatie van ammoniak gestart. Het geheel van onderzoeksopleiding en promotieonderzoek is beschreven in dit proefschrift en werd uitgevoerd onder leiding van prof. dr. R.A. van Santen.
Stellingen

behorende bij het proefschrift

Low Temperature Oxidation of Ammonia over Platinum and Iridium Catalysts

van

Arnoldus Cornelis Maria van den Broek

1. Het is opportunistisch om op basis van surface science experimenten te suggereren dat bij de industriële productie van salpeterzuur een hogere zuurstofconcentratie gebruikt zou moeten worden.

2. De conclusie dat de scherpe piek in het TPMS experiment van [Pt(NH$_3$)$_4$]NaY veroorzaakt wordt door verplaatsing van het complex naar de sodalietkooien van zeoliet Y kan niet kloppen omdat eenzelfde scherpe piek waargenomen wordt in zeoliet ZSM-5, die geen sodalietkooien bevat.
Dit proefschrift

3. De waarde van de conclusie dat een koper katalysator actiever is dan een platina katalysator in de oxidatie van ammoniak is zeer beperkt als het metaalgehalte van beide katalysatoren zeer verschillend is (platina 1.0 wt% en koper 7.3 wt%) en de deeltjesgrootte van de platina deeltjes bovendien niet bepaald is.

4. Het veel voorkomende gebruik van de standaarddeviatie als foutengrens geeft aanleiding tot verkeerde interpretatie van meetgegevens.

5. In de patentliteratuur worden vaak appels met peren vergeleken.
6. Kleine verschillen in activiteit bij een hoge conversie moeten hooguit tot voorzichtige conclusies leiden.  

7. Experimenten bij een lage druk hebben beperkt nut in het geval van oxidatie van ammoniak bij een lage temperatuur, aangezien de vorming van distikstofoxide pas wordt waargenomen bij experimenten uitgevoerd bij drukken hoger dan 100 Pa.

8. De invoering van concurrentie op het spoor heeft een ongewenste waardevermindering van de NS-jaarkaart tot gevolg.

9. Bij een trein die tussen Amsterdam en Antwerpen (170 km) nog drie maal stopt kan geen sprake zijn van een Hoge Snelheids Trein (HST).

10. Het is merkwaardig dat de temperatuur in winkels afgesteld lijkt te zijn op het personeel en niet op de klanten.