6-aminocapronitrile as an alternative monomer for the nylon 6 synthesis

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6-aminocapronitrile as an alternative monomer for the nylon 6 synthesis

PROEFSCHRIFT

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door

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geboren te Tilburg
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“Not to be absolutely certain is, I think, one of the essential things in rationality.” – Bertrand A.W. Russel, Am I an atheist or an agnostic?

Voor Suzanne
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Introduction

As the world’s first synthetic fiber and engineering plastic, nylon has a big influence on today’s society. Due to the unprecedented material properties, the introduction of nylon opened the door to all kind of novel products. Besides the value for today’s life, synthetic polyamides are also very important for the development of polymer and material science. The development of nylon-6,6 by Wallace Carothers, for example, provided the indisputable experimental prove for Staudinger’s hypothesis that chain molecules with a high molecular weight do exist. Today, nyons are still important engineering plastics and well-known for their fiber applications.

Nylon is the first synthetic, semi-crystalline polymer that is not strongly temperature sensitive in comparison with other polymers. A remarkable feature of most polyamides is that

* Although the definition of engineering plastics is not strict, it in general states that engineering plastics are thermoplastic polymers that behave according to the standard engineering equations for metals. Engineering thermoplasts have properties that are equal and in some cases even better than that of metals, more easy processing and lower weight for example. Therefore engineering plastics can replace metals. Usually engineering plastics retain their thermal and mechanical properties up to a minimum temperature of ca. 200°C.
they withstand high loads and tension for elongated periods of time over a large temperature range and in chemically aggressive environments. The initial development was directed to make a material that could be drawn into fibers and the first commercial products were therefore purely based on nylon fibers. Well-known examples of these initial products are toothbrushes, panties and parachutes. The fact that panties are also called nylons reflects the impact of the material, this is illustrated by the old advertisement shown in Figure 1. Due to the large window of processing conditions and the relative simplicity in which the material can be modified, the development of nylon for engineering plastic applications was started shortly after the introduction of the fiber. Up to now, nylon takes a prominent position within the family of engineering plastics.

![Diagram of AB and AABB nylon structures]

Figure 1.2. Schematic representations of AB- and AABB-type nylons and their most important examples.

Initially the term nylon only covered linear, aliphatic chains with regularly repeating amide functionalities, \(-\text{C}(=\text{O})-\text{NH}\)-. Currently, however, nylon is a generic term for aliphatic and semi-aromatic polyamides. Depending on the monomers used, polyamides can be of the AB- or AABB-type. AB-type polyamides are homopolymers with only one amide bond per repeating unit and AABB-type polymers are alternating copolymers with two amide bonds per repeating unit, see Figure 1.2. Nylon-6 is the major representative of the AB-type polyamides and nylon-6,6 is the major representative of the AABB-type polyamides.

Nylon-6 and nylon-6,6 are the first two commercial polyamides and are still the most important polyamides with respect to their production volumes. Both nylon-6,6 and nylon-6 were developed in the 40’s of the last century, respectively by Wallace Carrothers at DuPont and by Paul Schlack at I.G. Farben. Together, these polyamides account for more than 95% of the total amount of nylon used in the world, and nylon-6 is responsible for 59% of this quantity. The future success of nylons is determined by the continuous innovation of properties, reduction of production costs, further improvement
of the quality, and a reduction of the environmental impact of both monomer and polymer synthesis. Especially the production of the monomer for nylon-6, \(\varepsilon\)-caprolactam (CL), should be improved. An important note should be made that the enduring myth of producing large amounts of inorganic waste per kilogram of CL does not hold any longer, as today the produced \((\text{NH}_4)_2\text{SO}_4\) is a valuable fertilizer. However, avoiding the use of hydroxyl amine for the nylon-6 synthesis is still a big improvement, because of its explosive behavior and cost. Together with the fact that nylon-6 is one of the polyamides with the largest production scale, the improvement of the chemistry for synthesis of nylon-6 starting from the raw materials has a broad bearing.

**The currently applied route to nylon-6**

Industrially, nylon-6 is made out of the monomer CL. Besides 6-aminocaproic acid, that is sometimes used on lab scale, no other monomers are applied for the nylon-6 synthesis. The concise representation of the multi-step reaction scheme from the raw material benzene to nylon-6 is shown in Figure 1.3.

![Figure 1.3. \(\varepsilon\)-Caprolactam synthesis from benzene.](image)

The nylon 6 route via the consecutive manufacturing of the intermediates cyclohexanone oxime and CL out of the raw material benzene accounts for more than 95% of the produced nylon-6. Cyclohexanone is often considered as the starting material for the nylon-6 synthesis. However, cyclohexanone itself is an intermediate that is produced either by the oxidation of cyclohexane (~60%) or by the hydrogenation of phenol (~40%). The direct production of cyclohexane resulting from the fractional distillation of crude oil is too low to fulfill the demand. Therefore most of the cyclohexane is produced by hydrogenation of benzene. As the amount of phenol

---

\[ A \text{ complete overview of all the applied processes for the synthesis of } \varepsilon\text{-caprolactam out of the raw materials can be found in the book “Industrial Organic Chemistry” by Weissermel and Arpe. All the routes to } \varepsilon\text{-caprolactam that were ever used and are under development are described in Ullmann's Encyclopedia of Industrial Chemistry.} \]
produced by the cracking of oil can also be neglected, phenol is mainly produced via the cumene process. Cumene in its turn is again obtained from benzene. The main raw material for the nylon-6 synthesis is therefore benzene, and starting from benzene it takes 5 process steps to obtain nylon-6.

In general a perceived disadvantage of the applied route is the large amount of sulphuric acid and ammonia produced as side products in the cyclohexanone ammoxidation and during the Beckmann rearrangement, see Figure 1.4. However, the actual disadvantage is the use of hydroxylamine, because of its cost and explosiveness.

![Figure 1.4. The equilibrium of the cyclohexanone ammoxidation with hydroxylammonium sulphate and the Beckmann rearrangement of cyclohexanone oxime to CL.](image)

Until recently, there was no hydroxylamine-free route to CL available. However, Sumitomo recently started the full-scale production of CL without co-producing any hydroxylamine.6 This plant combines Enichem's direct ammoxidation of cyclohexanone (Figure 1.5) with the vapor-phase Beckmann rearrangement.5;7 However, the peroxide used is still explosive like hydroxylamine.

![Figure 1.5. The direct, catalytic ammoxidation of cyclohexanone with NH₃ ad H₂O₂.](image)

**Hydrolytic ring opening polymerization of ε-caprolactam**

Several polymerization techniques for the polymerization of CL exist, but the most commonly used polymerization method is the hydrolytic ring opening polymerization. Anionic polymerizations are only applied for specialty products, which only account for a small fraction of the world-wide production of nylon-6. The hydrolytic ring opening polymerization consists of three equilibrium reactions, as shown in Figure 1.6. Initiation of the polymerization proceeds by the hydrolysis of a small part of the present CL. The direct addition of CL to the amine end-group of a growing chain subsequently increases the molar mass, which implies a ring opening polymerization of CL. Condensation of two linear polymer molecules also results in a molar mass increase, becoming important when the CL concentration has become low. A substantial initial water concentration is
advantageous for the ring-opening of CL, but eventually the removal of the same amount of water is required to promote the polycondensation to high molar mass nylon 6.

Note that the ring opening polymerization of CL occurs by the attack of the carbonyl of CL by the free electron pair of the primary amines generated in step A. The generated carboxylic acid groups catalyzes the ring opening polymerization.

Figure 1.6. The three equilibrium reactions that are involved in the water-initiated polymerization of ε-caprolactam. A) Caprolactam hydrolysis, B) the addition of caprolactam to a polyamide chain and C) condensation of two polyamide chains.

To obtain nylon-6 with good properties, a minimum weight average molar mass of 15,000 – 20,000 g/mol is required. An unfortunate but unavoidable characteristic feature of polycondensation reactions is that very high conversions are required to obtain appreciable molar masses. The required minimum molar mass obtained with this polymerization mechanism results in the requirement that the conversion should be larger than 99.25% with complete selectivity for the condensation product, starting with a 100% pure monomer. Every deviation from this requirement results in a polymer with reduced molar mass and inferior properties.

Figure 1.7. The equilibrium reaction responsible for cyclic oligomers, 

The synthesis of high molecular weight nylon-6 is hampered by the equilibrium between the monomer (reaction B of Figure 1.6) and higher, cyclic oligomers (see Figure 1.7) with the polymer. The CL and higher, cyclic oligomers are formed by ‘back-biting’ reactions of the amine end group with an amide group in the main chain. Increasing the polymerization temperature has a negative effect, as the equilibrium of Figure 1.7 shifts
to the right and equilibrium B of Figure 1.6 shifts to the left with increasing polymerization temperature. The equilibrium amount of cyclic oligomers (mainly CL) can increase to more than 10 wt% for a polymerization temperature of 280°C.\(^1\) Such large amounts of CL and higher cyclic oligomers present in the end product make the product sticky and the properties are inferior. Therefore, the nylon-6 has to be always purified by extraction after the polymerization. As a result, amount of space and equipment allocated for the polymer extraction and the recycling of the monomer is generally larger than for the polymerization unit itself. Extraction and recycling of both the monomer and cyclic oligomers, therefore, accounts for considerable additional operational costs.

The commercial production of nylon-6 usually proceeds through a two step, continuous process, e.g. as represented by Figure 1.8.\(^8\) In the first part a small amount of the CL is hydrolytically ring-opened, followed by the direct ring opening polymerization of CL. About 85% of the CL is converted into a pre-polymer in this step. The polymerization is continued with the further condensation in a vertical reactor, in which the polymer moves slowly downwards with increasing viscosity at temperatures between 250 °C and 270 °C. The polymer is subsequently withdrawn at the bottom, the extruded polymer strand is cooled down (‘crystallized’) in water and cut into chips. Finally the chips are sent to the warm water extractor, where monomer and low molecular weight products are removed from the product. These extracted products are recycled in subsequent polymerization runs. The high molecular weight polyamide chips are dried with a hot, inert gas in a last step.

![Diagram](Figure 1.8. A representative polymerization process for nylon-6 a) Feed tank; b) VK tube; c) Pourer; d) Pelletizer; e) Water bath; f) Extractor; g) Dryer.\(^8\))
**Directions in the improvement for the ε-caprolactam synthesis**

Since the state of the art of the nylon-6 production is still far from optimal, a lot of effort is invested into both the development of improved and completely novel processes. There are two main approaches to improve the CL production, namely i) the improvement of the CL synthesis with cyclohexanoneoxime as the intermediate and ii) the use of butadiene as an alternative feedstock for the synthesis of CL (Figure 1.9).

![Diagram of nylon-6 developments](image)

**Figure 1.9. The main directions of nylon-6 developments.**

Although the use of butadiene has a comparable price to benzene, it allows the use of NH₃ to incorporate nitrogen in the monomer. The use of NH₃ is a big advantage compared to the use of hydroxylamine.

**Catalytic process improvements for the current caprolactam route**

A very interesting discovery is the direct synthesis of CL out of cyclohexanone using micro porous aluminophosphates, as depicted in Figure 1.10, as hydroxyl amine is generated in situ and formed out of NH₃ and air as the reactants. The principle behind this one-step, solvent-free process is the use of a bifunctional, heterogeneous nanoporous catalyst, which contains isolated acid and redox sites. This well-characterized catalyst generates hydroxylamine at the redox sites, simply using air as the oxidant. The hydroxylamine is subsequently converted with cyclohexanone into cyclohexanoneoxime. CL is finally formed as a result of a catalytic conversion of the oxime at the Brønsted acid sites. The developed systems convert cyclohexanone into CL with a 65 to 78% selectivity in air at 80 °C. The big improvement of this process in comparison with the
conventional processes is the in situ hydroxylamine generation and the absence of ammonium sulfate formation during the Beckmann rearrangement.

Figure 1.10. The direct synthesis of ε-caprolactam out of cyclohexanone and ammonia with microporous aluminophosphates.11

An innovative method, but hardly explored yet is the formation of cyclohexanone oxime directly out of cyclohexane, see Figure 1.11.12 The formation of cyclohexanone oxime is observed when cyclohexane is reacted with tert-butyl nitrite in the presence of a catalytic amount of imide. The consumed tert-butyl nitrite can be regenerated from tert-butyl alcohol with NO2 for example. However, the yield of cyclohexanone oxime obtained with this method is still low and the use of NO2 should be avoided.

Figure 1.11. Nitrosation of cyclohexane with tert-butyl nitrite.

Besides the two methods schematically presented in Figure 1.10 and Figure 1.11, there are other new developments in the field of the catalytic cyclohexanone ammoximation13,14 and the catalytic Beckmann rearrangement.15-26 The development of the Beckmann rearrangement using a supercritical water microreaction system is an example of these new developments, which allows the formation of CL with appreciable selectivity in the absence of any acid.27 However, the design of a liquid phase, bulk process operating at temperatures above 400°C remains problematic.

**Alternative routes with butadiene as raw material**

The use of butadiene as a starting material for the nylon synthesis is very attractive, since it is relatively cheap and its use strongly reduces the amount of inorganic waste. Two best explored routes so far for the synthesis of CL out of butadiene are shown in Figure 1.12.5 The upper route of Figure 1.12 uses alkoxy carbonylation followed by
Nylon 6 synthesis

hydroformylation and reductive ammination and the bottom route applies hydrocyanation to increase the length of the alkyl chain. The alkoxy carbonylation of the upper route is still problematic and rhodium catalyzed hydroformylation is very expensive, which limits the potential of the upper route. Although the selective hydrogenation of adiponitrile into 6-aminocapronitrile (ACN) is not fully optimized yet, the chemistry is already well developed. This increases the chance for industrial application of the bottom method appreciably.

Figure 1.12. Butadiene-based routes to ε-caprolactam or nylon-6.

The ε-caprolactam synthesis out of butadiene using hydroesterification.

The CL synthesis out of butadiene via 6-aminohexanoate as depicted in Figure 1.12 are: i) the hydroesterification of butadiene to methyl-3-pentenoate, ii) the isomerisation of methyl-3-pentenoate to methyl-4-pentenoate followed by the hydroformylation of methyl-4-pentenoate to methyl-5-formylvalerato (this is preferably done in a single step), iii) the reductive amination of methyl-5-formylvalerato to methyl-6-aminohexanoate and iv) the cyclization of 6-aminohexanoate. Both BASF28-30 and a joint group of DSM and DuPont researchers31-34 developed this route, but the process has not been commercialized so far.

The hydroesterification of butadiene with carbon monoxide and methanol is performed using a cobalt28 or palladium complex.35 Both catalysts result in high yields of methyl-3-pentanoate and negligible amounts of by-products. As the palladium catalyst has a detrimental effect on the subsequent transformation, it has to be separated from the reaction mixture and recycled.

In the following step, the methyl-3-pentenoate is in situ isomerized to methyl-4-pentenoate and the internal functionalized olefin is directly hydroformylated to methyl-5-formylvalerato with the homogeneous catalyst. All possible reaction pathways for methyl-3-pentenoate with CO and H2 are shown in Figure 1.13.33 The isomerisation can be performed by reactive distillation, using a zeolitic or pyridine based catalyst,29 and using ionic liquids, which simplifies the recycling of the homogeneous catalyst.36,37
similarities between the possible reaction pathways for the hydroformylation reaction of methyl-3-pentanoate, as shown by Figure 1.13, give rise to a low selectivity.

![Figure 1.13. The different reaction pathways in the hydroformylation of methyl-3-pentanoate, with the desired pathway captured by the frame.](image)

Methyl-5-formylvaleroate is subsequently transformed into methyl-6-aminohexanoate or 6-aminohexanoic acid (not shown). The reductive amination of methyl-5-formylvaleroate can be conducted either in the liquid or in the gas phase, using hydrogenation catalysts in the presence of both NH\textsubscript{3} and H\textsubscript{2}.\textsuperscript{5} Cyclization of 6-aminohexanoate to CL forms the final step of this route, which proceeds with a 99.1% selectivity at a conversion of about 97%.\textsuperscript{38;39} The hydrolysis of methyl-5-formylvaleroate into 5-formylvaleroic acid has also been reported, which is then followed by the reductive amination and the subsequent cyclic amidation to CL.\textsuperscript{31;34}

The caprolactam synthesis out of butadiene using hydrocyanation

The CL synthesis out of butadiene via ACN consists of the following three steps, as shown in Figure 1.12: \textit{i}) the hydrocyanation of butadiene (which is actually a three step process), \textit{ii}) the selective mono-hydrogenation of adiponitrile and \textit{iii}) the hydrolytic amidation of ACN, furnishing CL. Although it is not efficient to introduce two nitrogen atoms first and to remove one of them in a subsequent step, the hydrocyanation route has more potential than the hydroesterification step, as the chemistry is better accessible than the hydroesterification route. Adiponitrile via hydrocyanation of butadiene is an existing process.

1. Hydrocyanation

The most commonly applied method to produce adiponitrile is the addition of two molecules of hydrogen cyanide to one butadiene molecule, a process that is developed
and commercialized by DuPont. The formation of hydrogen cyanide is mainly accomplished by the ammoxidation of methane, but large amounts of HCN are also formed as a byproduct of the acrylonitrile synthesis. Other known routes to adiponitrile are the dimerization of acrylonitrile and the dehydrative amination of adipic acid. However, these routes have not been commercialized.

2. Hydrogenation

The selective catalytic hydrogenation of adiponitrile towards primary amines is extensively studied, both directed to the partial and complete hydrogenation of adiponitrile to ACN as well as to hexamethylenediamine, respectively. The main problem with the primary amine formation through nitrile hydrogenation is the formation of secondary and tertiary amines as side products.

![Diagram of selective hydrogenation of adiponitrile](image)

Figure 14. The selective hydrogenation of adiponitrile into 6-aminocapronitrile via the intermediate imine.

The formation of a primary amine consists of the addition of two dihydrogen molecules to one nitrile moiety via an intermediate imine, as shown in Figure 14. The secondary amine is formed when the imine reacts with an already formed primary amine followed by hydrogenation, as shown in Figure 1.15. In similar way a tertiary amine is formed by the reaction of the imine with an already formed secondary amine.

![Diagram of secondary and tertiary amines formation](image)

Figure 1.15. The overhydrogenation of 6-aminocapronitrile and the formation of secondary amines

The formation of secondary and tertiary amines is dependent on the nature of the metal catalyst and in general increases in the order of Co< Ni< Ru< Rh< Pd< Pt. The metals Co, Ni and Ru are therefore preferred for the selective hydrogenation of adiponitrile into primary amines. In industry, the hydrogenation is mostly performed in
the liquid phase, at high hydrogen pressures and with the use of Raney Nickel.\textsuperscript{53-55} A large number of attempts have been made to replace Raney Ni by catalysts with a cleaner preparation, but it appears difficult to avoid deactivation of the catalyst systems.\textsuperscript{50}

Besides the aforementioned secondary and tertiary amine formation, the selective hydrogenation of adiponitrile into ACN is also complicated by the hydrogenation of the second nitrile, as depicted in

![Diagram of adiponitrile hydrogenation](attachment:diagram.png)

Figure 1.15. The main reason for this problem is that there is no chemical preference for the hydrogenation of only one nitrile. With the formation of hexamethylenediamine being a consecutive reaction, the selectivity to ACN increases with decreasing hydrogenation conversion.\textsuperscript{45} This confines processes to be operated at low conversions and complicates the comparison of the selectivities of different catalytic systems.

Other by-products of the adiponitrile hydrogenation are azepine derivatives, especially tetrahydroazepine. These azepines are not easily separated from the reaction mixtures and cause undesired limitation of the molecular weight of the targeted polymers, colouring and branching. Specific purification methods of the product mixtures are therefore necessary.\textsuperscript{56,57}

3. Hydrolytic amidation to caprolactam

ACN is a good alternative precursor for the production of CL, as shown by Figure 1.16. Independent of the use of a catalyst the processes reported operate at temperatures of 300°C and higher.\textsuperscript{58-61} However, at these temperatures the conversion of the uncatalyzed reaction is already appreciable.\textsuperscript{62} Without the use of a catalyst, for example, a 10 mol% aqueous solution of ACN results in 93% CL yield after one hour reaction at 300°C, which raises doubt about the effectiveness of the added catalysts.\textsuperscript{61}

Table 1 shows a selection of the best catalytic systems and their performance for the conversion of ACN into CL. The results shown are all obtained in gas phase processes with high catalyst loadings and high water content of the reactor feed. A further
comparison is difficult due to the differences in e.g. residence times and reaction temperature.

\[
\text{H}_2\text{N} \quad \text{N} \quad + \quad \text{H}_2\text{O} \quad \xrightarrow{[\text{MO}_x]} \quad \text{N} \quad \text{H} \quad + \quad \text{NH}_3
\]

Figure 1.16. Caprolactam synthesis out of 6-aminocapronitrile and water (MO\textsubscript{x} = a metal oxide, as shown Table 1).

**Table 1. A comparison of the catalyst systems used in the gas-phase cyclization of 6-aminocapronitrile.**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base catalyst</th>
<th>Additives</th>
<th>T\textsubscript{reaction} (°C)</th>
<th>Yield (%)</th>
<th>Remarks</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>-</td>
<td>305</td>
<td>92</td>
<td></td>
<td>63</td>
</tr>
<tr>
<td>2</td>
<td>ZrO\textsubscript{2}</td>
<td>-</td>
<td>360</td>
<td>88.5</td>
<td>7.5 g ACN/h</td>
<td>58</td>
</tr>
<tr>
<td>3</td>
<td>ZrO\textsubscript{2}</td>
<td>PO\textsubscript{4}\textsuperscript{3-}</td>
<td>360</td>
<td>94.0</td>
<td>Idem</td>
<td>58</td>
</tr>
<tr>
<td>4</td>
<td>ZrO\textsubscript{2}</td>
<td>PO\textsubscript{4}\textsuperscript{3-} + Mn\textsuperscript{4+}</td>
<td>360</td>
<td>97.9</td>
<td>Idem</td>
<td>58</td>
</tr>
<tr>
<td>5</td>
<td>ZrO\textsubscript{2}</td>
<td>SO\textsubscript{4}\textsuperscript{2-} + Mn\textsuperscript{4+}</td>
<td>360</td>
<td>85.1</td>
<td>Idem</td>
<td>58</td>
</tr>
<tr>
<td>6</td>
<td>TiO\textsubscript{2}</td>
<td>-</td>
<td>280</td>
<td>98.9</td>
<td>0.07 g ACN/(ml\textsubscript{cat} \cdot h)</td>
<td>60</td>
</tr>
<tr>
<td>7</td>
<td>ZrO\textsubscript{2}</td>
<td>-</td>
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<td>92.2</td>
<td>Idem</td>
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<tr>
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<td>Nb\textsubscript{2}O\textsubscript{5}</td>
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<td>91.0</td>
<td>Idem</td>
<td>60</td>
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<tr>
<td>10</td>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>1.5% TiO\textsubscript{2} + 1.5% Fe\textsuperscript{3+}</td>
<td>300</td>
<td>99.7</td>
<td>1 g ACN/(g\textsubscript{cat} \cdot h)</td>
<td>59</td>
</tr>
</tbody>
</table>

**An alternative for the ring-opening polymerization of caprolactam: The direct polymerization of 6-aminocapronitrile**

The direct nylon-6 production out of the monomer ACN, see Figure 1.17, obtains a lot of industrial attention as an alternative for the polymerization of CL.\textsuperscript{65-72} Instead of synthesizing, purifying and subsequently polymerizing CL as discussed before, ACN is directly polymerized during the hydrolytic amidation without the isolation of CL. In comparison with the applied, five process steps starting from benzene, this route results in a reduction with two process steps, which yields a significant gain with respect to the energy and resource consumption and waste production. This method is therefore especially attractive.
Figure 1.17. The process steps for the formation of nylon-6 starting from butadiene without the formation of caprolactam as an isolated intermediate.

Figure 1.17 depicts the three process steps to make nylon-6 via the direct polymerization of ACN. These steps are i) the complete hydrocyanation of butadiene (a three step process), ii) the selective hydrogenation of the formed adiponitrile and iii) the hydrolytic polymerization of ACN.

The nylon-6 production out of the alternative monomer ACN has to obey the same restrictions as every arbitrary polycondensation reaction. The monomer has to be very pure, the conversion of the co-reactive group at the end of the polycondensation reaction has to be over 99.25%, and side reactions are not allowed. Leaving out the intermediate isolation of CL saves a process step, but increases the required control in comparison with the polymerization of CL, as the nitrile has to be transformed in situ too.

The overall chemistry involved in the polycondensation of ACN is bound to the complete transformation of equimolar amounts of a nitrile, a primary amine and water into an N-substituted carboxylic amide, with ammonia as the only other reaction product, see Figure 1.20. Although the discovery of the polymerization already dates back to the early days of the nylon development, the knowledge about the synthesis of polyamides out of amine and nitrile functionalities is limited, and to the best of our knowledge, is almost completely covered by patents only.

Figure 1.18. The effect of side reactions of the amine functionality during the polymerization of 6-aminocapronitrile.

The complete hydrolysis of the nitrile groups is required to obtain a high molecular weight nylon-6. A major constraint for the conditions used for the nitrile hydrolysis is that the applied method should not result in side reactions of the primary amine. As primary amines can form secondary and tertiary amines (vide supra), this can lead to
branches and chain stoppers for the polymerization of ACN, as shown in Figure 1.18. The resulting loss of stoichiometry due the secondary and tertiary amine formation also reduces the molecular weight.

\[
\begin{align*}
\text{RC}l \text{O} \text{O} \text{O} \text{OR} \text{OR} \text{OR} \text{OR} \text{OH} \text{NH}_2 & \quad \rightarrow \quad \text{RN} \text{RN} \text{H} \text{O} \text{OR} \text{OR} \\
\text{Decreasing reactivity towards nucleophilic substitution}
\end{align*}
\]

Figure 1.19. The order of reactivity towards nucleophilic substitution.

N-alkyl amides are generally made by the acylation of amines.\textsuperscript{73} As depicted in Figure 1.19, the polycondensation of amide functionalized monomers is already less advantageous than the polycondensation of a carboxylic acid functionalized monomer due to its higher chemical stability. The hydrolysis of a nitrile with an amine is, however, even more difficult, as nitriles are less reactive than amides. Hence, if nitrile functionalities are to be used with an appreciable performance, specific actions have to be taken to activate the nitrile.

\[
\begin{align*}
\text{nH}_2\text{N} \text{N} \text{N} + \text{H}_2\text{O} \quad & \quad \rightarrow \quad \text{nH}_2\text{N} \text{N} \text{N} \text{O} \text{O} \text{OH} \\
\text{6-aminocapronitrile} & \quad \rightarrow \quad \text{nylon 6}
\end{align*}
\]

Figure 1.20. The Polymerization of 6-aminocapronitrile.

Despite the potential of the method to produce N-substituted amides out of nitriles and amines, the formation of N-alkyl amides out of nitriles and amine reagents obtained only little attention in the literature so far. Except for some dinitriles and acetonitrile,\textsuperscript{74,75} the combined hydrolysis-aminolysis reaction of a nitrile group with primary and secondary amines requires a catalyst to give substituted amides and ammonia as the products.\textsuperscript{75-78} So far, the best results were obtained using the Lewis acid RuH\(_2\)(PPh\(_3\))\(_4\).\textsuperscript{76} Nevertheless, quantitative formation of N-alkyl amides out of the corresponding nitrile and amine, crucial for the synthesis of polyamides, has only been achieved for N-methyl- and N-hexyl piperidones.\textsuperscript{76} The possible routes for the formation of N-alkyl amides out of
nitrile and amine functionalities with water are shown in Figure 1.21. The knowledge about the separate reactions is, however, limited and the importance of the possible routes is therefore difficult to appreciate.

![Chemical Reaction Diagram](image)

**Figure 1.21. The possible chemistry for the formation of N-alkyl amides out of a nitrile and an amine.**

To activate the nitrile the reaction temperature can be increased, a catalyst can be used, both homogeneous and heterogeneous, or enzymes can be used. For the nitrile hydrolysis catalyzed by homogeneous mineral acids or bases, high concentrations of the acid or base are required.\(^{79}\) This should be prevented due to its corrosive effect on equipment. The use of biocatalysts is interesting, but the scarcity of suitable and well-characterized nitrile-converting enzymes is a barrier to their application.\(^{80}\)

A relatively simple method to enhance the reaction rate and to reach the required complete nitrile hydrolysis is the application of temperatures above 200°C.\(^{62,81-86}\) However, the application of high temperatures has its drawbacks, as high temperatures often lead to the formation of secondary or tertiary amines out of the primary amine, especially when catalysts are used.\(^{87,88}\) The operating temperature is limited by the ceiling temperature of nylon-6 around 280°C and above 320°C cracking reactions start to play a role. Working at not too high temperatures is therefore the only solution to this problem. To compensate for the decrease in hydrolysis rate at lower temperatures, the hydrolytic amidation of a primary amine with a nitrile should therefore be effectively catalyzed.

The best results up to now for the polymerization of ACN are obtained with a two step process. In the first step a high nitrile conversion is obtained using a catalyst and in the second step the molar mass is further increased by condensation by completely removing both water and ammonia.\(^{71}\) A heterogeneous TiO\(_2\) catalyst is applied for the nitrile hydrolysis, combined with the continuous addition of water and removal of aqueous ammonia. After two hours of hydrolysis at 270°C and 30 bar in the first step and
2 hours condensation at 270°C and 1 bar, a product with a relative viscosity of 2.95 in 96% sulphuric acid is obtained. This viscosity corresponds to an average $M_n$ of approximately 16,000 g/mol.

Besides the specific application for the production of nylon-6 out of ACN, the method can also be applied for the formation of AABB polyamides out of monomers based upon dinitriles and diamines.\textsuperscript{87,89,90} However, the polycondensation of dinitriles and diamines introduces an extra complication regarding the required exact stochiometric ratio of dinitrile and diamine in the reaction mixture. Only with exact stochiometric amounts of the diamine and the dinitrile a high molecular weight product can be produced. In contrast to dinitrile/diamine systems, stoichiometry is intrinsically present for the polycondensation of aminonitriles.

**Aim and outline of this thesis**

The preceding discussion clearly demonstrates that the development of novel processes for the nylon-6 production out of the raw material butadiene has distinct advantages over the current process. Especially the polymerization of ACN is a major improvement compared to the current polymerization of CL and has good perspectives. The work described in this thesis is therefore directed towards the development of viable chemistry for the synthesis of nylon-6 out of ACN on a large scale, resulting in an initial process design.

Activation of the nitrile using an elevated temperature, and/or homogeneous or heterogeneous catalysis is first studied to identify the most promising system. The comparison of the different methods is performed using a model reaction, consisting of a monofunctional aliphatic nitrile, pentanenitrile, and a monofunctional primary amine, hexylamine, in an aqueous environment. In Chapter 2 the behavior of the model reaction is studied at rather mild hydrothermal conditions and using the catalyst RuH$_2$(PPh$_3$)$_4$, previously reported in the literature.\textsuperscript{76} In Chapter 3 the results for the screening of a number of heterogeneous catalysts is discussed and the performance of the best catalysts is further investigated. A zirconium based heterogeneous catalyst appears to be the best system for a viable process. As not much is known about the catalyzed nitrile hydrolysis, the nitrile hydrolysis at the metal oxide surface is studied with infrared spectroscopy. The insights gained from this study are reported in Chapter 4.

In Chapter 5 the polymerization of ACN testing several different conditions is discussed, using the most promising heterogeneous catalyst.

Chapter 6 combines the obtained chemical knowledge for the design of a process for the polymerization of ACN on a large scale. The process design is based on logical
criteria with consideration of the extreme cases. In this way a concise picture is drawn about the state of the art.

Reference List

Nylon 6 synthesis

64. BASF A.-G., Mohrschladt, R., WO Patent 2000020488, 1999
Chapter 1

90. BASF A.-G., Ohlbach, F., DE Patent 19935398, 1999
**Introduction**

Thanks to its excellent physical properties, nylon-6 is one of the most widely used engineering plastics. However, ε-caprolactam production based on hydroxylamine as the raw material is environmentally unfriendly.¹ ² Nylon-6 formation out of 6-aminocapronitrile (ACN) as a monomer, see Eq. (2.1), is an attractive alternative that received considerable attention, especially from industry.³⁻²⁰ So far the knowledge about the chemistry involved for the combined nitrile hydrolysis and amine amidation of ACN is still limited and a better understanding of the (fundamental) reaction steps involved is therefore required to develop a viable process for the production of high molecular weight nylon 6 out of ACN.

Patent literature about the process of making nylon 6 out of monomers containing an amine and a nitrile functionality already dates back to the early 1940’s.¹² Nevertheless, except for a considerable number of patents, the open literature contains only a few papers covering the synthesis of polyamides out of amine and nitrile functionalities,²¹⁻²² which requires very high loadings of the expensive homogenous catalyst and a solvent. Note that both methods reported only lead to polyamides of moderate molecular weight.
As the system reported by Murahashi et al. is highly diluted, the main product out of ACN is ε-caprolactam.\textsuperscript{21}

The chemistry involved in the hydrolysis and the polycondensation of ACN is captured by the reaction of equimolar amounts of an unactivated nitrile, a primary amine and water leading to N-substituted carboxylic amide, see Eq. (2.2). The process requires two chemical steps, which are (i) the hydrolysis of the nitrile and (ii) the amidation of the amine.

\begin{equation}
\text{n H}_2\text{N} + \text{H}_2\text{O} \rightarrow \text{H}[\text{N} - \text{O}]_n \text{NH}_3 - \text{H}_2\text{O}
\end{equation}

\begin{equation}
\text{Nitrile Activation}
\end{equation}

The literature about the nitrile hydrolysis is dominated by studies on the selective formation of the terminal amide\textsuperscript{23-47} and by studies on the mechanism of nitrile hydrolysis.\textsuperscript{46-61} Despite the potential of the method, the formation of N-alkyl amides out of nitriles and amine reagents obtained only little attention so far.

Except for some specific dinitriles and acetonitrile,\textsuperscript{62,63} the combined hydrolysis-aminolysis reaction of a nitrile group with primary or secondary amines requires a catalyst to give a substituted amide and ammonia as the products.\textsuperscript{21,63-65} So far, the best results were obtained using the Lewis acid RuH\textsubscript{2}(PPh\textsubscript{3})\textsubscript{4} and generally the conversions were good but not 100\%.\textsuperscript{21} The complete conversion of the nitrile and the amine and complete selectivity towards the corresponding N-alkylamides is a prerequisite for the formation of high molecular weight polyamides.

Besides the influence of the catalyst, large differences in activity have been observed with different temperature and substrate combinations.\textsuperscript{21,63,64} Murahashi et al. could obtain high yields, however, this required 24 hours reaction time at 160 °C with 3 mol\% of RuH\textsubscript{2}(PPh\textsubscript{3})\textsubscript{4} and a solvent.\textsuperscript{21} De Benneville et al. demonstrated that 8 hours reaction time at 150 °C is sufficient to obtain 83\% yield of the desired product using H\textsubscript{2}S as a catalyst.\textsuperscript{63} Although the reaction is performed neat, 25 mol\% of H\textsubscript{2}S is required and this is not of practical use. The best catalyst performance so far has been reported by Cobley et al.\textsuperscript{64} With a 30 times lower catalyst loading than used for the ruthenium system, a
homogeneous platinum complex is capable of producing 89% of N-substituted amide under the same conditions as used by Murahashi. The only, but important, conclusion that can be drawn from the literature available so far is that the N-alkyl amide synthesis out of a nitrile and an amine substrate is promising. However, a thorough understanding of the mechanisms involved is absent and such understanding is crucial to optimize the system, especially for the highly demanding synthesis of high molecular weight nylon 6 out of ACN.

A relatively simple method to enhance the reaction rate to reach the required complete nitrile hydrolysis is to increase the temperature. However, an increased temperature has its drawbacks, as high temperatures often lead to the formation of secondary or tertiary amines out of the primary amine, especially when catalysts are used. The formation of secondary and tertiary amine and loss of primary amine is a major problem when these side reactions occur during the production of nylon. Secondary and tertiary amines lead to branching and even a small amount of primary amine conversion into secondary or tertiary amine leads to a deviation from the stoichiometric ratio of nitrile and amine. Note that working with stoichiometric amounts of nitrile and amine functionalities is crucial for the production of high molecular weight polyamide. Formation of secondary and tertiary amines is suppressed by lowering the temperature. To compensate for the decrease in hydrolysis rate at lower temperatures, the amidation of a primary amine with a nitrile should therefore be catalyzed effectively.

In the present chapter we describe interesting aspects concerning the uncatalyzed and ruthenium catalyzed formation of an N-substituted amide from an unactivated, aliphatic monofunctional nitrile and an aliphatic, monofunctional primary amine. The system is chosen as a model for the formation of nylon 6 out of ACN. The objective is to elucidate the bottlenecks for high yield N-alkyl amide formation out of an aliphatic, primary amine and an aliphatic nitrile. As a stoichiometric amount of functional groups is required to obtain a polyamide with a high molecular weight, the reaction parameters that are studied are restricted to equimolar amounts of nitrile and amine. The combined nitrile hydrolysis and amidation has been studied, both without a catalyst at mild hydrothermal conditions and with RuH₂(PPh₃)₄ as a catalyst at lower temperatures.

**Experimental procedures**

**General procedures and considerations**

All reactions and manipulations involving organoruthenium complexes were performed in an argon atmosphere using standard Schlenk techniques or in a nitrogen
filled glovebox, and the product mixtures were worked up in open flasks in air. The reaction products were identified using $^1$H NMR. Conversions of substrates and selectivities for product formation were determined by gas chromatography using p-xylene as an internal standard. The product mixtures were analysed using a CP 9000 gas chromatograph (GC) equipped with a 30m x 0.32mm id, capillary CP volamine column and a FID detector. The sample was injected at 120°C and after a stabilisation temperature of 1 minute the temperature was raised with 15°C/min to 290°C. All single point experiments were performed in duplo.

**Autoclave set-up**

Hydrolysis experiments were performed in closed, stainless steel microreactors that contained glass inserts, as shown in Figure 2.1. Reaction mixtures were stirred with magnetic stirring bars. These autoclaves, with 7 mL internal volume, were made in house by the workshop of the Eindhoven University of Technology. Sealing during the reaction was ensured by Kalrez o-rings, as these Kalrez o-rings are resistant against the aggressive ammonia that was formed. The maximum operation temperature and pressure are 250°C and 60 bar, respectively. The internal reactor temperatures were controlled within ± 2°C by a heating mantle.

![Figure 2.1. The picture of a) the heating mantle with stainless steel microreactors and b) a picture of a single, complete microreactor.](image)

**Materials**

Pentanenitrile (99.5%, Aldrich), pentanoyl chloride (>97%, Merck), hexylamine (99%, Merck), pentanamide (99%, Acros), p-xylene (99+%, Aldrich), triphenylphosphine
N-alkyl amide formation via amine amidation of a hydrolyzed nitrile

(>99%, Fluka) and 1,3-bis(diphenylphosphine)propane (97%, Aldrich) were used without further purification. RuCl$_3$(H$_2$O)$_3$ and RuCl$_2$(PPh$_3$)$_3$ were obtained from Strem Chemicals and used as received. [RuCl$_2$(COD)]$_x$,$^{69}$ RuH$_2$(PPh$_3$)$_3$,$^{70}$ and RuH$_2$(PPh$_3$)$_4$,$^{71}$ were synthesized according to the literature procedures.

**Standard procedure for the neat hydrolysis of pentanenitrile in the presence of hexylamine**

In order to ensure a realistic model for the chemistry involved for the combined hydrolysis and polycondensation of ACN, we restrict ourselves to a solvent free system consisting of equimolar amounts of pentanenitrile and hexylamine in aqueous environment to form N-hexyl pentanamide, see Eq. (2.3). These aliphatic substrates with long alkyl chains restrict the amount of water used to avoid the risk of phase separation.

\[
\begin{align*}
\text{CH}_3\text{C} = \text{N} &+ \text{H}_2\text{N} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{C} = \text{N} - \text{NH}_3 \\
1 & + 1 \\
\end{align*}
\]

The reaction mixture of pentanenitrile (8.6 mmol, 0.71 g), hexylamine (8.6 mmol, 0.87 g), water (17.2 mmol, 0.31 g) and RuH$_2$(PPh$_3$)$_4$ (0.5mol%, 4.3 µmol, 49 mg) was first prepared in an inert atmosphere. At room temperature the homogeneous reaction mixture was charged into a 7 mL stainless steel autoclave containing a glass insert. The autoclave was then heated to a set temperature, which was kept constant during the reaction. After the preset reaction time the reaction vessels were removed from the heating mantle and immersed in an ice/water bath to quench the reaction. The experiments were checked for leaks by weighing the autoclave before and after each reaction. After cooling, the reactors were opened and the content was removed and homogenised with ethanol if necessary. Each reactor was rinsed twice with ethanol. The conversion and yield were determined with GC analysis using p-xylene as an internal standard. To investigate the influence of the concentration on the course of the reaction, the initial concentrations of the various components were varied.

For the catalyst-free experiments at elevated temperature, the reaction mixture was biphasic at room temperature for 10 equivalents of water compared to the amount of nitrile. The phase behaviour for these experiments is not known and therefore these data give only a qualitative insight into the global kinetics.
Hexylamine amidation experiments with pentanamide

The system as shown in Eq. (2.4) has been used to study the amidation. The reaction mixture consisting of pentanamide (7.4 mmol, 0.75 g), hexylamine (7.4 mmol, 0.99 mL) and water (14.8 mmol, 0.27 mL) was first brought into a reactor insert in an inert atmosphere. The rest of the procedure was the same as for the hydrolysis experiments.

\[
\begin{align*}
\text{NH}_2 + \text{H}_2\text{N} + \text{H}_2\text{O} & \quad \text{O} \\
\text{1} & \quad \text{1} & \quad \text{x}
\end{align*}
\]

(2.4)

For the hexylamine amidation with pentanamide under dry conditions, pentanamide was dried using azeotropic toluene distillation and hexylamine was dried by distillation over sodium hydroxide. The complete reactor was dried in an oven before use.

N-hexyl pentanamide synthesis

Pentanoyl chloride (0.51 mol, 61.2 g) was added dropwise to a solution of hexylamine (1.02 mol, 103 g) in diethyl ether (300 mL) and left overnight. The product mixture was distilled under vacuum, extracted with acidified water and brine and dried over Na$_2$SO$_4$. A 97% pure product was obtained, used for product identification. Orange, red oil; $^1$H NMR (300 Mhz, CDCl$_3$) $\delta$ 6.30-6.40 (s, 1H) 3.17 (td, $J_t= 7$ and $J_d= 6$ Hz, 2H), 2.14 (t, $J= 7$Hz); $^{13}$C NMR (300 MHz, CDCl$_3$) $\delta$ 173.3, 39.3, 36.2, 31.3, 29.4, 27.8, 26.4, 22.3, 22.2, 13.7, 13.6

Results and discussion

Nitrile activation using hydrothermal conditions

Since hydrothermal nitrile hydrolysis is a well known process in organic chemistry we first studied its applicability for the formation of nylon 6 using pentanenitrile and hexylamine as model reagents. Figure 2.2 shows the conversion-time history for the reaction of pentanenitrile with 10 equivalents of water at 230°C. For the nitrile-water mixture only, pentanenitrile is hardly hydrolysed. This hydrolysis behaviour is completely in line with literature observations, for which temperatures of at least 300°C are used to obtain complete nitrile hydrolysis under hydrothermal conditions. In a large excess of water for example, a reaction temperature of 250°C resulted in only a

---

* Reactions were performed without a primary amine as well as with a stoichiometric amount of n-hexylamine.
20% propionitrile conversion after 6 hours,\textsuperscript{49} while 3 hours at 330°C and 6 hours at 300°C resulted in the complete propionitrile conversion.

![Conversion-time history for the pentanenitrile hydrolysis](image)

**Figure 2.2.** The conversion-time history for the pentanenitrile hydrolysis without hexylamine (●) and with a stoechiometric amount of amine (▲) at 230 °C.

However, in the presence of n-hexylamine a steadily increasing conversion of pentanenitrile with time is observed, see Figure 2.2. The presence of the amine clearly promotes the nitrile hydrolysis. Nevertheless, rather high temperatures are required, as a temperature reduction to 160°C results in only 8% of hydrolysed pentanenitrile after 22 hours.

Hydrolysis enhancement due to the reactant hexylamine is interesting, as nitrile hydrolysis without the use of additives requires high reaction temperatures. Since nitrile hydrolysis is known to be both acid and alkaline catalyzed,\textsuperscript{59,60} the distinct improved hydrolysis rate of pentanenitrile is most probably due to the basicity of the amine. An acid catalyzed process is not likely to take place, due to the buffering effect of amines.\textsuperscript{50} In contrast, for alkaline catalyzed nitrile hydrolysis and amine amidation, the formation of ammonia counterbalances the consumption of amine, thus maintaining the basicity of the system.\textsuperscript{50} The nitrile hydrolysis combined with amine amidation is very advantageous, as the amine is both a catalyst and a reactant.
Figure 2.3. The (a) first and (b) second order Delplot for the hydrothermal pentanenitrile hydrolysis in the presence of hexylamine. Reaction products: pentanamide (▲), N-hexyl pentanamide (●) and pentanoic acid (◆).

The main products of the nitrile hydrolysis in the presence of amine are the corresponding terminal amide, pentanamide, and the N-alkyl amide, N-hexyl pentanamide, as can be observed in Figure 2.3. With a maximum error on the total mass balance of 2%, no loss of selectivity is observed for pentanenitrile and hexylamine under these conditions. The maximum amount of the corresponding carboxylic acid formed is less than 1% based on the initial amount of nitrile and is only detected at higher conversions. In contrast, the major product of the nitrile hydrolysis at hydrothermal conditions in the absence of amine is the carboxylic acid, and hydrolysis of nitriles into the terminal amide is requires the use of a selective catalyst. The small amount of carboxylic acid formed in the reaction of pentanenitrile, n-hexylamine and water can be rationalised by the relatively slow hydrolysis of the pentanamide compared to the fast consumption of the formed carboxylic acid by acylation of hexylamine. This difference in kinetic constants of the reaction rates prevents the built up of appreciable amounts of carboxylic acid, as shown by Eq. (2.5). An important conclusion that can be drawn from these results is that the system has a strong thermodynamic preference for the formation of the N-substituted amide over the carboxylic acid.
N-alkyl amide formation via amine amidation of a hydrolyzed nitrile

As shown in Figure 2.3a, the relation between the selectivity and the conversion shows a clear product composition development. At the beginning of the reaction the terminal amide is the major product and after 25% conversion a selectivity of 90% for N-hexyl pentanamide is obtained. Although pentanamide remains present, it only contributes less than 10% to the total yield at higher conversions.

Figure 2.3a is also considered as the first-rank Delplot, which allows the assignment of the reaction rank to the different products involved. The initial selectivity of pentanamide tends to unity, which implies that the amide is the primary product of the reaction network. The zero intercept of N-hexyl pentanamide shows that it is a higher-rank product.

Figure 2.3b shows the second-rank Delplot for the pentanenitrile hydrolysis in the presence of hexylamine at 230°C, which allows sorting of higher rank products in the reaction network. As the y-intercept of pentanamide in the secondary Delplot goes to infinity for zero conversion, the assignment of pentanamide as the primary product is confirmed. As N-hexyl pentanamide has a finite, positive value of the y-intercept, it is the product of the consecutive amidation of the terminal amide. The observations allow the formulation of a consecutive reaction mechanism, as shown in Eq. (2.5).

Hexylamine amidation with pentanamide

Although amine acylation is the most widely used method for preparing N-substituted amides, terminal amides as acylation source are hardly reported. The two possible routes for the amine amidation with a terminal amide in aqueous environment are depicted by route A and B in Eq. (2.5). The first step for route A is the hydrolysis of the amide to the carboxylic acid, followed by the formation of the ammonium salt, as shown in Eq. (2.6). The ammonium salt dehydrates at high temperature, enhanced by water

† The relatively high scattering for the selectivity at low conversions is due to the strong effect of the experimental error on the selectivity for low conversions.
‡ Amidine intermediates are not excluded, but not observed and therefore omitted in Eq. 2.5.
removal. The direct amine amidation using a terminal amide, route B of Eq. (2.5), needs some method of activation.\textsuperscript{76,78} As reported by Mares \textit{et al.},\textsuperscript{77} the products of the reactions of 6-aminocaproic acid amide in aqueous solution at 200°C show an analogy to the product composition development for the hexylamine amidation with hydrolyzed nitrile. Although an excess of water was present, the main product of the 6-aminocaproic acid amide conversion was caprolactam and an appreciable amount of its dimer was also formed, while a relatively small amount of hydrolysis product was obtained.

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

Note that the amide bond formation from a carboxylic acid and an amine is unfavourable in aqueous environment due to the supposedly preferred amide hydrolysis. This opinion makes it even more surprising that the N-alkyl amide formation is preferred over the carboxylic acid formation.\textsuperscript{79} The origin for this unexpected behavior can be the organic nature of the reaction mixture, which influences the equilibrium of Eq. 2.6.

The results for the neat hexylamine amidation with pentanamide for 180°C and 230°C are collected in Figure 2.4a. As expected the amidation rate at low temperatures is low. At 180°C it takes more than 5 hours to reach an 80% conversion. At 230°C the initial rate is high, as the same 80% conversion is already reached within 2 hours, however, further progress of the reaction is slow. The stepwise removal of ammonia from the reaction mixture further increases the N-hexyl pentanamide yield. Although no complete ammonia removal could be achieved, the yield increased from 85% without ammonia removal to 93% with three ammonia removal cycles, which is an indication for the presence of an equilibrium.
Figure 2.4. Hexylamine amidation with a) pentanamide performed at 180°C (▼) and at 230°C (●) and b) pentanoic acid. Hexylamine amidation with starting with 85% pentanamide and 15% pentanoic acid is performed at 180°C (▲). The amidation of n-hexylamine with pentanoic acid is performed at 180°C (▲) and at 230°C (●). (Closed system)

The amine amidation with pentanoic acid is much faster than with pentanamide, as shown in Figure 2.4. Within 5 hours a 95% yield is reached at 180°C, and at 230°C a yield of 94% is already reached within 1 hour. However, no significant increase of the N-hexyl pentanamide yield is observed for longer reaction times. The time constant for the amidation is significantly higher for the carboxylic acid than for the terminal amide, which is in line with the relative stability of the two compounds. Further, the carboxylic acid is completely consumed within one hour for a reaction mixture consisting of 85% pentanamide and 15% pentanoic acid and a stoichiometric amount of hexylamine. Both results are in agreement with our observation that only small amounts of carboxylic acid are formed in the model reaction of pentanenitrile with hexylamine and water at high temperature.
Figure 2.5 shows the results of the amidation of hexylamine with pentanamide, both dry\textsuperscript{§} as in aqueous environment. The results clearly demonstrate that water has only a minor influence on the amidation step. The initial rate of hexylamine amidation with pentanamide is somewhat higher in the absence of water than in the presence of water. A possible reason may be dilution when water is used. However, the addition of water increases the final amide conversion. For the water-free reaction conditions a 76\% conversion was reached, while with 10 equivalents of water over 90\% of amide was converted after 22 hours at 140\°C. The formation of 1.5\% of carboxylic acid suggests that this increased conversion can be assigned to the formation of intermediate carboxylic acid according to route A in Eq. (2.5). A strong contribution of route A to the total reaction is illustrated by the experiment with 10 equivalents of water. For this experiment a maximum amount of 15\% carboxylic acid is observed besides N-hexyl pentanamide, which decreases again for the further progression of the reaction. As the addition of water does not have a distinct effect on the amide consumption rate, the amide hydrolysis into the corresponding carboxylic acid does not proceed fast. However, the formation of pentanoic acid as well as the increased N-hexyl pentanamide yield, compared to the water-free experiments, show that the amide hydrolysis does occur. N-hexyl pentanamide and pentanoic acid comprise the total conversion of pentanamide and hexylamine, which excludes side reactions. Although amide functionalities are rather robust, they can be hydrolyzed into their corresponding carboxylic acids. In principle terminal amides can

\textsuperscript{§} Although the reactors are dried as good as possible, a trace of water adsorped to the wall of the metal reactors can not be excluded.
even be dehydrated to their nitrile analogues. In Table 1 the results are collected for the stability of pentanamide at 140°C against hydrolysis and dehydration as depicted by Eq. (2.7). As expected, pentanamide is stable for prolonged periods of time and the addition of water results in only a small amount of carboxylic acid formation. The dehydration of pentanoic amide is not observed.

\[
\text{HN}\text{-alkyl amide formation via amine amidation of a hydrolyzed nitrile}
\]

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

(2.7)

Table 1. Pentanamide stability towards hydrolysis and dehydration (Eq. (2.6)).

<table>
<thead>
<tr>
<th>Entry</th>
<th>[H\textsubscript{2}O] (molar equivalents)</th>
<th>[RuH\textsubscript{2}(PPh\textsubscript{3})\textsubscript{4}] (mol%)</th>
<th>Y\textsubscript{PN} (%)</th>
<th>Y\textsubscript{PA} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0\textsuperscript{b}</td>
<td>-</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0\textsuperscript{b}</td>
<td>1</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>-</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>16</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>-</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>1</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>2</td>
<td>0</td>
<td>10</td>
</tr>
</tbody>
</table>

\textsuperscript{a} 22 hours and 140°C, \textsuperscript{b} dried pentanamide used, \textsuperscript{c} Yield pentanenitrile, \textsuperscript{d} Yield pentanoic acid

Varying the amine concentration does not influence the amine amidation. Increasing the amount of hexylamine from 1 equivalent to 8 equivalents in the presence of 2 equivalents of water did not result in an increase of the N-hexyl pentanamide yield after 12 hours reaction at 140°C. To check if the pentanamide hydrolysis is stimulated by the presence of the amine, triethylamine is added to a mixture of pentanamide and water. As no effect of the amine concentration on the amidation is observed, the possibility of N-hexyl pentanoic amide formation via the pentanoic acid (route A of Eq. (2.5)) is strengthened. The addition of an equimolar amount of triethylamine did not affect the pentanamide hydrolysis in the presence of 2 equivalents of water after 12 hours at 140°C. The amide hydrolysis is therefore not enhanced due to the presence of the primary amine.

The stability of N-hexyl pentanamide is checked for hydrolysis and ammonation. Both hydrolysis and ammonation of the N-hexyl pentanamide are not observed after 22 hours at 140°C.
A preliminary conclusion

The observed phenomena for the N-hexyl pentanamide synthesis out of pentanenitrile, n-hexylamine and water at mild hydrothermal conditions can be summarized as follows. Nitrile hydrolysis requires harsh conditions, but the presence of the primary amine reduces the activation barrier for hydrolysis leading to considerably lower time constants for reaction at 230°C. Nitrile hydrolysis in the presence of hexylamine mainly results in the formation of the corresponding N-substituted carboxylic acid amide. The terminal amide is initially the main product, due to its chemical stability. However, the time constant for the amine amidation is higher than the time constant of the nitrile hydrolysis, as no further build-up of pentanamide is observed. Amidation of hexylamine with pentanamide in an aqueous environment is the second step of the reaction network for the formation of N-hexyl pentanamide using pentanenitrile and hexylamine. No matter whether the amidation proceeds via the intermediate carboxylic acid (route A in Eq. (2.5)) or via the direct amidation of the terminal amide (route B in Eq. (2.5)), the consecutive reaction is not so fast that the pentanamide is undetectable. Results for the amine amidation with hydrolysed nitrile demonstrate that the amidation of the primary amine with a terminal amide proceeds in aqueous environment. The reaction scheme as depicted by Eq. (2.5) combines all these observed features for the hexylamine amidation with pentanamide in an aqueous environment.

More insight into the reaction mechanism of the N-alkyl amide formation out of a terminal amide and primary amine in the presence of water is obtained by studying the neat reaction of pentanamide with hexylamine separately. The terminal amide is either directly amidated with hexylamine or first hydrolyzed to the corresponding acid. Note that the time constant for the amidation of the carboxylic acid seems high compared to the time constants of the amide hydrolysis. As the amide amination is not influenced by the amine, the product N-hexyl pentanamide is mainly formed via the hydrolysis of the terminal amide (Eq. (2.5), route A). This is supported by the formation of carboxylic acid for higher conversions, as the amidation rate is decreased due to a low amine concentration. However, the direct amidation of hexylamine with pentanoic acid amide can not be excluded. The relative values of the time constants for the nitrile hydrolysis, amide hydrolysis and the amine amidation with the carboxylic acid formed are in good agreement with the general order of reactivity towards nucleophilic substitution for carboxylic acid derivatives. Limitations for the yields are the required low water concentration and the built up of ammonia pressure in our system. Ammonia removal during the amidation reaction was very cumbersome due to the experimental scale, but partial ammonia removal undoubtedly resulted in an improved performance.
Although the neat n-hexylamine amidation with pentanenitrile proceeds at 230°C, the outcome is not satisfactory. An increased reaction temperature seems to be the most obvious solution, however, a recent study on the thermal cyclization of 6-aminocaproic acid showed a dramatic drop in the selectivity for caprolactam. At 350°C the selectivity for caprolactam and 6-aminocaproic acid amide out of ACN dropped below 80%, and a conversion of 70% is reached. This loss of selectivity may be due to the formation of secondary amines, which has been observed at elevated temperatures. Hence, solutions for a highly selective nitrile hydrolysis and amidation at much lower temperature have to be found. A possible solution that will be discussed next is the use of a catalyst to improve the nitrile hydrolysis. A homogeneous ruthenium catalyst for which complete amidation of amines with hydrolyzed nitriles has been reported, is studied to improve the system.

Ruthenium catalyzed nitrile hydrolysis and amine amidation

The concentration-time history for the solvent free reaction of pentanenitrile with n-hexylamine and 2 equivalents water, catalyzed by RuH$_2$(PPh$_3$)$_4$ at 140°C, is shown in Figure 2.6a. The only reaction product up to a nitrile conversion of 60% is the terminal amide (see Figure 2.6b). Distinct amounts of N-hexyl pentanamide are only observed for high nitrile conversions, as is clearly demonstrated by the results collected in Figure 2.6b. In analogy with the uncatalyzed reaction the terminal and coupled amide are the main products. The observed sequential process as depicted in Eq. (2.5) is even more pronounced for the ruthenium catalyzed hexylamine amidation with hydrolysed pentanenitrile than for the hydrothermal conditions. Although the same consecutive reaction steps are observed, a dramatic change in rate determining step occurs. Whereas the nitrile hydrolysis is rate-limiting for the hydrothermal conditions, this step is effectively catalyzed by the ruthenium compound. As a consequence the amidation reaction is now the rate limiting step. The large amount of terminal amide formed is in agreement with the known selective hydrolysis of nitriles into the terminal amide by RuH$_2$(PPh$_3$)$_4$ catalysis. No carboxylic acid is observed during the whole course of the reaction.
Figure 2.6. The (a) concentration-time diagram for the RuH$_2$(PPh$_3$)$_4$ catalyzed n-hexylamine amidation with pentanenitrile and 2 equivalents of water, and (b) the corresponding selectivity-conversion plot: normalized concentration pentanenitrile (●), pentanamide (▲) and N-hexyl pentanamide (◆).

The use of a ruthenium catalyst clearly has a strong accelerating effect on the nitrile hydrolysis compared to the hydrothermal hydrolysis. With only 0.5 mol% RuH$_2$(PPh$_3$)$_4$, 60% conversion is already reached within 2 hours at 140°C, while this requires 12 hours at 230°C for the uncatalyzed reaction.

In order to assess if there is a possible effect of the added amine on the reaction rate, the hydrolysis reaction was also carried out in the absence of hexylamine. Pentanenitrile does not dissolve appreciably in water without amine present and to compare the hydrolysis rate a homogeneous system is required. Therefore the hydrolysis, both in the absence and presence of amine, was performed in dimethoxy ethane. Although the hydrolysis rate is lower due to dilution and perhaps solvent effects, a clear increase in rate is observed for the experiment in the presence of n-hexylamine. After 2 hours at 140°C with 0.5 mol% of RuH$_2$(PPh$_3$)$_4$, 10% conversion of pentanenitrile is obtained in the presence of n-hexylamine against 5% conversion without amine.
Figure 2.7. Conversion-time histories for the hexylamine amidation with a stoechiometric amount of pentanamide at 140°C with (●) and without (▲) 0.5 mol% RuH2(PPh3)4 (2 equivalents of water present)

Figure 2.6 clearly shows that the amine amidation has become the rate determining step for the ruthenium catalyzed process, which suggests that ruthenium only poorly catalyzes the amidation or not at all. The effect of the RuH2(PPh3)4 upon the amidation is therefore studied. Figure 2.7 compares the uncatalyzed and ruthenium ‘catalyzed’ amidation. The addition of 0.5 mol% RuH2(PPh3)4 clearly does not influence the formation of N-hexyl pentanamide and therefore the effect of ruthenium is restricted to the nitrile hydrolysis.

Eq. (2.8) shows the possible reaction routes that are in agreement with the observations. Although RuH2(PPh3)4 already catalyzes the nitrile hydrolysis, the hydrolysis rate is further enhanced by the addition of amine. Three possible origins for this increased reaction rate are identified. The first reason for this enhanced hydrolysis rate may be due to the fact that the amine acts as a cocatalyst, which shifts the required proton exchange to liberate the formed amide. Secondly, another option might be the activation of the ruthenium complex by the substitution of one phosphine ligand by the amine, which results in a more open and more active complex. A third origin for the
increased nitrile hydrolysis rate by n-hexyl amine could be the formation of a metal amidine, which is subsequently hydrolysed to an amide, see Eq. (2.8) route II.\textsuperscript{80} In our opinion the most plausible origin for the increased reaction rate would be that the amine acts as a cocatalyst, as ruthenium is well known for the use in hydrogen transfer reactions with imines.\textsuperscript{81}

Direct hydrolysis of the amidine to the N-alkyl carboxylic amide is a conceivable route to N-alkyl amides according to Murahashi \textit{et al.}\textsuperscript{82} and Cobley \textit{et al.}\textsuperscript{64} However, the direct hydrolysis of the amidine to the N-alkyl carboxylic amide does not correspond to the observed formation of the terminal amide. Additionally, the hydrolysis of the amidine should lead to a terminal amide and not directly to an N-substituted amide, as n-hexylamine is a better leaving group than ammonia.\textsuperscript{**} Although no conclusive judgement can be made about the amidine activation of the nitrile hydrolysis, the direct N-alkyl amide formation through the hydrolysis of an amidine is excluded.

**Different ruthenium systems**

The sensitivity to air of the ruthenium dihydride is a limitation for the applicability of the method. More easily accessible ruthenium systems are therefore tested for their performance and the results are collected in Table 2. Although the more stable RuCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{4} is less active in the nitrile hydrolysis in the absence of amine, it shows a slightly higher conversion than the dihydride in the presence of amine. This triggered us to use [Ru(COD)Cl\textsubscript{2}]\textsubscript{x}, which is easy to synthesize and very stable. [Ru(COD)Cl\textsubscript{2}]\textsubscript{x} is active, but its activity is less than that of RuCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{4}. The addition of triphenylphosphine to [Ru(COD)Cl\textsubscript{2}]\textsubscript{x} resulted in the same performance as found for RuH\textsubscript{2}(PPh\textsubscript{3})\textsubscript{4}.

Although catalyst development is no objective of the project, a quick screening of some ligands was performed, in the reaction shown by Eq. (2.9). Addition of electron donating tricyclohexylphosphine and electron withdrawing tripentafluorophenylphosphine to [Ru(COD)Cl\textsubscript{2}]\textsubscript{x} resulted in a lower activity than the combination of [Ru(COD)Cl\textsubscript{2}]\textsubscript{x} with triphenylphosphine. The use of the bidentate ligand 1,3-bis(diphenylphosphino)propane (DPPP) did not result in an improved yield either.

\textsuperscript{**} The product of amidine hydrolysis is determined by the character of the leaving group of the amine.\textsuperscript{83-85} Similar behaviour is observed for the hydrolysis of a polyamidine.\textsuperscript{86}
N-alkyl amide formation via amine amidation of a hydrolyzed nitrile

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

\[ \text{H}_2\text{N} + \text{N} \]

\[ \text{O} + \text{N} \]

Table 2. Comparison of different catalyst precursors\(^\text{a}\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conv (VN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>([\text{Ru(COD)Cl}_2])(_x)</td>
<td>60%</td>
</tr>
<tr>
<td>2</td>
<td>([\text{Ru(COD)Cl}_2])(_x) + 3\text{PPh}_3)</td>
<td>80%</td>
</tr>
<tr>
<td>3</td>
<td>(\text{RuCl}_2(\text{PPh}_3)_3)</td>
<td>85%</td>
</tr>
<tr>
<td>4</td>
<td>(\text{RuH}_2(\text{PPh}_3)_3)</td>
<td>80%</td>
</tr>
<tr>
<td>5</td>
<td>([\text{Ru(COD)Cl}<em>2])(<em>x) + 3\text{PCl}</em>{18}\text{F}</em>{15})</td>
<td>56%</td>
</tr>
<tr>
<td>6</td>
<td>([\text{Ru(COD)Cl}<em>2])(<em>x) + 3\text{PCl}</em>{18}\text{H}</em>{30})</td>
<td>66%</td>
</tr>
<tr>
<td>7</td>
<td>([\text{Ru(COD)Cl}_2])(_x) + 1\text{DPPP})</td>
<td>73%</td>
</tr>
<tr>
<td>8</td>
<td>([\text{RuCl}_2(\text{p-cymene})]_2)</td>
<td>59%</td>
</tr>
<tr>
<td>9(^b)</td>
<td>-</td>
<td>8%</td>
</tr>
</tbody>
</table>

a. 3h, 160°C b. 23h at 160°C.

The results show that a combination of an air-stable ruthenium precursor with triphenylphosphine results in a system with an activity comparable to that of \(\text{RuH}_2(\text{PPh}_3)_4\), which makes the method more accessible. Although experimentally more easily applicable systems also show a good performance, strong improvements of the yield are not obtained. Therefore the origin of the decline in nitrile hydrolysis rate with increased nitrile conversion was studied.

**Improving the ruthenium catalyzed nitrile hydrolysis**

It was found that the initial hydrolysis rate is dependent on the water concentration. At 140°C the initial rate is about a factor 1.4 higher when 2 equivalents of water are used instead of one equivalent. The reaction order for water can not exactly be determined, as the accuracy of the obtained values for the initial hydrolysis rates is not high enough due to the uncertainty in the extrapolation. At 140°C the initial turnover frequency is \(1.8 \times 10^2\) \(\text{mol}_{\text{pentanenitrile}} \times \text{mol}_{\text{Ru}}^{-1} \times \text{h}^{-1}\) with 2 equivalents of water and the rate decreases by a factor 20 within 2 hours. This reduction in hydrolysis rate is observed for the ruthenium catalyzed hydrolysis of nitrile, both with and without (not shown) amine present. However, the decrease of the nitrile hydrolysis activity is more pronounced in the presence of amine. The strong decrease in hydrolysis rate with reaction time occurs for catalyst concentrations ranging from 0.05 to 1.0 mol%, see Figure 2.8, for temperatures ranging from 100 °C to 180 °C, see Figure 2.9, and for 1, 2 and 10 equivalents of water (not shown).
Figure 2.8. The nitrile conversion for the model reaction with 0.05 mol% (●), 0.02 mol% (▲), 0.5 mol% (▼) and 1.0 mol% (▲) RuH2(PPh3)4. The shown curves are only guides for the eye.

As shown in Figure 2.8, the ruthenium catalyst concentration has a strong effect on the maximum conversion. However, the strong reduction in hydrolysis rate is observed with time for all catalyst concentrations ranging from 0.05 mol% to 1.0 mol%, as the major part of the nitrile reacts within 4 hours. With 2.5 mol% of ruthenium a 98% nitrile conversion can be obtained, but for a viable process lower catalyst loadings are required.

Figure 2.9 shows the conversion-time history of the nitrile hydrolysis with 0.5 mol% ruthenium catalyst at different temperatures. The results plotted in Figure 2.9 point to an increase of the final conversion with temperature. After 2 hours of reaction at 180°C the nitrile conversion exceeds 85%, compared to a 70% conversion at 160°C for the same reaction time. A higher reaction temperature thus seems to be more attractive to obtain the required high conversions, rather than increasing the catalyst concentration.

However, in the case of ruthenium catalyzed nitrile hydrolysis and amidation, at temperatures equal to or higher than 160°C, side reactions become significant. It was reported that ruthenium catalysts effectively enhance the formation of secondary and tertiary amines from primary amines at elevated temperatures. Indeed, a part of the discrepancy in amine conversion and N-hexyl pentanamide yield corresponds well to the amount of dihexylamine formed during the reaction at temperatures higher than 160°C. Although amine disproportionation forms no real threat in organic synthesis, for polycondensations even small amounts of secondary amines lead to branches and loss of selectivity. Moreover, the stoichiometric balance is disturbed, which is deleterious for the required high molar mass.
N-alkyl amide formation via amine amidation of a hydrolyzed nitrile

Plausible reasons for the strong observed catalyst deactivation are the decomposition of the catalyst or the inhibition of the active metal species by the formed products. The addition of a mixture of nitrile, amine and water to a mixture which had reacted for 19 hours resulted in about 60% hydrolysis of the extra added nitrile in an additional 3 hours. The observed renewed activity excludes the possible explanation that deactivation is due to decomposition of the active ruthenium species and points to a reversible inhibition process. The reversible character of the activity decrease is also supported by the observation that a stepwise addition of the catalyst in time results in the same conversion compared to the experiment for which the same total amount of catalyst is initially added.

The reduced activity is therefore most probably the result of the competitive adsorption of the amides at the ruthenium center, see Figure 2.10. To unravel the deactivation mechanism, the influence of the effect of pentanamide, N-hexyl pentanamide and ammonia on the hydrolysis activity was studied. Application of a partial ammonia pressure at the start of the reaction did not lead to a decrease of the hydrolysis activity. It is not surprising that ammonia has no effect, since the strong decrease of the hydrolysis activity is observed before appreciable amounts of N-substituted amides and ammonia are formed. The decrease of the catalyst performance upon addition of the pentanamide or N-hexyl pentanamide (as shown in Figure 2.10) is much more pronounced than the decrease that can be expected as a result of merely the dilution of the neat system. So the terminal and N-hexyl pentanamide play a dominant role in the catalyst deactivation. Note that competitive amide addition to ruthenium phosphines in a nitrile-water mixture has been reported in literature.90,91 The competitive binding of
pentanamide to the ruthenium complex is a typical example of reversible product inhibition.

![Graph showing nitrile conversion vs. initial amount of pentane amide added](image)

**Figure 2.10.** The observed reduction in nitrile conversion after one hour reaction time with increasing initial amount of pentane amide added, both for a reaction mixture with (▼) and without (▲) n-hexylamine. 0.5 mol% RuH2(PPh3)₄, T=140°C

**Ruthenium catalyzed amide dehydration and hydrolysis**

As the amide competes with the nitrile for the coordination to the ruthenium metal, an equilibrium can also exist between a ruthenium nitrile species and a ruthenium amide. The role of amide dehydration as part of the nitrile hydrolysis mechanism has not been extensively studied, as dehydration is generally not observed. However, note that the actual reason for the observed deactivation can be the existence of an equilibrium between the nitrile hydrolysis and amide dehydration. The existence of an equilibrium is quite well possible, as ruthenium phosphines dehydrate amides in the absence of water, and this is strongly enhanced by the removal of water by using urea.

With 1 mol% of RuH₂(PPh₃)₄ the formation of the dehydration product is clearly observed at 140 °C, see Table 1. The water formed due to the hydrolysis is capable of some carboxylic acid formation. But also in the presence of 1 equivalent of water, some pentanenitrile is formed from the corresponding amide. Increasing the amount of water to 10 equivalents is enough to make the quantification of the dehydration impossible. These results show that the nitrile hydrolysis catalyzed by RuH₂(PPh₃)₄ is an equilibrium reaction, as shown in Eq. (2.10), and confirms that pentanamide adsorbs competitively with nitrile onto the catalyst. The appearance of this equilibrium might well be due to the low amounts of water used.
Equation (2.10) combines all the observations for the system consisting of a nitrile, a primary amine and water with RuH$_2$(PPh$_3$)$_4$ as a catalyst precursor. The desired reduction of the amount of catalyst results in a decrease of the final yield, which is caused by reversible product inhibition of the active species. The decrease in hydrolysis rate with lower catalyst loadings can be counterbalanced by using increased temperatures. However, increased temperatures result in side reactions of the primary amine, which would result in a non-stoichiometric amount of functional groups in a polymerization reaction of ACN, and in branched and low molar mass nylon 6. Hence, although very useful for the organic synthesis of N-substituted amides out of nitriles and amines, ruthenium is no suitable catalyst for the direct polycondensation of monomers containing both amine and nitrile functional groups (like ACN). The use of the air stable ruthenium species [Ru(COD)Cl$_2$]$_x$ together with triphenylphosphine shows a comparable activity to RuH$_2$(PPh$_3$)$_4$ and allows an easier experimentation

Conclusions

The synthesis of N-hexyl pentanamide from pentanenitrile and hexylamine was studied under mild hydrothermal conditions and with the use of ruthenium catalysts. The reaction proceeds through two consecutive major reactions, independent of the use of a catalyst. The first reaction is the nitrile hydrolysis to the terminal amide, and subsequently the amide acylates the amine. The presence of the reactant amine enhances the nitrile hydrolysis as compared to the plain nitrile hydrolysis. At elevated temperatures this activation is sufficient to obtain an appreciable hydrolysis rate in the absence of any further additives. However, the hydrolysis rate is not high enough for the application in polymerizations. The rate determining step is the nitrile hydrolysis.

The total picture for the hexylamine amidation with hydrolyzed nitrile under hydrothermal conditions was summarised before, but the most important conclusions are:
i) the reaction mainly forms N-hexyl pentanamide and ii) the slow nitrile hydrolysis is the rate determining step.

RuH2(PPh3)4 can be used to catalyze the nitrile hydrolysis, but has no distinct influence on the amine amidation. As reversible product inhibition of the active catalytic species restricts the nitrile conversion, homogeneous ruthenium phosphine is no suitable catalyst for the polymerization of 6-aminocapronitrile.

Reference List

N-alkyl amide formation via amine amidation of a hydrolyzed nitrile
Heterogeneous catalyzed
nitrile hydrolysis and subsequent
amine amidation

Introduction

The crucial requirement for the polymerization of 6-aminocapronitrile into high molecular weight nylon 6 is the complete conversion of the nitrile functionality into an N-substituted amide. With the aim to reach this condition, two methods to improve the performance of the nitrile hydrolysis were evaluated in Chapter 2. The first method was based on the use of a mild hydrothermal process and the second method was based on the use of a homogeneous ruthenium catalyst. Although high conversions were obtained, both systems did not result in complete nitrile hydrolysis. However, the study resulted in an indepth insight in the mechanistic aspects of the reaction, which can now be used to study the nitrile hydrolysis by heterogeneous catalysis. A big advantage of heterogeneous catalysis is that it in general dramatically simplifies the process operation in comparison to homogeneous catalysis, most importantly with respect to the catalyst separation from the final product.
Except for the patent literature there is not much attention for the heterogeneously catalyzed formation of N-substituted amides out of nitrile and amine functionalities, the reaction that captures all features of the polymerization of 6-aminocapronitrile. The formation of ethyl esters, using benzonitriles and ethanol as substrates and several zeolites as catalysts, is the only study in the open literature that concerns a heterogeneously catalyzed nitrile reaction with two nucleophiles.\(^1\) A number of patents consider the gas-phase conversion of an aliphatic amino-nitrile into the corresponding N-substituted amide using metal oxides, mainly aimed at the synthesis of the corresponding lactams.\(^2\)\(^-\)\(^7\) The operating temperature is typically near or above 300\(^\circ\)C. However, under these conditions the uncatalyzed nitrile hydrolysis already proceeds with a decent rate, making it difficult to measure the effect of the oxide.\(^8\) Furthermore, the process requires a highly dilute system to obtain the lactam, which corresponds to a large excess of water in the process.

Since we intend to make nylon 6 out of 6-aminocapronitrile using heterogeneous catalysis we can only use small amounts of water. While our work was in progress, BASF published patents describing the polymerization of 6-aminocapronitrile, using TiO\(_2\) as the heterogeneous catalyst.\(^9\)\(^,\)\(^10\) Although this is claimed to be a good working system, nothing is disclosed about the mechanisms involved and not to mention about the characteristics and the amounts of the catalyst used. Hence, a lot can still be learned and improved with respect to heterogeneously catalyzed N-substituted amide bond formation using nitriles and amines as substrates.

Contrary to the heterogeneously catalyzed formation of N-substituted amides using nitrile hydrolysis, the use of heterogeneous catalysis for nitrile conversion into its corresponding terminal amide is getting more and more attention.\(^11\)\(^-\)\(^18\) The best heterogeneous systems for this reaction described so far are ruthenium hydroxide on alumina\(^11\) and magnesium supported copper.\(^12\) Although these systems also seem very attractive for the polymerization of 6-aminocapronitrile, the presence of the amine functionality in this system is expected to dramatically affect the behavior of the acidic catalysts. For example, the abovementioned ruthenium on alumina fails completely due to amine induced leaching of the ruthenium from the acidic Al\(_2\)O\(_3\) surface.\(^*\) The comparison of the most trivial heterogeneous catalysts is therefore still of relevance.

\(^*\) Although ruthenium on Al\(_2\)O\(_3\) is highly active for the selective nitrile hydrolysis,\(^11\) with our system a 30% loss of amine selectivity in the conversion of hexylamine into N-hexyl pentanamide is observed after 2 hours at 160\(^\circ\)C. Furthermore, the presence of nitrile, amine and water results in leaching of the metal as a clear coloured reaction mixture was observed, due to ruthenium in solution.
In this chapter we describe a study aimed at identifying whether heterogeneous metal oxide catalysts, other than TiO$_2$, can catalyze the nitrile hydrolysis to full conversion and possibly catalyze the subsequent amine amidation too.

**Experimental**

**Catalysts**

The catalysts studied were several modifications of faujasite (Y) and beta (β) zeolite, amorphous silica alumina, zirconia, titanium dioxide and niobium acid. All zeolites were calcined for 6 hours at 550°C in air before use. The surface area and pore size for the metal oxides is given in Table 1.

<table>
<thead>
<tr>
<th>Physical property</th>
<th>TiO$_2$</th>
<th>ZrO$_2$</th>
<th>Nb$_2$O$_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcination temp. °C</td>
<td>300</td>
<td>300</td>
<td>200</td>
</tr>
<tr>
<td>BET Surface area m$^2$.g⁻¹</td>
<td>201</td>
<td>288</td>
<td>193</td>
</tr>
<tr>
<td>Pore diameter nm</td>
<td>5.8</td>
<td>4.9</td>
<td>4.3</td>
</tr>
</tbody>
</table>

NaY was obtained from Akzo Nobel (Arnhem, The Netherlands) and has a silica to alumina ratio of 2.5 and a surface area of 500 m$^2$.g⁻¹. Zeolite HY was synthesized via ionexchange of NaY with NH$_4$NO$_3$ followed by calcination to deammonate the formed NH$_4$Y. Hβ was obtained from Zeolist Int. (Valley Forge, USA) and has a silica to alumina ratio of 37.5 and a surface area of 680 m$^2$.g⁻¹.

To avoid the formation of clustered copper species during the synthesis of Cu(I)β and Cu(II)β, the use of solid state ion exchange and a high Si/Al ratio for the zeolite was chosen. The complete ion exchange procedure was fully performed in a nitrogen atmosphere. Before ion exchange the zeolite was first calcined in situ. Subsequently, the zeolite was well mixed with an equivalent amount to 2wt% of Cu(I)Cl and Cu(II)Cl$_2$ to obtain Cu(I)/β and Cu(II)/β loaded with 2 wt% of metal, respectively. The obtained mixture was then heated for 2 hours at 500°C under a nitrogen flow. In this way the hydrogen was replaced with copper and the HCl formed was removed with the gasflow.

Amorphous silica was obtained from Dilip (Eindhoven, The Netherlands).

Zirconia was prepared from a commercial available precursor (MEL XZ01247/01) acquired from Mel Chemicals (Manchester, UK) by calcination at 300°C in an air stream for 6 hours. SEM micrographs indicated an average particle size of 5-10 µm.
Niobium oxide (HY 340) was acquired from CBMM Ltd (Araxá, Brazil) and was used after calcination at 200°C in a air stream for 6 hours.

Titanium oxide was prepared from a commercial available precursor (FinnTi S150) acquired from Kemira (Pori, Finland) by calcinations at 300°C in an air stream for 6 hours. SEM micrographs indicated an average particle size of 4-10 µm.

**BET analysis**

The specific surface area (BET) and average pore size of the oxides were determined on a Micromeretics ASAP 2020 instrument. To desorb contaminating molecules (mainly water) from the catalyst surface, the catalyst was first pretreated at 200°C under vacuum for over 2 hours. For the determination of the BET surface area, the value of $p/p_0$ in the range $0 < p/p_0 \leq 0.3$ was used. For the pore size measurements, the value of $p/p_0$ was further increased to 1 and subsequently reduced to 0.14.

**Nitrile hydrolysis with subsequent transamination**

The hydrolysis experiments were performed in closed, stainless steel microreactors using a solvent free system consisting of equimolar amounts of pentanenitrile and hexylamine in aqueous environment, as discussed in Chapter 2. The reaction mixture consisting of pentanenitrile (8.6 mmol, 0.71 g), hexylamine (8.6 mmol, 0.87 g), water (17.2 mmol, 0.31 g) and 0.2 g of the heterogeneous catalyst was prepared in an inert atmosphere. The internal standard was p-xylene (3.56 mmol, 0.36 g). The rest of the experimental procedure was identical to the procedure applied in Chapter 2. Sufficient stirring of the mixture was used to avoid external mass or heat transport limitations for the reactions on the catalyst surface. For the analysis of the reaction mixture with GC the product mixture diluted with ethanol was filtered to remove the heterogeneous catalysts.

For the catalyst screening all the catalyst tests were performed in duplo and the results presented is the average of the conversion and selectivity.

**Results and discussion**

**Catalyst screening**

To simplify the catalyst screening for the polymerization of 6-aminocapronitrile, a model reaction was used. The model reaction consists of nitrile hydration to the amide followed by transamidation with hexylamine, as shown in Figure 3.1. Obviously, one would like to remove NH$_3$ from the mixture to push the equilibrium to the product side, but for practical reasons the reactions had to be performed in a closed system. From an
application point of view, all catalyst systems tested were chosen because of their availability or their ease of preparation. The results from the model reaction, obtained after 2 hours at 230°C, are shown in Table 2. Like in Chapter 2, the selectivity for the nitrile hydrolysis is determined by the combined yield of the terminal amide and N-hexyl pentanamide. Although no significant pentanoic acid formation is observed (<1%) for any of the different systems tested, the small deviation from complete nitrile selectivity is caused by pentanoic acid.† The nitrile conversions can be completely assigned to the catalytic effect of the oxide surfaces, as nitrile hydrolysis is not observed for the non-catalyzed reference experiment (Entry 1 of Table 2).

![Figure 3.1. The initial reaction mixture composition for the model reaction of hexylamine with hydrolyzed pentanenitrile and the quantified reaction products.](image)

**Table 2. The performance of the different catalyst systems for the reaction shown in Figure 3.1.**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>$X_{PN}^b$ (%)</th>
<th>$X_{HA}^b$ (%)</th>
<th>$S_{PN}^c$ (%)</th>
<th>$S_{HA}^d$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>HY</td>
<td>2</td>
<td>15</td>
<td>&gt;99</td>
<td>13</td>
</tr>
<tr>
<td>3</td>
<td>Amorphous SiO$_2$/Al$_2$O$_3$</td>
<td>3</td>
<td>9</td>
<td>&gt;99</td>
<td>44</td>
</tr>
<tr>
<td>4</td>
<td>NaY</td>
<td>11</td>
<td>10</td>
<td>99</td>
<td>90</td>
</tr>
<tr>
<td>5</td>
<td>Hβ</td>
<td>44</td>
<td>54</td>
<td>99</td>
<td>80</td>
</tr>
<tr>
<td>6</td>
<td>Cu(I)β</td>
<td>53</td>
<td>65</td>
<td>99</td>
<td>80</td>
</tr>
<tr>
<td>7</td>
<td>Cu(II)β</td>
<td>32</td>
<td>46</td>
<td>99</td>
<td>67</td>
</tr>
<tr>
<td>8</td>
<td>TiO$_2$</td>
<td>86</td>
<td>79</td>
<td>&gt;99</td>
<td>100</td>
</tr>
<tr>
<td>9</td>
<td>ZrO$_2$</td>
<td>93</td>
<td>84</td>
<td>&gt;99</td>
<td>100</td>
</tr>
<tr>
<td>10</td>
<td>Nb$_2$O$_5$</td>
<td>84</td>
<td>78</td>
<td>&gt;99</td>
<td>100</td>
</tr>
</tbody>
</table>

$a$ 2 hours, 230°C, 0.29 g PN, 0.35 g HA, 0.13 g H$_2$O and 0.2 g catalyst, $b$ $X_{PN}$ and $X_{HA}$ are, respectively, the conversions of pentanenitrile and hexylamine, $c$ $S_{PN} =$ the selectivity for the conversion of pentanenitrile into pentanamide and N-hexyl pentanamide, $d$ $S_{HA} =$ the selectivity for the conversion of hexylamine into N-hexyl pentanamide.

† The presence of the carboxylic acid does not form a problem for the polymerization of 6-aminocapronitrile.
As zeolites showed their power for both the nitrile hydrolysis\textsuperscript{15,18} and the nitrile hydrolysis combined with the condensation of alcohols,\textsuperscript{1} we started by testing a number of zeolitic systems. To avoid a decreasing diffusivity with the formation of polymers, the zeolites used are restricted to the large pore size forms faujasite and beta to enhance diffusion. In addition to the silica based zeolites, an amorphous silica alumina was also screened.

Unfortunately, all silica based systems, entries 2 - 5 of Table 2, have a low activity for the nitrile hydrolysis, mostly in combination with a bad selectivity for the amine amidation. A part of the difference between the hexylamine conversion and the N-hexyl pentanamide yield is accounted for by the formation of dihexylamine, e.g. 4\% of the 11\% loss of selectivity for H\(\beta\) consisted of dihexylamine. The not identified part of the difference between the amine conversion and the N-hexyl pentanamide yield are assumed to consist of the corresponding tertiary amine and imines, both the result of side reactions.\textsuperscript{20} Although different reaction conditions are used, the side reaction of the primary amine is \textit{a posteriori} not a big surprise for zeolitic systems, as these zeolites are industrially used to catalyze for example the disproportionation of methylamine into dimethylamine and trimethylamine.\textsuperscript{21} Despite the fact that amorphous alumino-silicates and sodium faujasite show no loss of selectivity for the amine conversion into N-alkyl amide, their activities are very low. The beta zeolite (entry 5 of Table 2) has a distinctly higher activity than the faujasite zeolite (entries 2 and 4), but the obtained conversion is still not sufficient.

Impregnation of zeolites with metal ions has resulted in many effective catalysts and could also be a solution to enhance the nitrile hydrolysis. As copper is cheap and known to catalyze the nitrile hydrolysis,\textsuperscript{4,12} the H\(\beta\) zeolite was loaded with both Cu(I) and Cu(II) (entries 6 and 7 of Table 2).\textsuperscript{‡} Although both Cu(I) and Cu(II) modified zeolites catalyze the model reaction, the nitrile conversion was by far not quantitative and the selectivity for the amine conversion into N-hexyl pentanamide was also unsatisfactory. Cu(I)\(\beta\) gives a slight increase in nitrile conversion, but the yellow color of the solution suggests leaching of copper from the zeolite. Although the use of Cu(II) is more convenient than Cu(I) from an application point of view, impregnation of the \(\beta\)-zeolite with Cu(II) resulted in a decrease of the nitrile conversion, as well as in a reduced amine selectivity.

\textsuperscript{‡} Using 5 mol\% of the Cu(I)Cl, Cu(II)Cl\(_2\) and Cu(I)acetate salts as a catalyst for the model reaction for 4 hours at 140\(^\circ\)C resulted in a maximum obtained nitrile hydrolysis of 35\%, in the case of Cu(I)Cl. There was no distinctive loss of selectivity for Cu(I)Cl.
Summarizing, zeolites are unsuitable for the polymerization of 6-aminocapronitrile as they do not give a quantitative nitrile conversion. Furthermore, the amine moiety is not solely converted into the corresponding N-substituted amide bond either. The secondary amines formation is devastating for the aimed polymerization process, since they lead to branched products and loss of stochiometry.

Besides the zeolites, three well-known metal oxides, ZrO\textsubscript{2}, TiO\textsubscript{2} and Nb\textsubscript{2}O\textsubscript{5} (entries 8 - 10 of Table 2), were also tested. As mentioned before, TiO\textsubscript{2} was recently reported to be an effective heterogeneous catalyst for the combined hydrolysis and amidation of 6-aminocapronitrile.\textsuperscript{9} ZrO\textsubscript{2} was chosen as Zr is in the same group of the periodic table as Ti, and is known to be a good catalyst for hydrolysis reactions.\textsuperscript{22,23} Nb\textsubscript{2}O\textsubscript{5} was chosen for the high acid strength of its hydrated surface, a characteristic property though to be beneficial for the studied process.\textsuperscript{24}

All three metal oxides show a high conversion of the nitrile. ZrO\textsubscript{2} proves to be even more active than TiO\textsubscript{2}, and a nitrile conversion of 93% was already reached under conditions that are far from optimal, viz. 2 hours at 230°C in a closed system. The three metal oxide systems show excellent selectivity for the conversion of hexylamine into N-hexyl pentanamide. Unlike the microporous zeolites, the oxides are known to be mesoporous. This might be advantageous for the targeted application, being the polymerization of 6-aminocapronitrile into high molar mass nylon 6. During the hydrolysis of 6-aminocapronitrile the formation of oligomers can not be prevented.\textsuperscript{§} The hydrolysis rate will therefore suffer less of diffusion limitation in the case of bigger pore diameters.

Although zirconium dioxide has a quite neutral surface, it has a surprisingly good catalytic performance for the nitrile hydrolysis. This intriguing contradiction has been observed several times before for other reactions and is attributed to a unique property, namely the coexistence at the surface of acidic and basic sites. Due to the strong cooperative effect of these acid and base sites at the surface,\textsuperscript{25} zirconium oxide is known as a bi-functional acid-base catalyst.\textsuperscript{26}

\textsuperscript{§} The first process step for the nylon 6 synthesis out of 6-aminocapronitrile is directed to the full hydrolysis of the nitrile and requires water. As the amine amidation is restricted due to the presence of water, the product mixture of the first step will not contain high molecular weight polyamide chains. However, the formation of nylon 6 oligomers can not be excluded.
Figure 3.2. Conversion-time history for the model reaction at 180°C with 0.2 g ZrO₂ (▲), TiO₂ (◆), and Nb₂O₅ (●).

Rate profile of the metal oxide catalyzed reaction between n-hexylamine and pentanenitrile

The conversion-time history and the composition development of the systems based on the three metal oxides (TiO₂, ZrO₂ and Nb₂O₅) are followed at 180°C, as shown in Figure 3.2 and Figure 3.3. The order of the nitrile conversion with respect to metal oxide at 180°C (Figure 3.2) is the same as the order in conversion after 2 hours at 230°C (Table 2). ZrO₂ has a significantly higher activity for the nitrile hydrolysis than both TiO₂ and Nb₂O₅. With ZrO₂, more than 50% conversion is reached within 2 hours, even at a temperature as low as 180°C.** In spite of a lower hydrolysis rate in the reaction catalyzed by TiO₂ and Nb₂O₅, their reaction rate is still appreciable at 180°C. Note that at 180°C a more pronounced difference in activity is observed between TiO₂ and Nb₂O₅, than is expected from the conversions after 2 hours at 230°C (compare Figure 3.2 and Table 2).

As shown in Figure 3.3, ZrO₂ and TiO₂ (not shown for brevity) show a very similar composition development, which is completely different compared to that obtained by Nb₂O₅. Despite the different composition developments, a complete mass balance is

** Sulfonated ZrO₂ (not shown for brevity) was also tested for its performance at 180°C, but showed a much lower nitrile hydrolysis rate than the other three oxides. After 18 hours the conversion did not exceed 40%. 
obtained for all three reactions only taking pentanamide and N-hexyl pentanamide into account. No appreciable amounts of pentanoic acid had thus been formed.

In accordance with the product development observed for the hydrothermal reaction (Chapter 2), pentanamide is initially the major product in the reaction catalyzed by Nb$_2$O$_5$, as shown in Figure 3.3a. Extrapolation of the pentanamide selectivity to zero conversion according to the Del-plot methodology identifies the terminal amide as the initial product.$^{27}$ Although pentaneamide is the initial product, N-hexyl pentanamide becomes the major species with increasing conversion, comprising more than 90% of the converted nitrile after 18 hours. This behavior is comparable to the composition development for the mild hydrothermal conditions, as described in Chapter 2. The pentanenitrile is first hydrolyzed to the pentanamide and subsequently amidates the hexylamine, as shown in Figure 3.4.

N-hexyl pentanamide is the sole product from the start of the reaction with ZrO$_2$ or TiO$_2$ as a catalyst, in strong contrast to Nb$_2$O$_5$. Only for nitrile conversions higher than 50% a small amount of the terminal amide is observed in the reaction catalyzed by the group 4 metal oxides. The terminal amide concentration remains small, despite the fact that the amount of pentanamide increases somewhat with higher conversions. For a nitrile conversion of 85%, 4% of pentanamide and still less than 1% of acid are formed as the only side products.

---

Figure 3.3. Selectivity development of pentanamide(●) and N-hexyl pentanamide(♦) with nitrile conversion for the model reaction with (a) 0.2 g Nb$_2$O$_5$ and (b) 0.2 g ZrO$_2$ at 180°C.
Despite the initial absence of pentaneamide using ZrO$_2$ and TiO$_2$, the formation can still be explained relying on the reaction scheme of Figure 3.4. The initial absence of pentanamide is due to the fact that both ZrO$_2$ and TiO$_2$ not only catalyze the nitrile hydrolysis, but also accelerate the rate limiting step involved for the transamination, reaction II of Figure 3.4. According to this reasoning, the reaction rate of the amine acylation should therefore initially be higher than the nitrile hydrolysis rate and decline faster than the nitrile hydrolysis rate. The next paragraph shows that the oxides enhance the terminal amide transamination and explains the stronger decline of the transamination rate compared to the decrease of the nitrile hydrolysis rate. This change in rates explains the eventual terminal amide formation.

The effect of the oxides on the amine acylation with a terminal amide

The dramatic difference in composition development for the reaction mixtures with Nb$_2$O$_5$, TiO$_2$ and ZrO$_2$ is intriguing. As pentanamide is the primary product for the model reaction with Nb$_2$O$_5$, the acylation of hexylamine with pentanoic amide in aqueous environment was performed separately (Figure 3.5) to further probe the origin of this difference. The acylation experiments were restricted to Nb$_2$O$_5$ and ZrO$_2$, as i) the same composition development was observed of TiO$_2$ and ZrO$_2$, and ii) ZrO$_2$ is more interesting due to its better performance compared to TiO$_2$. Since N-hexyl pentanamide is the main product for the model reaction catalyzed by ZrO$_2$, the temperature was lowered to 140°C in the hope to trace possible reaction intermediates.
Heterogeneous catalyzed nitrile hydrolysis and subsequent amine amidation

\[ \text{H}_{\text{N}} + \text{H}_2\text{N} \rightarrow \text{H}_2\text{O} + \text{N}_2 \]

Figure 3.5. The transamination of pentanoic amide with hexylamine in aqueous environment.

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

Figure 3.6. Conversion-time diagram (a) for the reaction of pentanamide with hexylamine in the presence of water and ZrO$_2$ (△) or Nb$_2$O$_5$ (●). The uncatalyzed acylation reaction at 140°C (dashed line) is added as a reference. The selectivity development with the conversion (b) is shown for pentanoic acid (○ = ZrO$_2$ and ● = Nb$_2$O$_5$) and N-hexyl pentanamide (◇ = ZrO$_2$ and ■ = Nb$_2$O$_5$).

As shown in Figure 3.6, both Nb$_2$O$_5$ and ZrO$_2$ enhance the amide conversion compared to the reaction without the oxides. While with ZrO$_2$ most of the amide is already converted within 1.5 hour at 140°C, the pentanamide consumption with Nb$_2$O$_5$ shows a gradual increase over more than 6 hours. After 1.5 hour the pentanamide conversion catalyzed by Nb$_2$O$_5$ is only 17%, compared to more than 70% with ZrO$_2$. The maximum amide conversion after 23 hours is 93% for both ZrO$_2$ and Nb$_2$O$_5$ as equilibrium is reached for the closed system. This conversion corresponds with a product mixture consisting of 91% of N-hexyl pentanamide and 2% of pentanoic acid.

ZrO$_2$ catalyzes the hexylamine amidation with pentanamide more effectively than Nb$_2$O$_5$. This supports our assumption that for all oxide systems the N-substituted amide formation using pentanenitrile and hexylamine is a consecutive, two step process. In the ZrO$_2$-catalyzed reaction the intermediate pentaneamide does not accumulate due to the
very fast transamination reaction. This is probably also true for TiO₂, but does not occur with Nb₂O₅.

While some pentanoic acid is also always present in the niobium oxide catalyzed reaction, N-hexyl pentanamide is always the major product during the hexylamine acylation with pentanamide.†† In contrast to the low amounts of pentanoic acid measured using Nb₂O₅, a 19% yield of pentanoic acid is obtained with ZrO₂ for the lowest amide conversion measured. The carboxylic acid is, however, consumed again at higher conversions.

To improve the understanding of the mechanisms involved for the heterogeneously catalyzed 6-aminocapronitrile polymerization with ZrO₂, the origin of the unexpected acid formation using ZrO₂ is discussed. The high initial amount of pentanoic acid is surprising, since hardly any carboxylic acid was observed in the combined nitrile hydrolysis and amidation (Figure 3.3). The 19% pentanoic acid yield shows that ZrO₂ also enhances the pentanamide hydrolysis. This is supported by the hydrolysis of pentanamide in the absence of hexylamine, as a stable 30% yield of pentanoic acid is obtained in the amide hydrolysis with ZrO₂ after 15 hours at 140°C.‡‡ The high initial carboxylic acid yield in the amine acylation shows the importance of the acylation route consisting of the successive amide hydrolysis and transamination (route IIb in Figure 3.4). Although the subsequent acylation with the carboxylic acid also proceeds satisfactorily without the addition of zirconia, amine acylation with carboxylic acid is enhanced by hydrated zirconia.²⁸ Although route IIb is probably far more important than route IIa, the results do not exclude the direct hexylamine acylation with pentanamide. Performing the acylation of hexylamine with pentanamide under dry conditions could be a test for the direct acylation reaction, however, water can not be totally excluded due to the use of a hydrated zirconia.

An equilibrium in the amide hydrolysis, as shown in Figure 3.7, is often observed.²⁹-³¹ The results of Takahashi et al. in the ZrO₂ catalyzed liquid phase transformation of a carboxylic acid and ammonia into the corresponding terminal amide support the presence of the equilibrium,²⁸ as ZrO₂ even accelerates the amide formation from the acid. The amide hydrolysis yield is probably restricted to 30% due to this equilibrium and the

†† For the uncatalyzed amidation the only observed product is N-hexyl pentanamide.

‡‡ The pentanamide is hardly hydrolyzed at 140°C without the addition of the oxide (Chapter 2).
equilibrium explains why the yield of carboxylic acid is strongly dependent on the acylation yield. The equation for the amide consumption shown in Figure 3.7 clearly visualizes the dynamic behaviour of the acylation reaction. Initially mainly pentanamide is present, resulting in a high carboxylic acid formation rate. However, with increasing N-alkyl amide yield less pentanamide is available for the formation of the carboxylic acid and more ammonia is around accelerating the amide formation from the acid. While initially the amount of acid increases, at a certain time the amount of pentanoic acid will start to decrease again. This reasoning clearly describes the observed behaviour of the carboxylic acid.

\[
- \frac{d[\text{amide}]}{dt} = k_f \cdot [\text{amide}] \cdot [H_2O] - k_b \cdot [\text{acid}] \cdot [\text{NH}_3]
\]

Figure 3.7. The amide hydrolysis equilibrium and the equation for the amide consumption for the amidation reaction.

The equilibrium also explains the formation of pentanamide at the end of the reaction in the reaction between pentanenitrile and hexylamine (Figure 3.4), although pentanamide is initially absent. As the amidation rate decreases, the terminal amide amount increases with increasing nitrile conversion. Almost no pentanoic acid is formed in the model reaction, probably due to the use of only 2 equivalents of water.

A schematic representation of all the separate surface reactions is shown in Figure 3.8. First the nitrile is irreversibly hydrolyzed to the terminal amide. Pentanamide is subsequently hydrolyzed to the corresponding carboxylic acid, strongly dependent on an equilibrium. The reaction sequence is finished with the acylation of hexylamine with the carboxylic acid. The direct amidation of the primary amine with the terminal amide is left out of the scheme, as it is expected to be less important. N-hexyl pentanamide is not hydrolyzed or ammonolyzed under these conditions without the use of a catalyst.

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§§ Chapter 4 deals in more detail with the nitrile hydrolysis on a zirconia surface.
Chapter 3

Figure 3.8. Schematic representation of the surface reactions involved for the formation of N-alkyl amide out of a nitrile, a primary amine and water, using ZrO$_2$ as the catalyst, with 1: the nitrile hydrolysis; 2: the amide hydrolysis; 3: the carboxylic acid amidation.

**Complete nitrile hydrolysis with increased temperature**

So far ZrO$_2$ turned out to be both the most active oxide and a highly selective catalyst for the combined nitrile hydrolysis and transamination. Although very promising, the 93% nitrile conversion obtained within 2 hours at 230°C (see Table 2) is not sufficient for the conversion of 6-aminocapronitrile into a high molar mass nylon 6. In order to see whether the required 99+% nitrile conversion can be obtained at all, the conversion-time history of the model reaction using ZrO$_2$ is followed at 180°C, 210°C and 230°C for reaction times exceeding 2 hours, as shown in Figure 3.9. A high initial nitrile hydrolysis rate is obtained at all temperatures, declining strongly at higher conversion.

The origin of the decreased nitrile hydrolysis can be product inhibition. This hypothesis is supported by the strong chemisorption of terminal amides on a zirconia surface (Chapter 4). Another reason could be diffusion limitation, as intraparticle mass transport becomes rate limiting at high conversions. The effective diffusion coefficients of a multicomponent, liquid system, however, are difficult to relate to composition changes of the reaction mixture. It is thus hard to identify the origin of the inhibition.
Heterogeneous catalyzed nitrile hydrolysis and subsequent amine amidation

Figure 3.9. The conversion-time histories of the reaction of valeronitrile with hexylamine in aqueous environment with 0.2 g ZrO₂, T=180°C (●), 210°C (♦) and 230°C (▲)

Even in a closed system, however, a 99% nitrile conversion with complete selectivity of the amine conversion into N-hexyl pentanamide is obtained within 6 hours at 230°C, fulfilling the requirement for the polymerization of 6-aminocapronitrile.

Conclusions

A number of zeolitic systems and metal oxides were screened for the polymerization of 6-aminocapronitrile into nylon 6 using a model reaction. The zeolites showed an insufficient performance. All zeolites induced low nitrile conversions and, in general, a bad selectivity for the conversion of hexylamine into N-hexyl pentanamide. The metal oxides ZrO₂, TiO₂ and Nb₂O₅, however, induced high nitrile conversions together with complete selectivity for the hexylamine acylation into N-hexyl pentanamide.

The analysis of the composition development for the conversion of a nitrile and a primary amine into an N-alkyl amide with use of these metal oxides showed that the nitrile is first converted into pentanamide and subsequently reacts with hexylamine in all reactions catalyzed by the three oxides. A distinct difference in amidation rate between Nb₂O₅ and ZrO₂ was observed for the hexylamine acylation with pentanamide. The difference is due to the capability of ZrO₂ to effectively catalyze the transamination, while Nb₂O₅ has not such a strong effect on this reaction. The catalyzed transamination of pentanamide using ZrO₂ is ascribed to a two step process, of which the first step is most importantly enhanced. The two successive steps are the amide hydrolysis and the acylation of the hexylamine with the formed carboxylic acid. The equilibrium for the
amide hydrolysis has a strong influence on the composition development of the N-hexyl pentanamide formation out of pentanenitrile, hexylamine and water.

As the goal is to reach complete nitrile hydrolysis with ZrO$_2$ as the catalyst, the conversion-time history was followed at an elevated temperature of 230°C. This temperature is high enough to reach the desired nitrile hydrolysis conversion of over 99% within acceptable time and without loss of amine selectivity! These conditions offer good perspectives for the use of ZrO$_2$ in the polymerization of 6-aminocapronitrile to high molar mass nylon 6.

**Reference List**

Acetonitrile hydrolysis
on a hydrous zirconia surface

Introduction

Although a high reaction temperature (230°C) is still required, the commercial ZrO$_2$ described in Chapter 3 performed exceptionally well in the N-hexyl pentanamide synthesis from a nitrile, a primary amine and water. The reaction route is initiated by the hydrolysis of the nitrile. Typically, the catalytic cycle for nitrile hydrolysis on an oxide surface is thought to consist of three successive steps, as schematically shown for acetonitrile in Figure 4.1.$^{1,2}$ After adsorption on the metal oxide surface, the nitrile is hydrolyzed and the final amide is formed upon proton exchange with water. The catalytic cycle is completed by acetamide displacement with acetonitrile. Acetonitrile adsorption on zirconia attracted considerable attention, especially with respect to the hydrolysis behavior.$^{3-5}$ However, the effect of the surface conditions in relation to the catalytic cycle has not been studied in great detail yet.
Figure 4.1. A schematic representation of the catalytic cycle for the nitrile hydrolysis on a zirconia surface, with \( i \) the acetonitrile adsorption, \( ii \) the nitrile hydrolysis and \( iii \) acetamide formation upon proton exchange with water.

Infrared (IR) spectroscopy in combination with probe molecules is a well-known and appreciated technique for the surface site characterization of heterogeneous catalysts.\(^6\) An advantage of IR in surface studies is that the observed surface characteristics are dramatically simplified in comparison to the real surface composition, as it only visualizes the adsorbed surface species and not the complex oxide surface itself. Surprisingly, on various metal oxides the probe molecule acetonitrile already exhibits surface reactions at room temperature, which is identified as the acetonitrile hydrolysis by the reaction products acetamide and acetic acid.\(^3\);\(^4\);\(^7\)-\(^13\) Despite the observation of room temperature nitrile hydrolysis on an unmodified metal oxide surface, effective, liquid phase nitrile hydrolysis using a heterogeneous catalyst requires elevated temperatures.\(^14\)-\(^18\) This rather surprising contradiction between the surface hydrolysis at room temperature observed with infrared spectroscopy and the stringent conditions required for the liquid phase catalyzed nitrile hydrolysis strangely enough did not get any attention so far.

In this chapter the effect the surface hydration has on the three steps of the catalytic cycle, nitrile adsorption, nitrile hydrolysis on the zirconia surface and desorption of the hydrolysis products, is studied. This approach an important allows the identification aspect responsible for the difference between the reaction temperature required for the hydrolysis at the surface and the temperature required for the effective catalyzed nitrile hydrolysis is identified. Note that the study of the surface chemistry with IR spectroscopy limits the reactants to gaseous substances.
Experimental

Zirconia used was obtained by calcination of a commercially available precursor (MEL XZ01247/01, Mel Chemicals) at 573 K for 6 h in an air stream. The zirconium oxide obtained is mainly amorphous and exhibits a specific surface area of 288 m²·g⁻¹.

Infrared spectra were recorded using a Bruker IFS 113v spectrophotometer equipped with a DTGS detector. The controlled atmosphere transmission cell was connected to a stainless steel vacuum system, pumped by a turbomolecular pump with a base pressure better than 1·10⁻⁶ mbar. All IR spectra were recorded at 303 K with a 1 cm⁻¹ resolution. The zirconia material was pressed in a self-supporting wafers (~9.5 mg·cm⁻¹). Before the start of the surface studies, the zirconia was treated by dynamic vacuum. Due to the largely irreversible nature of some of the surface reactions, virgin samples of (virtually) constant thickness were used for each IR experiment.

Acetonitrile was used as a reactant for infrared studies. Due to the strong complication of the CN region for the protonated form of acetonitrile (CH₃CN) by Fermi resonances between the ν(CN) and the combination δₛ(CH₃) + ν(CC) frequencies, the deuterated form of acetonitrile (CD₃CN) is more appropriate for infrared studies than CH₃CN.¹⁹ The CD₃CN (liquid, 99.9 %, Aldrich) was purified by several freeze-pump cycles before use.

Results and discussion

Surface dehydroxylation of zirconia

The infrared spectrum of zirconia (Figure 4.2) contains a wealth of information about the surface species, especially with respect to surface hydroxides, carbonates and adsorbed water.²⁰⁻²³,* The two strong absorption bands at ~3770 cm⁻¹ (OH-T) and ~3685 cm⁻¹ (OH-B) are assigned to the stretching modes of terminal and bridged hydroxide species, respectively.²⁴ The second monolayer consisting of physisorbed water is not fully covered, as otherwise the unperturbed hydroxides would not be observed.²¹ The high frequency part of the spectrum is dominated by a very broad and unresolved absorption band (<3600 cm⁻¹) due to OH stretching modes of both undissociated water molecules and surface hydroxyl species, interacting by hydrogen bonding.²¹ A schematic representation of the surface species present on a hydrated zirconia surface is depicted in Figure 4.3.

* For a more elaborate discussion of the hydrated zirconia surface Appendix A should be consulted.
Figure 4.2. The ZrO$_2$ spectra I) immediately after reaching vacuum in the IR chamber, II) after 10 min vacuum and III) after another 110 min vacuum.

The absorption bands in the region of 1800 – 1000 cm$^{-1}$ are characteristic for surface carbonates, resulting from carbon dioxide chemisorption from the air.$^{21,23,25-27}$ Unfortunately, air contact can not be avoided with commercial zirconia precursor and the surface carbonates are thus always present. As the zirconia is only calcined at a mild temperature, the carbonates cannot be removed without changing the surface characteristics of the oxide either. Hence, this represents a situation of the catalytic surface which is not too deviant from the one relevant to catalysis.$^{21,23}$ Note that although Aboulayt et al. do not consider the presence of surface carbonates in their study of adsorbed acetonitrile on a zirconia surface,$^5$ their presence can not be excluded.$^\dagger$

Among the carbonate bands, the bending deformation mode of undissociated water with weak intensity at $\sim$1630 cm$^{-1}$ is observed. The band at 1630 cm$^{-1}$ is complex and broad and contains contributions of both multilayer physisorbed (liquid-like) H$_2$O and from water coordinated to zirconia.$^{21}$ However, due to the perturbation of the bending vibration by co-adsorbed carbonates, this water band has a weaker intensity compared to the intensity obtained from a completely carbonate free sample.$^{21}$

$\dagger$ The difference spectra shown by Aboulayt et al. do not allow the exclusion of surface carbonates, although these surface species are certainly not removed by the used pretreatment.
Acetonitrile hydrolysis of a hydrous zirconia surface

Figure 4.3. A schematic representation of a highly hydrated zirconia surface, T = a terminal surface hydroxyl group and B = a bridged hydroxyl group.

With prolonged evacuation time an increase in transmission is observed for the whole measured IR range (4000 – 1000 cm\(^{-1}\)), due to decreasing scattering losses with removal of physisorbed water. Upon evacuation at 303 K, a strong decrease in intensity of the broad unresolved band (<3600 cm\(^{-1}\)) and the band at 1630 cm\(^{-1}\) is observed, showing the removal of adsorbed water. The signal intensity of terminal hydroxides increases with elongated evacuation. With prolonged evacuation time, the band at 3770 cm\(^{-1}\) increases about 15% in 10 min and after another 110 min a further increase is observed. This increase in intensity is due to a decrease in hydrogen bonding of the terminal hydroxyls with the removal of physisorbed water. In contrast to the band at 3770 cm\(^{-1}\), the band at 3685 cm\(^{-1}\) corresponding to vicinal OH groups does not change in intensity after prolonged evacuation. As the disappearance of appreciable amounts of surface carbonates only starts at evacuation temperatures above 470K,\(^{21}\) the surface carbonate concentration is assumed to be independent of the current surface pretreatments.

As the observed changes in the surface species present at the zirconia surface only concern molecular water, the difference in surface characteristics after prolonged evacuation at room temperature is completely ascribed to a difference in degree of surface hydration. Mainly the second monolayer of adsorbed water is removed, as it has only a weak interaction with the oxide surface in comparison with the first monolayer of water. A lower coverage of the second surface layer is therefore the main difference between the zirconia evacuated for different periods.

The first step of the catalytic cycle for nitrile hydrolysis is the activation of the nitrile by adsorption. IR spectroscopy permits linking the surface chemistry of a real catalyst to the behavior of a catalytic reaction on a macroscopic scale. However, as a result of the required vacuum for surface studies with IR spectroscopy, the degree of surface hydration for surface studies is much lower than for the catalyzed nitrile hydrolysis in practice. The degree of surface hydration is therefore the main difference between the nature of the zirconia surface in surface studies and in catalysis. The difference in the
The degree of surface hydration is used to obtain more insight in the nitrile adsorption on a zirconia surface.

**Acetonitrile adsorption on the zirconia surface**

The molecular adsorption of CD$_3$CN on a zirconia surface gives rise to four adsorption bands in the IR spectrum, as shown in b. The bands positioned at 2299 cm$^{-1}$ and at 2262 cm$^{-1}$ are according to literature data ascribed to the stretch vibration of acetonitrile, $\nu$(CN), both bound to Lewis acidic zirconia sites$^{3-5}$ and liquid like acetonitrile,$^{28}$ respectively.

![Figure 4.4](image-url)

**Figure 4.4.** a) The wavenumber range from 4000 – 3000 cm$^{-1}$ for the successive application of vacuum and acetonitrile pressure, 10 min evacuation of the zirconia (v1), 3 mbar acetonitrile pressure initially (p1), 10 min acetonitrile pressure (p2), directly after evacuation of the acetonitrile pressure (v2) and after another 110 min evacuation (v3). b) The IR spectra for the range of 2350 – 2050 cm$^{-1}$ directly after introduction of 1.7 mbar of CD$_3$CN acetonitrile, on a zirconia surface evacuated for 10 min and another 110 min.

The theoretical frequencies of the symmetrical stretch vibration, $\nu_s$(CD$_3$), and the asymmetrical stretch vibration, $\nu_{as}$(CD$_3$), of the methyl group are respectively equal to 2113 and to 2250 cm$^{-1}$. In comparison to gaseous CD$_3$CN, they are shifted to lower wavenumbers by 12 and 7 cm$^{-1}$. According to an ab initio study, electron density perturbation in the CD$_3$ group caused by CD$_3$CN interaction with an electron-acceptor site,$^{31}$ leads to insignificant upward shifts of the CD stretching frequencies. Therefore, the downward shift has to be due to a weak interaction with the oxide channel wall, as the small widths of the $\nu_s$(CD$_3$) and $\nu_{as}$(CD$_3$) and the $\nu_{as}$(CD$_3$) degeneracy$^{28}$ imply the absence of any specific interaction of the CD$_3$ group. Small frequency shifts of 10 – 15 cm$^{-1}$ for the CD stretching vibration are usually observed for organic molecules perturbed
Acetonitrile hydrolysis of a hydrous zirconia surface

by dispersion interactions in going from gas to liquid. These $\nu_{s}(\text{CD}_3)$ and $\nu_{as}(\text{CD}_3)$ bands are therefore believed to be characteristic for physisorbed acetonitrile.

The behaviour of the hydroxide region upon acetonitrile adsorption and desorption shows i) the complete disappearance of the unperturbed hydroxide signals upon adsorption and ii) the complete reappearance upon evacuation, as shown in a. This shows that the surface hydroxyls are not consumed upon nitrile adsorption on a hydrated surface, in contrast to the observations reported by Aboulayt et al. for a dehydrated surface.5

While still highly hydroxylated after 120 min. calcination at 303K, the amount of zirconia coordinated acetonitrile increases more than 65% in comparison to the amount of coordinated acetonitrile on a zirconia surface activated by only 10 min. evacuation, as shown in a. This increase can be rationalized by a shift of the equilibrium concentrations of the equilibrium depicted in Figure 4.6 with a decreased amount of absorbed water. Hence, a more dehydrated surface results in a distinctly higher amount of bound acetonitrile than the less dehydrated surface. In contrast to the behavior of the bound acetonitrile, a small decrease is observed in the intensity of the stretch vibration of the physisorbed acetonitrile and the symmetrical stretch vibration of the methyl group. For a liquid phase system consisting of nitrile molecules and water only a small amount of nitrile will probably adsorb due to the strong competition with water.

With evacuation of the sample chamber, the signal of coordinated acetonitrile is almost completely removed again, independent of the surface pre-treatment. Only 3% of the signal intensity obtained from the adsorbed acetonitrile pressure of 1.7 mbar remains after evacuation. This shows that the adsorption of bound acetonitrile is mostly reversible on a hydrated zirconia surface.

The band at 2113 cm$^{-1}$ does not show a dependence on the degree of surface hydration, demonstrating the effect of adsorption on the $\nu_{s}(\text{CD}_3)$ band of the coordinated acetonitrile. The perturbation of $\nu_{s}(\text{CD}_3)$ band could be due to deuterium abstraction, resulting in the formation of surface OD-species. The $\nu(\text{OD})$ is characterized by an absorption band at 2700 cm$^{-1}$. As no OD formation is observed, the deuteria of the acetonitrile methyl is not abstracted. The disappearance of the $\nu_{s}(\text{CD}_3)$ of coordinated acetonitrile, probably results from the H-bonding with neighboring surface hydroxyls. This view is strengthened by the acidic character of the acetonitrile protons, which stimulates the interaction with other polar species.

The zirconia surface used for the catalytic nitrile hydrolysis will always be highly hydrated, as at least stochiometric amounts of water are required to completely convert an
amount of nitrile. This limits the amount of absorbed acetonitrile activated for hydrolysis, and consequently decreases the observed hydrolysis rate.

Figure 4.5b represents a Langmuir adsorption isotherm of acetonitrile on the zirconia surface.\(^4\) The quantities of zirconia coordinated (2299 cm\(^{-1}\)) and physisorbed acetonitrile (2262 cm\(^{-1}\)) follow a similar trend. A more than 3 times higher pressure (from 2.9 mbar to 9.7 mbar) only results in a 60% increase of both physisorbed and zirconia coordinated acetonitrile and the actual dependence is even smaller.\(^5\) A similar pressure dependence of both bound as physisorbed acetonitrile suggests the presence of a rapid established equilibrium between the physisorbed and Lewis-bound acetonitrile.

Although Aboulayt et al. ascribe the nitrile adsorption to ligand displacement, the surface activated at 423 K probably consists of some coordinatively unsaturated surface (cus) zirconium ions too due to the removal of bound water.\(^5\) These cus zirconium ions are also capable of bounding acetonitrile and increase the amount of adsorbed acetonitrile.

Furthermore Aboulayt et al observed the irreversible disappearance of the hydroxyl group vibration, which they attribute to irreversible ligand displacement.\(^5\) However, for a

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\(^4\) The dependence of the amount of absorbed acetonitrile on the acetonitrile pressure can not be determined for the 120 min evacuated zirconia due to a high consumption rate of the absorbed acetonitrile.

\(^5\) A small amount of nitrile hydrolysis cannot be avoided during the adsorption analysis, which results in a decreased amount of bound acetonitrile as will be discussed later.
Acetonitrile hydrolysis of a hydrous zirconia surface

hydroxylated surface the irreversible disappearance of the hydroxyl group vibration is more convincingly accounted for by reversible disappearance due to perturbation of the vibration of adsorbed acetonitrile initially, followed by the irreversible consumption by nitrile hydrolysis. Morterra et al. ascribe the acetonitrile adsorption of a hydroxylated surface more specifically to the ligand displacement of zirconia bound water. The amount of bound acetonitrile is strongly dependent on the hydration degree of the surface, as an increased amount of physisorbed water is competitive with physisorbed acetonitrile for Lewis acid coordination, as schematically shown in Figure 4.6.

![Figure 4.6. A schematic representation of the competition between the surface adsorption of acetonitrile and water, dependent on the physisorbed amounts.](image)

An increasing degree of surface hydration thus results in a decline of the absorbed amount of bound acetonitrile. As the nitrile hydrolysis rate is obviously strongly dependent on the amount of activated adsorbed acetonitrile, the observed hydrolysis rate for liquid phase catalysis is probably strongly restricted by a low amount of bound acetonitrile. However, in addition to the effect on the amount of adsorbed acetonitrile, the degree of surface hydration can also affect the nitrile hydrolysis rate of coordinated acetonitrile. This is very interesting as it is the second step of the catalytic cycle. To elucidate the effect of the surface hydration degree, the hydrolysis of adsorbed acetonitrile is now investigated.

The dependence of the nitrile hydrolysis rate on the surface hydration

The surface reaction of bound acetonitrile at 313 K is evidenced by a decrease of the intensity of the v(CN) band at 2299 cm$^{-1}$, as shown in Figure 4.7. Depending on the dehydroxylation degree of the surface and the contact time of acetonitrile, pronounced differences in the surface reactions of acetonitrile are observed. The decrease in coordinated acetonitrile can be the result of the surface site consumption only by hydrolysis products or a decrease of the acetonitrile pressure due to catalytic nitrile consumption. The decrease of the intensity of the v(CN) band due to the coordinated acetonitrile should according to the adsorption isotherm of Figure 4.5b correspond to a
conversion of about 70%. However, the amount of physisorbed acetonitrile does not change, as is clearly shown in . Furthermore, there is no distinct pressure change observed, which could hint to the formation of gaseous reaction products. The change in bound acetonitrile coverage is therefore ascribed to the consumption of surface sites and is not due to the complete consumption of the gaseous reactant resulting from a catalytic reaction.

Figure 4.7. Effect of the contact time on the adsorption bands of adsorbed CD$_3$CN, a) for the $\nu$(CN) bands and b) for the $\nu$(CD$_3$) region. The first spectrum is taken after the introduction of 1.87 mbar CD$_3$CN (i), the other spectra are recorded after increasing contact time with $\frac{1}{2}$ an hour.

Two kinds of competing surface reactions can account for the consumption of bound acetonitrile on a zirconia surface (Figure 4.8), that is nitrile hydrolysis and proton abstraction.$^{3,5,32}$ The carbanion formation by deuterium abstraction is characterized by a broadening of the adsorption bond at 2113 cm$^{-1}$ corresponding to [CD$_2$CN$^-$] and the formation of a broad OD band at 2170 cm$^{-1}$. The carbanion is not a stable surface species for highly hydroxylated surfaces,$^{3,4}$ and is therefore not observed. However, the formation of surface OD species due to the deuterium exchange of surface hydroxides as a result of the equilibrium between the carbanion and adsorbed acetonitrile is an indirect way to monitor the presence of this equilibrium. However, no OD band is observed, and there is therefore no indication that deuterium/proton abstraction plays a role in our system.$^{**}$

$^{**}$ The OD formation is observed for the acetonitrile adsorption on a surface dehydrated at 200$^\circ$C.
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Figure 4.8. The schematic representation of the competing surface reactions of Lewis coordinated acetonitrile on a zirconia surface, with arbitrary surface reaction intermediates for clarity.

The bands resulting from the surface reaction of bound acetonitrile are observed in the mid-IR range (1800 – 1000 cm\(^{-1}\)) as shown in Figure 4.9. These bands are according to literature data identified as the hydrolysis products.\(^{12,13}\) Five different signals are clearly visible, although the relative intensities vary depending on the reaction conditions. These bands are positioned at 1651, 1546, 1471, 1433, and at 1215 cm\(^{-1}\).

Figure 4.9. The development of the absorption bands of the nitrile hydrolysis products, after \(i\) 30 min (---), \(ii\) 60 min (----), \(iii\) 90 min (——) and \(iv\) 120 min of 1.7 mbar of acetonitrile pressure.

The assignment of the bands to specific surface acetamide species is not unambiguous. However, the observed bands elucidate some important aspects with respect to the catalytic cycle. The signal at 1651 cm\(^{-1}\) is assigned to molecularly adsorbed acetamide, as it shows a good resemblance to the bands of acetamide absorbed on TiO\(_2\).\(^7\) The other bands show a strong similarity with the bands Aboulayt et al. identified as two kinds of acetamide anion species (assigned \(\alpha\) and \(\beta\)) resulting from the nitrile hydrolysis on a zirconia surface. These two species are both characterized by a set of three bands denoted A, B and C, as shown in Figure 4.9.\(^5\) The good comparison of the positions of these bands with the results of Aboulayt et al. is surprising, as no distinct isotope effect is
observed since deuterated acetonitrile is used instead of protonated acetonitrile. The agreement is due to the fact that the hydrolyzed nitrile functionality is protonated by surface hydroxyl groups.

Figure 4.10. The time dependence of the intensity of the $\nu$(CN) signals at 2299 cm$^{-1}$ (△) and 2262 cm$^{-1}$ (◆) and the $\nu$(CD$_3$) signal at 2111 cm$^{-1}$ for a zirconia surface evacuated for a) 10 min and c) 2 hours. The difference of the spectra in the hydrolysis product region for every half an hour for a zirconia surface evacuated for b) 10 min and d) 2 hours. The roman numbers I to IV relate the change in amount of adsorbed acetonitrile to the change in amount of hydrolysis products present on the surface. $P_{\text{CN}}$ = 1.87 mbar, 9.6 mg ZrO$_2$. The first order fits for the nitrile consumption (—) are shown in Figure a) and c).

Due to the limited identification of the hydrolysis products, it is not possible to relate the formed reaction intermediates present on the oxide surface to a specific reaction mechanism. However, an important observation is that although the adsorbed acetonitrile is hydrolyzed on a zirconia surface, most of the products are only converted into an
Acetonitrile hydrolysis of a hydrous zirconia surface

acetamide anion and not fully converted into the molecular amide. So step iii of the catalytic cycle is not at all quantitative, even though an excess of molecular water is still present, which should permit the completion of the nitrile hydrolysis.

Difference spectra for the change in hydrolysis products with reaction time allow a better interpretation of the change in the product formation, than the accumulated view of Figure 4.9. shows the change in the amount of adsorbed acetonitrile species and the difference spectra for the hydrolysis product range, for two zirconia surfaces initially evacuated for 10 min and for 120 min. In spite of the different extinction coefficients of the surface species involved, the intensity increase of the hydrolysis products clearly follows the change in the amount of zirconium coordinated acetonitrile (\( \theta \)). With respect to the required water for the catalytic nitrile hydrolysis, the much lower nitrile consumption rate for the higher water coverage is very striking. A strong difference in intensity is observed for the absorption bands of the hydrolysis products for different initial surface pretreatments, as observed for monoclinic ZrO\(_2\) activated at beam temperature and at 523 K.\(^4\) The development of the absorbance bands in time for the hydrolysis product region is comparable to the behavior observed by Aboulayt \textit{et al.} and Morterra \textit{et al.}\(^4;5\) Except for the band positioned at 1434 cm\(^{-1}\) the change in intensity of the bands is initially high, independent of the surface pre-treatment. The absorption band at 1434 cm\(^{-1}\) has a relative constant intensity change, while the other bands show a strong decrease in intensity. A large difference for the two surface pre-treatments is especially observed for the absorption bands at 1547 and 1470 cm\(^{-1}\). These two bands increase more strongly for the more dehydrated surface. This abundant formation of nitrile hydrolysis products on the zirconia surface consumes surface sites available for acetonitrile absorption. As most of the hydrolysis products consist of ionic species, they have to form a molecular species first before they can desorb. This implies that the formation of molecular acetamide upon proton exchange of the anionic acetamide with water is the rate limiting step. The formation of the molecular acetamide might be dependent on equilibria.

A fit assuming first order kinetics for the nitrile coverage to the consumption rate of the adsorbed acetonitrile (Eq. 4.1) allows a comparison of the nitrile consumption rate for the two different surface conditions, independent of the nitrile coverage:

\[
\frac{d\theta_{\text{CD,CN}}}{dt} = -k_{\text{hydr}} \cdot \theta_{\text{CD,CN}} \tag{4.1}
\]

with \( \theta_{\text{CD,CN}} \) as the nitrile coverage and \( k_{\text{hydr}} \) as the first order rate constant for the coordinated nitrile consumption. The acetonitrile consumption for the two hour evacuated ZrO\(_2\) obeys a fit to a first order dependence with the amount of absorbed acetonitrile until
a conversion of about a 60% is reached, corresponding to a reaction time of about 1 h. For higher conversions the fit starts to deviate significantly from the actual nitrile consumption. The kinetics of the acetonitrile disappearance on the the zirconia surface evacuated for 10 min shows a distinct deviation of first order kinetics within 20 min contact time with acetonitrile, both for a 1.7 and 9.0 mbar (not shown for clarity) equilibrium pressure of acetonitrile. As more adsorbed water is available on the 10 min evacuated surface than on the 120 min evacuated surface, the faster deviation excludes that the formation of bound nitrile hydrolysis intermediates is dependent on the amount of adsorbed water.

The initial observed rate constant for the more hydrated surface is approximately one order of magnitude lower than for the dehydrated surface. If the nitrile is directly hydrolyzed by water, the initial observed rate constant of the more hydrated surface should be higher. The decrease in hydrolysis rate of the more hydroxylated surface therefore strengthens the conclusion that water does not directly hydrolyze the bound nitrile for the hydrolysis in surface studies. The hydrolysis thus occurs with a surface hydroxyl. The 25% higher terminal hydroxyl concentration for the more dehydrated surface compared with the more hydrated zirconia can account for the difference in observed rate constants for the different hydration degrees of the surface, supporting that the nitrile is hydrolyzed by surface hydroxyls.

In conclusion, the hydrolysis of adsorbed acetonitrile results in the abundant formation of acetamide species present at the oxide surface. Besides the fully hydrolyzed molecular acetamide, a large amount of ionic amide species are also formed as a result of partial surface hydrolysis. As these ionic surface species first have to form molecular surface species, they do not desorb and as a result they limit the amount of coordinated acetonitrile. Accounting for the decrease in adsorbed acetonitrile shows that the nitrile hydrolysis is faster on the dehydrated zirconia surface than on the more hydrated surface. The difference in concentration of terminal hydroxides can account for the difference in initial hydrolysis rate. Abundant formation of ionic hydrolysis products restrict the nitrile hydrolysis and should be desorbed to allow a catalytic reaction. The primarily formation of ionic hydrolysis products is the origin for the discrepancy between stringent conditions required for the catalyzed nitrile hydrolysis and the mild conditions required for the nitrile hydrolysis on the metal oxide surface. Although water does not have a big effect the further hydrolysis of the ionic species, activation of the further hydrolysis of the ionic species using temperature treatment could result in complete hydrolysis.
Hydrolysis product desorption

Figure 4.11 shows the evolution of the infrared bands of the hydroxyl range and the hydrolysis products after the treatment of the zirconia at an increased temperature. Upon a stepwise temperature program a gradual change in surface species is observed, which is a result of the hydrolysis of the acetamide surface ions into acetate species. This change is identified as the hydrolysis of the acetamide anion species into surface acetates. While there are still surface hydroxyls present to complete the catalytic cycle, the ionic products do not form molecular acetamide or acetic acid and therefore do not desorb upon a temperature treatment. This shows that the hydrolysis products are strongly bound to the zirconia surface.

Figure 4.11. The spectra of the surface hydroxyl region and the hydrolysis product region after the consecutive heating to 50°C (---), 150°C (– –) and 250°C (––) and cooling again.

The strong adsorption of the ionic acetamide and acetic acid species indicates the existence of product inhibition in the catalytic nitrile hydrolysis with this zirconia, probably resulting in a poor catalytic performance. However, for liquid phase system of Chapter 3, the nitrile hydrolysis proceeds in the presence of a primary amine. As the zirconia has a good catalytic performance for amine amidation with carboxylic acid, the amine is apparently capable of reacting with the formed surface species of the nitrile hydrolysis. In this way the catalytic cycle is completed.

Conclusions

The surface of the hydrated zirconia consists of two kinds of surface hydroxyls and is further fully covered with adsorbed and physisorbed water. Prolonged vacuum treatment allows a reduction of the degree of zirconia hydration by removal of physisorbed water.
When a zirconia surface is exposed to acetonitrile, coordinated and physisorbed acetonitrile species on the surface are observed. The amount of adsorbed acetonitrile depends on the degree of surface hydration, strongly increasing with decreasing degree of surface hydration. On the contrary, the amount of physisorbed acetonitrile is relatively independent of the hydration degree. The amount of absorbed and physisorbed acetonitrile are both not strongly dependent on the nitrile pressure. These results suggest that for the catalytic hydrolysis conditions the amount of activated nitrile is limited due to a high surface hydration degree.

For a highly hydroxylated zirconia surface, the only observed surface reaction of acetonitrile is hydrolysis. Proton abstraction to give carbanionic product is not observed. The hydrolysis rate is distinctively higher after dehydration of the zirconia surface. This higher rate of nitrile hydration can be correlated to a higher surface coverage of terminal hydroxides for a more dehydrated zirconia surface. This indicates that direct nitrile hydrolysis with molecular water is not occurring.

The resulting reaction products primarily consist of a number of ionic hydrolysis products, which consume surface sites available for the coordination of acetonitrile. As acteamide anions have to form molecular amide first before they can desorb, this results in product inhibition of the nitrile hydrolysis and consequently a decreased hydrolysis rate. As ionic hydrolysis products are mainly formed, the catalytic cycle for the nitrile hydrolysis on a zirconia surface is mainly incomplete. A temperature treatment at 523 K does not complete the catalytic cycle either, although an excess of water is still present. Upon the temperature treatment, the initial acetamide ion are rather converted into new products identified as acetate species, instead of forming molecular acetamide.

Summarizing, infrared spectroscopy clearly shows the effect of surface hydration on nitrile adsorption and hydrolysis of the adsorbed nitrile, the first two steps of the catalytic cycle for nitrile hydrolysis as represented by Figure 4.1. Both the adsorption as the surface hydrolysis of acetonitrile is obstructed by a higher hydration degree of the zirconia surface, resulting in a lower rate of nitrile hydrolysis for practical catalytic conditions compared to the hydrolysis rate of absorbed acetonitrile for the surface studies. Furthermore, the completion of the catalytic cycle is identified as an important bottleneck with respect to the catalyzed nitrile hydrolysis, as even at elevated temperature ionic hydrolysis species are still mainly present and they do not desorb. This result suggests a that strong effect of product inhibition due to formation of ionic surface species. However, the combination of elevated temperature with the presence of the primary amine for the polymerization of ACN apparently allows the completion of the
catalytic cycle, as observed in Chapter 3. Although the formation of distinct amounts of terminal amide for high nitrile conversions explain the decrease in hydrolysis rate.

Reference List

Chapter 4

Appendix. Description of a zirconia surface covered with water

A good understanding of surface characteristics is a prerequisite for well-founded conclusions about the observed surface reactions. A clear view of the possibilities and limitations of the applied spectroscopic technique with respect to the identification of the surface of zirconia is therefore required to relate the acetonitrile hydrolysis to surface properties.

The complete description of the surface composition in a vacuum environment requires the quantification of the amount of surface species present and the amount of coordinatively unsaturated surface (cus) sites. IR visualizes surface species, however, it can not directly show the presence of cus sites.\textsuperscript{34,35} With increased dehydration these cus cations and cus oxygen anions are typically exposed by metal oxide surfaces. IR does not distinguish between the species present on different surfaces and shows the sum of all species present. Water can not be quantified due to unknown extinction coefficient and the amount of hydroxides present can not be quantified without the use of other complementary techniques.\textsuperscript{36} Therefore the nitrile hydrolysis dependence on different surface hydration can only be qualitatively treated. The adsorption behaviour of the probe molecules is generally performed for highly dehydrated metal oxide surfaces. In such a case the adsorption and activation of organic molecules mainly concerns cus ion sites.\textsuperscript{34,37}

Due to the inevitable presence of water in catalytic hydrolysis experiments, an oxide surface typically has a high degree of hydration. Compared to other metal oxides, zirconia adsorps a lot of water\textsuperscript{38-40} and has a high hydroxide coverage of its surface.\textsuperscript{41} A distinction between adsorbed water can be based upon the distance to the zirconia surface, represented by monolayers. For clarity, a rigid distinction between the water layers higher than the second monolayer experience and lower than the second layer is assumed. As water layers higher than the second monolayer do not experience much influence of the metal oxide surface, they are readily removed upon introduction of the vacuum and the water observed with IR can therefore be attributed to the first two monolayers, schematically shown in Figure 4.3.

The water affecting surface reactions can be classified into three types: structural water (condensed hydroxyl groups), zirconia coordinated water and adsorbed water (also often named hydrogen bound water), in order of decreasing bond strength. It is known that on most ionic oxides the surface hydrated layer is made up of hydroxyls and of a variable amount of coordinated undissociated water. The second adsorption layer consists
of physisorbed water, which is expected to be more activated than bulk water.\textsuperscript{40} The first monolayer, the water layer closest to the zirconia surface, consists both of surface hydroxides and water coordinated to zirconia sites. Calculations show that a full monolayer of surface hydroxides is not formed on a tetragonal zirconia, due to an increase in hydroxylation energy with increasing hydroxide coverage.\textsuperscript{42} The amount of hydroxyls and adsorbed water depends on the crystal structure and the surface direction of the oxide surface.

Surface characteristics and the catalytic behaviour of zirconia are therefore very dependent on the preparation method, also with respect to the nature of the first monolayer of adsorbed water.\textsuperscript{43} And the nitrile hydrolysis on a zirconia surface is again dependent on the exact morphology of the zirconia.\textsuperscript{3,4} The mechanism of nitrile hydrolysis was therefore not unambiguous for every kind of zirconia. As the zirconia used in Chapter 3 performs well in the catalyzed N-hexyl pentanamide synthesis, the study is restricted to this kind of zirconia.
The polymerization of 6-aminocapronitrile

Introduction

Polycondensation of 6-aminocapronitrile (ACN) into high molecular weight nylon-6 (Figure 5.1) already attracted attention during the early days of this highly versatile polymer. In principle, the ACN route allows a cheaper and environmentally friendlier monomer synthesis of nylon-6 than the currently used monomer \( \varepsilon \)-caprolactam.\textsuperscript{1-8} The challenge for a route based on this alternative monomer is to obtain complete hydrolysis of the nitrile functionality without side reactions of the amine functionality. As shown in Chapter 2 and 3, the temperature required for nitrile hydrolysis is high and to achieve complete conversion a catalyst is required to activate the system. It was found that zirconia (ZrO\(_2\)) was the most promising catalyst for the hydrolysis of pentanenitrile combined with the subsequent amidation. The use of a porous ZrO\(_2\) could be successful in making high molecular weight nylon-6 and is therefore used to perform the polymerization of 6-aminocapronitrile.
Figure 5.1. The overall reaction for the synthesis of nylon-6 out of 6-aminocapronitrile

The most important developments with respect to the polymerization of ACN are unfortunately captured in patents and consequently no clear evaluation of the aspects affecting the polymerization is accessible.\textsuperscript{1-8} So far, the best product seems to be obtained by performing the nitrile hydrolysis and amine amidation in separate process steps, using a heterogeneous TiO\textsubscript{2} catalyst for the nitrile hydrolysis.\textsuperscript{6,7} The use of separate process steps for the nitrile hydrolysis and amine amidation are necessary to obtain a linear, high molecular weight nylon-6, as both reactions are contradictory with respect to the relation between complete conversion and the required amount of water. Moreover, the simultaneous presence of nitriles, amines and amides at elevated temperatures may cause side reactions.

In this chapter the polymerization of ACN using the zirconia catalyst is studied, and the results of the post-condensation of the hydrolysis product are discussed with respect to the development of the molecular weight distribution.

**Experimental procedures**

**6-aminocapronitrile**

High purity 6-aminocapronitrile (ACN) was kindly supplied by BASF. As the purity of the monomer is of crucial importance for the synthesis of high molecular weight polymers using a polycondensation reaction, the purity was checked. The best method appeared to be \textsuperscript{13}C NMR (Varian Inova 500, 125 MHz \textsuperscript{13}C), for which the high resolution spectrum of ACN is shown in Figure 5.2. No other signals than those expected for ACN are detectable, except for the carbon signal due to an impurity of the NMR solvent. Although \textsuperscript{13}C NMR is not very accurate for the determination of the purity of a compound of a mixture composition, the absence of a detectable impurity allows the statement that the ACN used is pure.
The polymerization of 6-aminocapronitrile

The polymerization of 6-aminocapronitrile (ACN) was performed in the presence of water above its boiling point, which requires a closed autoclave. As the small amount of catalyst available limits the size of the used autoclaves, the reactor set-up as discussed in Chapter 2 was used. A typical polymerization experiment was performed using 1 equivalent of ACN (0.90 g, 1 mL, 8.0 mmol), 2 equivalents of water (0.29 g, 16 mmol) and 0.40 g ZrO$_2$ (Melchem, MEL XZ01247/01) at a reaction temperature of 230°C. As the reactor set-up does not allow the polymer-catalyst separation in the melt, the separation was achieved by first dissolving the polymer product in formic acid. After removal of the zirconia catalyst by filtration, the polymer was precipitated by addition of water and separated from the liquid phase by ultracentrifugation for 1 hour at 40,000 rpm. It should be noted, that this method results in the loss of the low molecular weight fraction of the product.

The solid state post-condensation was performed by heating the finely ground polymer to 185°C for 24 hours under a nitrogen flow, using the method described in literature.$^9$

Nylon-66 synthesis out of adipamide and hexamethylenediamine

Equimolar amounts of adipamide (0.431g, 2.99 mmol) and 1,6-diaminohexane (0.347g, 2.99 mmol) were mixed and heated for the required reaction time at 230°C. This experiment was performed in a glass round bottom flask provided with a heating mantle, using a continuous flow of nitrogen to remove the ammonia and minimize side reactions that involve NH$_3$. 

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Figure 5.2. $^{13}$C NMR spectrum of 6-aminocapronitrile in CDCl$_3$. 

Nylon-6 synthesis out of 6-aminocapronitrile

The polymerization of ACN was performed in the presence of water above its boiling point, which requires a closed autoclave. As the small amount of catalyst available limits the size of the used autoclaves, the reactor set-up as discussed in Chapter 2 was used. A typical polymerization experiment was performed using 1 equivalent of ACN (0.90 g, 1 mL, 8.0 mmol), 2 equivalents of water (0.29 g, 16 mmol) and 0.40 g ZrO$_2$ (Melchem, MEL XZ01247/01) at a reaction temperature of 230°C. As the reactor set-up does not allow the polymer-catalyst separation in the melt, the separation was achieved by first dissolving the polymer product in formic acid. After removal of the zirconia catalyst by filtration, the polymer was precipitated by addition of water and separated from the liquid phase by ultracentrifugation for 1 hour at 40,000 rpm. It should be noted, that this method results in the loss of the low molecular weight fraction of the product.

The solid state post-condensation was performed by heating the finely ground polymer to 185°C for 24 hours under a nitrogen flow, using the method described in literature.$^9$

---

Nylon-66 synthesis out of adipamide and hexamethylenediamine

Equimolar amounts of adipamide (0.431g, 2.99 mmol) and 1,6-diaminohexane (0.347g, 2.99 mmol) were mixed and heated for the required reaction time at 230°C. This experiment was performed in a glass round bottom flask provided with a heating mantle, using a continuous flow of nitrogen to remove the ammonia and minimize side reactions that involve NH$_3$. 

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Polymer analysis

The molecular weight distribution of the synthesized nylon-6 was determined using size exclusion chromatography (SEC) with hexafluoroisopropanol (HFIP) as eluent. The SEC set-up consecutively consists of an eluent degasser (Alltech Elite), a gradient pump (Shimadzu, LC-10AD), an injector (Spark Holland, Midas), a two-column set (PSS, PFG Linear x1 7 µm 8 x 300 mm) in series and a differential refractive-index detector (DRI) (Waters, 2414). After injection of a 50 µL sample, the separation was established with a flow rate of 0.8 mL/min at a constant temperature of 40°C. The HFIP (Biosolve, AR-S grade) was recycled and distilled when necessary. For evaluation of the molecular weight distributions the DRI detector was used as a concentration detector. The calculated molecular weights were based on a calibration curve for poly methyl methacrylate standards (molar mass range 650 – 1.5·10^4 g·mol^-1) of narrow polydispersity (Polymer Laboratories) in HFIP.

The presence of nitrile functionalities in the polyamide product was assessed with transmission infra-red spectroscopy (Biorad, FTS 6000) on a thin polymer film, obtained by compression of a polymer particle with a diamond press.

Results and discussion

Before synthesizing nylon-6 out of ACN using ZrO₂, the uncatalyzed synthesis was performed as a reference first. Both time and amount of water were varied, as shown in Table 1.

Table 1. The molar mass distribution of the nylon-6 synthesized from 6-aminocapro nitrile without a catalyst at 230°C.

<table>
<thead>
<tr>
<th>Entry</th>
<th>ACN:H₂O</th>
<th>t [h:m]</th>
<th>M_n [g·mol⁻¹]</th>
<th>PDI [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1:2</td>
<td>8:30</td>
<td>1200</td>
<td>2.5</td>
</tr>
<tr>
<td>2</td>
<td>1:2</td>
<td>22:30</td>
<td>2100</td>
<td>1.6</td>
</tr>
<tr>
<td>3</td>
<td>1:10</td>
<td>8:30</td>
<td>1100</td>
<td>1.6</td>
</tr>
<tr>
<td>4</td>
<td>1:10</td>
<td>22:30</td>
<td>1300</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Although some oligomeric material is obtained, no high molecular weight is formed. The molecular weight is largely independent of the amount of water used and of the reaction time, although a smaller amount of water initially results in a higher polydispersity (Entry 1 of Table 1). After more than 22 hours with 2 equivalents of water (Entry 2 of Table 1) the polydispersity index (PDI) is similar to that obtained in the
polymerizations with 10 equivalents of water, but the number average molecular weight ($M_n$) is in this case about a factor two higher.

As the amount of water used seems to affect the polymerization of ACN, the ACN polymerization using the zirconia catalyst was also performed using varying amounts of water (Table 2). A distinct increase of the molecular weight is observed for all experiments in comparison to the polymerization without zirconia, showing that zirconia indeed catalyzes the nitrile hydrolysis of ACN, as was earlier observed for the studied model compounds (Chapter 3). In contrast to the uncatalyzed ACN polymerization, the polymerization catalyzed by ZrO$_2$ does not depend on the amount of water used, at least not within experimental error. The low PDI in comparison to Entry 1 of Table 1 can be rationalized by the fact that the zirconia also catalyzes the transamidation reaction.

### Table 2. The molar mass distribution of the nylon-6 synthesized from 6-aminocapronitrile, using ZrO$_2$ as the catalyst.$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>ACN:H$_2$O</th>
<th>$M_n$ [ g mol$^{-1}$]</th>
<th>PDI [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1:2</td>
<td>4100</td>
<td>1.4</td>
</tr>
<tr>
<td>2$^b$</td>
<td>1:2</td>
<td>4700</td>
<td>2.6</td>
</tr>
<tr>
<td>3</td>
<td>1:4</td>
<td>4000</td>
<td>1.4</td>
</tr>
<tr>
<td>4</td>
<td>1:8</td>
<td>4000</td>
<td>1.5</td>
</tr>
<tr>
<td>5</td>
<td>1:10</td>
<td>3900</td>
<td>1.4</td>
</tr>
</tbody>
</table>

$^a$ 230°C, 8 hours. $^b$ Nylon of entry 1 after 24 hours post-condensation at 185°C in the solid state

Although the use of the zirconia catalyst increases the molar mass, the molar mass is still small with respect to the required molar mass of about $15 \cdot 10^3$ g mol$^{-1}$. The most trivial origin for the formation of the low molecular weight nylon could be that the product obtained after the ACN hydrolysis still contains nitrile endgroups, besides amide or carboxylic acid end-groups. However, the infra-red spectrum of the product does not show a nitrile absorption band, which should be observed when nitrile end-groups would still be present due to incomplete hydrolysis. Residual nitrile end-groups can therefore not be responsible for the moderate molecular weight increase. As ZrO$_2$ is involved in all successive reaction steps to convert the nitrile functionality into the N-alkyl amide (Chapter 3), nitrile hydrolysis is apparently not limiting anymore for the molecular weight built up during the ACN hydrolysis.

The results of Chapter 3 indicate that if the nitrile hydrolysis is performed in a closed system, distinct amounts of amide functionalized oligomers can be expected. These are expected to have a lower amidation rate with the amine functionality than a carboxylic acid end-group, and could therefore be responsible for the limited molar mass built up.
Although the polymerization using amide functionalized monomers has been performed before, this was at a much higher temperature of 260°C.\textsuperscript{10,11} To avoid the influence of amide hydrolysis on the molar mass increase, the polycondensation was performed in the absence of water. Adipamide and hexamethylene diamide were used as a monomer, as 6-amino caproamide was not available (Figure 5.3).

![Figure 5.3. The polycondensation reaction of adipamide with hexamethylene diamine.](image)

After 24 hours reaction at 230°C a number average molecular weight of $7 \cdot 10^3$ g·mol\(^{-1}\) was obtained for the polycondensation of adipamide with 1,6-hexyldiamine. Although amide functionalized monomers may slow down the molecular weight build-up, they are obviously not responsible for the limited molecular weight after the pre-polymerization step.

The molecular weight is therefore probably limited due to the required presence of water during the ACN hydrolysis. A successive further amidation under water free conditions is therefore required to achieve the maximum molecular weight. As the amount of polymer product gained from the experimental method used (Entry 1 in Table 2) is too small to perform a melt polymerization, the semi-crystalline product was submitted to a solid state post-condensation (SSP) step (Entry 2 of Table 2).

The post-condensation only results in a minor increase of the number average molecular weight, but the polydispersity is distinctively higher, and a weight average molar mass of ca. 12000 g·mol\(^{-1}\) is reached. As shown in Figure 5.4, comparison of the molecular weight distributions of Entries 1 and 2 (Table 2) obtained by SEC shows that the nice Flory-Schulz shape of the SEC curve of the polyamide before solid state post-condensation is distorted. After post-condensation a bimodal distribution is obtained, with a high molecular weight tail.
The polymerization of 6-aminocapronitrile

Figure 5.4. The normalized molar mass distribution of the nylon before (——) and after solid state post-condensation (— —).

Two possible explanations for the limited molecular weight build-up are an inadequate post-condensation method (see further) or a loss of end-groups during the hydrolysis of ACN resulting from side reactions. Since the latter was not observed during the model reactions (see chapter 3) this option is unlikely. Therefore we feel that the slow amidation during the solid state post-condensation at 185 °C, which has to be performed below the melting temperature of the nylon-6 prepolymer is responsible for the relatively low $M_n$. Furthermore, one should realize that in a SSP the molecules present in the crystals do not participate in the post-condensation reaction. Only the mobile amorphous chains will undergo chain extension, and the low molar mass chains in the crystals stay relatively short. This also explains the broad PDI obtained after the SSP.

**Conclusion**

In comparison to the uncatalyzed hydrolysis of ACN, the use of the ZrO$_2$ catalyst significantly improves the molar mass build-up of the product nylon-6. However, the end product is still not the desired high molecular weight nylon-6, as a result of the presence of water required for the hydrolysis. This water prevents the molecular weight built-up. To obtain a high molecular weight, the water should be removed and the amine functionality should be further acylated. The product obtained after hydrolysis using ZrO$_2$ was therefore treated by solid state post-condensation to increase the molecular weight. However, this does not result in the expected substantial product improvement, most probably because the applied temperature of 185 °C is too low. Molecular weight limitation due to the presence of unreacted nitrile end-groups could be excluded on the basis of infra-red spectroscopy data. The presence of amide functionalities could also be canceled as the origin for the low molar mass obtained during the prepolymerization, as
amide functionalized monomer forms polymer with a higher molecular weight than obtained after the prepolymerization at 230°C. Unfortunately, no further evaluation of the origin is currently possible. However, the results show good perspectives for the system.

Reference List

Preliminary process
design for the polymerization of
6-aminocapronitrile

Introduction

For the synthesis of high molecular weight nylon-6 out of the monomer 6-aminocapronitrile (ACN), the nitrile functionality of ACN needs to be completely hydrolyzed and the amine functionality needs to be completely amidated (step I and step II in Figure 6.1, respectively). With respect to the complete and selective hydrolysis of the nitrile functionality, porous zirconia (ZrO$_2$) catalysts show a good performance, see Chapter 3. Zirconia catalysts therefore seem very attractive for the use in the production of nylon 6 out of ACN. However, up to now there is no insight in the characteristics of such a process. A preliminary design of a process using this heterogeneous catalyst is therefore very useful to identify the most important challenges for further development.
This chapter first considers the development of a process configuration based on chemical considerations. After establishing at a functional process configuration, the further process evaluation is focused on the description of the selective ACN hydrolysis, catalyzed by zirconia. As a result of the limited kinetic data and the expected change in mass transfer behavior at high nitrile conversions, only a rough evaluation of the reaction volume of the reactor is possible for a desired annual production of \(50 \cdot 10^3\) ton, which seems to be appropriate for an engineering plastic. However, even this rough evaluation is capable of identifying critical design aspects.

**The conceptual process configuration**

The requirements to obtain complete conversion in both the hydrolysis and the amidation reaction are in contradiction with each other with respect to the allowed water concentration. As a consequence the hydrolysis and acylation leading to the polymer have to be performed in at least two separate process steps, see Figure 6.2. The first process step is aimed at the complete nitrile hydrolysis with as little as possible amine amidation, and the second process step is aimed at the complete amine amidation, i.e. polycondensation, as the product of the nitrile hydrolysis can only acylation the amine,

---

* The patented process configurations also consist of at least two process steps.\(^{1,2}\)
Figure 6.2. The two step process for the nylon 6 synthesis out of 6-aminocapronitrile. 1: gas/liquid separator; 2: catalytic hydrolysis reactor; 3: buffer vessel; 4: evaporator; 5: polycondensation stage; 6: water separator and; 7: pump.

The reactor for the ACN hydrolysis is a solid/liquid (s/l) catalytic fixed bed reactor, batch-wise operated to control the required high, final nitrile conversion of the product mixture. A well mixed, batch wise operated slurry reactor does not seem to be a proper choice, as separation of the solid catalyst from the relatively viscous product liquid will meet serious difficulties.† So a batchwise operated, fixed bed solid/liquid reactor with recycle seems a proper choice to limit the resistance against heat and mass transfer, allowing operation of the hydrolysis reaction with intrinsic kinetics up to high conversions.

With increasing hydrolysis of the nitrile functionality of ACN, ammonia accumulates in the reaction mixture. Ammonia should be removed to allow reaction (2) in Figure 6.1 to proceed in a sufficient degree. In the first process step a continuous flow of water is therefore supplied to the reaction mixture to remove the ammonia.‡ The ammonia/water mixture is separated from the liquid reaction mixture on top of the reactor with a

† Due to high reaction temperatures in combination with water and ammonia, special attention should be paid to wear reduction for the process design.

‡ Ammonia can not be separately removed from the system.
gas/liquid separation column. Reuse of the produced ammonia improves the perspectives for the nylon-6 production out of ACN.

The product mixture of the first process contains no ACN anymore and is transferred to a buffer vessel to allow the transition from the batchwise operated nitrile hydrolysis to the continuously operated acylation. This intermediate vessel facilitates control of the polycondensation stage (reaction 3 in Figure 6.1), as the reaction mixture composition entering process step II is kept constant in this way. As the actual polycondensation is performed in the second process step, water has to be removed before the reaction mixture enters the polycondensation reactor. The water removal is performed by evaporation.

Process II in Figure 6.2 is almost completely similar to the polycondensation of partially hydrolyzed ε-caprolactam (CL) in a so-called Vereinfacht Kontinuierlich (VK) column, since it can be expected that at the process conditions a significant part of the hydrolyzed ACN is ring-closed to this nylon-6 monomer. The continuous production of nylon-6 out of CL in this reactor is typically modeled as a plug flow reactor. This comprehensive description of the polycondensation of CL in a VK-column can therefore be used to describe process step II in Figure 6.2.

As the development of a viable process for the complete hydrolysis of ACN (reaction 1 and 2 in Figure 6.1) is the most challenging part of the process configuration, the further analysis is limited to the design of the fixed bed reactor, process step I in Figure 6.2.

**Process description**

The degree of detail for the description of the fixed bed reactor is in the first place dependent on the requirements of conversion and selectivity, i.e. ~100% conversion of ACN into its hydrolyzed form, being the corresponding amino amide. However, as the degree of accuracy of available kinetic and transport data is limited, only the most basic model for a catalytic fixed bed reactor can be applied.

A complicating aspect of the ACN hydrolysis is that a large amount of amine is already acylation (reaction 3 in Figure 6.1) in the hydrolysis reactor, resulting in amine conversions higher than 90%. These high acylation conversions already result in a significant build-up of the molar mass during the ACN hydrolysis, which can be clearly visualized by the average degree of polymerization versus amine conversion dependence on amine conversion according to a Flory-Schulz distribution, as shown in Figure 6.3.

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Figure 6.3. a) The development of the number average degree of polymerization ($\bar{P}_n$) with increasing amine conversion, related to the process operation given in Figure 6.2. b) Theoretical mole fraction of i-mer ($f_i$) distribution according to a Flory-Schulz distribution for the given degree of polymerization ($i = P_n$) for 80% (--), 90% (— — ) and 95% (—⋅⋅) amine conversion.

Figure 6.3a shows that up to an 75% amine conversion oligomer formation is very limited. For higher amine conversions a gradual increase is observed for the degree of polymerization and a steep rise occurs for amine conversions above 90%. The presence of high amounts of water during the hydrolysis of ACN restricts the maximum amine amidation in the first process step to 95%. However, this would still result in an average degree of polymerization of about 20 repeating units. As a result of the existence of a chain length distribution, a significant fraction of chains with a degree of polymerization higher than 20 monomer residues is already formed, as shown in Figure 6.3b. Although this phenomenon is only occurring at a high degree of nitrile hydrolysis, the molar mass built-up in the last stage of the hydrolysis reaction strongly influences both the viscosity and diffusion rates in the reaction mixture.

A recipe based on a 1:2 molar ratio of ACN ($C_6H_{12}N_2$, 112.2 g/mol) and water (18.0 g/mol) is applied to evaluate the mass transfer resistances in the fixed bed reactor. Thus, the mixture consists of 76 weight% ACN and 24 weight% of water. Note, that the amount of water used is not crucial, as the excess hot water can be reused to extract the low molecular mass fraction of the product nylon in a later stage. The hydrolysis process is operated at a constant temperature of 250°C to obtain a hydrolysis rate sufficiently high

\[\text{This is an indispensable step, since at the envisaged polycondensation temperature of 250°C some 10 wt% of } \varepsilon\text{-caprolactam and low molar mass oligomers are present in the polycondensation equilibrium.}\]
Preliminary process design for the polymerization of 6-aminocapronitrile

for complete ACN conversion within a reaction time of at most 4 hours. Before the reactor design can be further evaluated, the kinetic behavior and mass transport have to be evaluated first to arrive at the best catalyst morphology for the process operation.

**The kinetic model for the catalyzed nitrile hydrolysis**

There are no good physicochemical models available to describe the ACN hydrolysis kinetics using a heterogeneous catalyst. As the molecular weight build-up at high ACN conversions complicates the acquisition of reliable experimental data, the formulation of a comprehensive kinetic model for the ACN hydrolysis using a heterogeneous catalyst is difficult.

The description of the kinetic behavior is therefore based on the measured rate of the model reaction between pentanenitrile and hexylamine, see Chapter 3. Up to ~90% nitrile conversion (Chapter 3) the reaction seems to obey zero-order kinetics as the conversion rate of pentanenitrile is independent of conversion. However, at higher conversions the hydrolysis rate declines strongly. This decline is most probably due to product inhibition of the catalyst at high conversions (Chapter 4), but the actual reason is not yet identified.

As there is no comprehensive model available based on all fundamental reaction steps occurring in the model reaction, we have chosen for a very global kinetic model, i.e. zero-order kinetics for conversions up to 90% and first order kinetics for conversions exceeding 90%.

** The influence of the water concentration was not investigated, however, a description of the concentration dependence of the ACN hydrolysis rate on water is not required as the continuous water flow used for the ammonia removal during the ACN hydrolysis allows the assumption of a constant water concentration in process step I. The rate constants reported in Table 1 are obtained by extrapolation of the rate constants of the specific conversion regimes at 250°C, using Arrhenius’ law. The rate coefficients in Table 1 have been derived from experiments with catalyst particle sizes ≤ 5 μm, so intrinsic kinetics is obeyed, even at 250°C.

** The rate constants are obtained by using the following mass balance for the ACN consumption:

\[
V_l \cdot \frac{dC_{\text{ACN}}}{dt} = -k_{n}^{V} \cdot (\text{obs}) \cdot C_{\text{ACN}}^{n} \cdot V_{\text{cat}}
\]
Figure 6.4. The Arrhenius-plots used for the determination of the a) zero-order rate constant used for conversions up to 90% nitrile conversion and b) the first order rate constant for higher nitrile conversion at 250°C.

Table 1. The rate coefficients per unit catalyst volume for the power-law fit to the experimental data, extrapolated to 250°C.

<table>
<thead>
<tr>
<th>Conversion range (%)</th>
<th>$r_{\text{ACN}}$</th>
<th>$n$</th>
<th>$k_{\text{ACN}}^{\text{V,n}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 – 90</td>
<td>$k_{\text{ACN}}^{\text{V,0}}$ (obs)</td>
<td>0</td>
<td>$2.5 \cdot 10^1$ [mol·m$^3$·m$_{\text{cat}}$·s$^{-1}$]</td>
</tr>
<tr>
<td>90 - 100</td>
<td>$k_{\text{ACN}}^{\text{V,1}}$ (obs)·$C_{\text{ACN}}$</td>
<td>1</td>
<td>$2.2 \cdot 10^{-3}$ [m$^3$·m$_{\text{cat}}$·s$^{-1}$]</td>
</tr>
</tbody>
</table>

The effect of mass transport

For a fixed bed reactor with large particles (e.g. diameters in the order of 10 mm) reaction rates may be limited by mass transfer from the liquid phase to the outer particle surface and by diffusion into the pores of the catalyst particles. These transport phenomena are usually related to inter- and intra particle mass transfer resistances. Figure 6.5 shows the concentration profiles of a reactant A (e.g. ACN) around and inside a porous catalyst particle.
Preliminary process design for the polymerization of 6-aminocapronitrile

Figure 6.5. A) A schematic representation of the different zones for mass transport and b) Three concentration profiles for the reactant from the bulk liquid to the center of the spherical catalyst particle. The concentration profiles are representative for I) no mass transfer limitations, II) only intraparticle mass transfer limitation and III) both inter and intra particle mass transfer limitation.

A key parameter for the estimation of the mass transfer resistances is the diffusion coefficient of the limiting reactant (i.e. ACN). Fick’s law is a valuable tool to describe diffusion phenomena. However, the experimental determination of the Fickian diffusion coefficient is difficult for the required conditions. Fick’s law is furthermore not capable of describing the effect of molar mass build-up on the diffusion rate of the reactant, which can have an appreciable effect at high ACN conversions. A recently developed extended Maxwell-Stefan model is capable of describing the effect of chain length on the diffusion rate, however, for the moment this model is much too complex with respect to the lack of accuracy of the intrinsic kinetic data of the molecular zirconia catalyzed hydrolysis of ACN. Rough estimates of the resistances of mass transfer are carried out with an initial value of the molecular diffusion coefficient of ACN of $1 \cdot 10^{-9} \text{m}^2\text{s}^{-1}$. To evaluate the effect of increasing molecular weight, the effect of a decreasing diffusion coefficient is considered.

**Intraparticle mass transfer**

Concentration gradients inside the catalyst particle (Figure 6.5, concentration profile II and III) due to low intraparticle diffusion rates generally lead to a lower reaction rate than expected on the basis of the concentration on the outer particle surface, as shown in Figure 6.5b, concentration profiles I and II.†† If the observed reaction rate per catalyst volume is lower than the expected reaction rate according to intrinsic kinetics, this is

†† For reaction orders >0, concentration gradients lead to limitation of the reaction rate.
called intraparticle diffusion limitation. To assess intraparticle diffusion limitation effects for a porous solid, the effectiveness factor ($\eta$) should be used, which is the ratio of the actual reaction rate and the reaction rate observed when intrinsic kinetics are obeyed. Unfortunately, analytical solutions for the dependence of the effectiveness factor on the characteristic dimensions of the catalyst particle requires knowledge of the true kinetic behaviour of the system.

As a reliable, thorough description of our system is not available, the existence of intraparticle diffusion limitation is estimated using the extended Weisz-Prater criterion. The extended Weisz-Prater criterion allows a judgement whether or not intraparticle diffusion limitation is significant for the observed reaction rates. The criterion is based on the assumption of irreversible kinetics and of diffusion according to Fick’s first law, and this criterion uses the effective diffusivity coefficient in contrast to the molecular diffusion coefficient. The effective diffusion coefficient accounts for the diffusion through a catalyst volume, which is different from diffusion through the pure reaction mixture due to the pore tortuosity and pore diffusion. When the criterion is obeyed, an effectiveness factor of $\geq 0.95$ holds.$^{10}$ The key parameter for the criterion is the Weisz-modulus, $\Phi_{WP}$. Diffusion limitation is not significant for power law kinetics (i.e. $r_{\text{nitrile}} = k \cdot C_s^n$) if:$^{11}$

$$\Phi_{WP} = \frac{r_{\text{ACN}} \cdot (A_{\text{cat}} / V_{\text{cat}})^2}{D_{\text{e,ACN}} \cdot C_{\text{ACN}}^S} \ll \frac{1}{n} \quad n > 0$$  \hspace{1cm} (6.1)

In Eq. (6.1), $n$ stands for the reaction order in ACN, $r_{\text{ACN}}$ represents the reaction rate, $A_{\text{cat}} / V_{\text{cat}}$ stands for the surface area per volume catalyst particle, $D_{\text{e,ACN}}$ stands for the effective diffusivity and $C_{\text{ACN}}^S$ stands for the surface concentration. The used parameter values are shown in Table 2. For zero-order kinetics the criterion is: $\Phi_{WP} << 6$.

Table 2. The values used for the determination of diffusion limitation effects for the hydrolysis of ACN catalyzed by porous zirconia.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film thickness catalyst layer</td>
<td>V/A</td>
<td>$1 \cdot 10^{-4}$</td>
</tr>
<tr>
<td>Effective diffusion coefficient of ACN</td>
<td>$D_{\text{e,ACN}}$</td>
<td>$2 \cdot 10^{-10}$</td>
</tr>
<tr>
<td>Surface concentration of ACN</td>
<td>$C_{\text{ACN}}^S$</td>
<td>$6.1 \cdot 10^3$</td>
</tr>
</tbody>
</table>
Intrinsic kinetic behavior is desired for the operation of the heterogeneously catalyzed process. A simple use of the catalyst would be in the form of spherical particles, completely consisting of the zirconia catalyst material. To allow proper process operation, sphere diameters of at least 5 mm are required (for smaller spheres the column is too densely packed). However, as the Weisz-prater criterion for intrinsic kinetics is not obeyed, diffusion limitation is expected, see Figure 6.6.

Diffusion limitation can be avoided by decreasing the ratio of catalyst volume over surface area. The catalyst should therefore be used in the form of a thin active layer, e.g. immobilized on solid spheres or structured internals (for example Sulzer SMV packing). A catalyst layer of 100 µm allows process operation in the intrinsic kinetic regime and will therefore be used. The further analysis of the reactor design is limited to a spherical solid support with a diameter of 5 mm.

With molar mass build-up for ACN conversions higher than 75%, the effective diffusion coefficient of the reactant is expected to decrease. As the Weisz-modulus is inversely proportional to the effective diffusivity, a strong decrease in diffusivity, e.g. a factor ten, will only result in a ten times higher value for the Weisz-modulus. A decrease of the effective diffusion coefficient with a factor of ten does not result in intraparticle diffusion limitation for high ACN conversions and a catalyst film thickness of $1 \times 10^{-4}$ m.

---

Figure 6.6. The results for the extended Weisz-Prater criterium for the zero-order range for initial concentration (— —) and 90% conversion ( — — ) and for first order kinetics (— — — — )

---

‡‡ The use of Raschig rings is not a good option, because there is risk of stagnant liquid in the inner space in the rings.
Resistance to mass transfer from liquid to particles

The mass transfer from the bulk liquid to the outer catalyst surface is described by ideal radial mixing in the bulk fluid, and the rate of mass transfer is largely dependent on the fluid properties (i.e. density and viscosity) and the liquid velocity. The mass transfer resistance is typically characterized by the mass transfer coefficient, \( k_c \). For packed beds the mass transfer from the bulk liquid to the catalyst particles can be estimated with the relation:

\[
\text{Sh'} = 1.0 \cdot (Re')^{1/2} \cdot Sc^{1/3}
\]

as formulated by Thoenes and Kramers.\(^{13}\) The dimensionless numbers are defined as:

\[
\text{Sh'} = \frac{k_c \cdot d_p}{D_{\text{ACN}}} \cdot \left( \frac{\varepsilon_b}{1 - \varepsilon_b} \right); \quad \text{Re'} = \frac{u \cdot d_p \cdot \rho}{\mu \cdot (1 - \varepsilon_b)}; \quad \text{Sc} = \frac{\mu}{\rho \cdot D_{\text{ACN}}}
\]

Table 3 shows the used parameter values and Figure 6.7 shows the dependence of the mass transfer coefficient on the Reynolds number. The superficial velocity of \( 5 \cdot 10^{-2} \, \text{m} \cdot \text{s}^{-1} \) corresponds to 10 minutes per pass for a 30 m high reactor.

**Table 3. Applied conditions for the determination of the mass transfer coefficient using the Thoenes-Kramers relation.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bed porosity ( \varepsilon )</td>
<td>0.5 ([-])</td>
</tr>
<tr>
<td>Catalyst particle diameter (d_p)</td>
<td>( 5.2 \cdot 10^{-3} ) ([\text{m}])</td>
</tr>
<tr>
<td>Fluid viscosity (\mu)</td>
<td>( 1 \cdot 10^{-3} ) ([\text{Pa} \cdot \text{s}])</td>
</tr>
<tr>
<td>Superficial velocity (u)</td>
<td>( 5 \cdot 10^{-2} ) ([\text{m} \cdot \text{s}^{-1}])</td>
</tr>
<tr>
<td>Molecular diffusion coefficient ACN (D_{\text{ACN}})</td>
<td>( 1 \cdot 10^{-9} ) ([\text{m}^2 \cdot \text{s}^{-1}])</td>
</tr>
<tr>
<td>Density reaction mixture (\rho)</td>
<td>( 18 \cdot 10^3 ) ([\text{mol} \cdot \text{m}^{-3}])</td>
</tr>
</tbody>
</table>

The occurrence of inter particle mass transfer limitation is checked by comparing the resistance against mass transfer with the resistance against reaction. The resistance against mass transfer is:

\[
\frac{1}{k_c \cdot (A_{\text{cat}} / V_{\text{cat}})}
\]

where \( A_{\text{cat}} / V_{\text{cat}} \) stands for the specific outer surface of the catalyst (for spherical particles \( A_{\text{cat}} / V_{\text{cat}} = 6 / d_p \)). The resistance against reaction is:
Preliminary process design for the polymerization of 6-aminocapronitrile

Figure 6.7. The dependence of the mass transfer coefficient as a function of the Reynolds number.

\[
\frac{C_{\text{ACN}}}{r_{\text{ACN}}} \quad (6.5)
\]

where \( r_{\text{ACN}} \) stands for the reaction rate per unit volume of the catalyst. The resistance against mass transfer from the bulk liquid to the outer surface of the catalyst particles is negligible if:

\[
\frac{1}{k_c \cdot (A_{\text{cat}} / V_{\text{cat}})} << \frac{C_{\text{ACN}}}{r_{\text{ACN}}} \quad (6.6)
\]

Using the design specifications, the resistance against reaction is a factor 100 larger than the external resistance against mass transfer. Interparticle mass transfer limitation can consequently be neglected.

Unfortunately, there are no adequate correlations to relate the viscosity of a water–nylon-6 oligomer solution to the water concentration and the average molecular weight of the oligomer. However, a ten times higher viscosity results in a \( \text{Re}' \) of 45, for which the Thoenes-Kramer relation still holds. For this 10 times higher viscosity the mass transfer coefficient is only a factor 3 lower and therefore does not strongly influence the external mass transfer, see Figure 6.7.

**Reactor evaluation**

The reactor volume for the hydrolysis of ACN is calculated for a production volume of 50\( \cdot 10^6 \) kg nylon-6 per year (= 8000 operation hours). This capacity is comparable to capacities for currently used nylon 6 plants, based on the polymerization of CL. The residence time covering the whole process shown in Figure 6.2 is taken at 20 hours: 4
hours for process step 1, 4 hours for the charging and emptying the reactor of process step 1, and 12 hours for process step 2. The 12 hour residence time for process step 2 is typical for the polymerization of CL in a VK-column.

To be able to produce $50 \cdot 10^6$ kg/annum of high molecular weight nylon 6, $22.7 \cdot 10^7$ kg of ACN should be hydrolyzed up to at least 99.5% conversion within the 4 hours available for step 1. To avoid problems with the catalyst utilization, the ACN hydrolysis is operated at a pressure at which the reaction mixture is completely in the liquid phase.\footnote{The pressure of water at 250°C is 40 bar. As ammonia is continuously removed, this will not form a problem.}

The reaction rate is assumed to be independent of the ACN concentration for conversions up to 90%, and for conversions higher than 90% the reaction is assumed to be first order in ACN. The ACN conversion per pass is small. Both aspects allow the description of the concentration development as an ideally mixed batch reactor, as captured by Eq. (6.7).

$$V \frac{dC}{dt} = -V_{cat} \cdot r_n$$

(6.7)

Calculated by an iterative process, an amount of 4.15 m$^3$ ZrO$_2$ is required to fulfill the operation requirements, for which the corresponding ACN conversion-time history is shown in Figure 6.8. With this catalyst loading, a 90% ACN conversion was already reached within 30 minutes, and within 3 hours from the start of the hydrolysis a 99.6% ACN conversion is already reached. For an additional hour reaction time, the conversion only increases to 99.8%. Although this increase by 0.2% is small in absolute terms, it is crucial for obtaining the desired high molar mass nylon-6 in the subsequent polymerization reaction. The total required reactor volume is 67 m$^3$ for a 50% bed porosity.

The pressure drop over the bed is calculated using the Ergun relation, see Eq. (6.8). As shown in Table 4, the pressure drop is only 5 bar, which is allowed for the process operation.

$$\Delta P = \frac{150 \cdot \mu \cdot (1 - \varepsilon_b)^2}{d_p^2 \cdot \varepsilon_b^3} \cdot u + \frac{1.75 \cdot \rho \cdot (1 - \varepsilon_b) \cdot L}{d_p^2 \cdot \varepsilon_b^3} \cdot u^2$$

(6.8)
Preliminary process design for the polymerization of 6-aminocapronitrile

Figure 6.8. The conversion-time history for process step 1.

Table 4. Design specifications of the batchwise operated plug flow reactor for ACN hydrolysis, with complete recycle.

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid volume</td>
<td>32.4 [m$^3$]</td>
</tr>
<tr>
<td>Catalyst particle volume</td>
<td>34.6 [m$^3$]</td>
</tr>
<tr>
<td>ZrO$_2$ volume</td>
<td>4.15 [m$^3$]</td>
</tr>
<tr>
<td>Pressure drop</td>
<td>5 [Bar]</td>
</tr>
</tbody>
</table>

The large volume of the catalytic bed (34.6 m$^3$) can be strongly reduced by dividing the ACN hydrolysis over two separate reactors. In the first reactor the ACN is hydrolyzed to 90% and in the second step the product mixture is further hydrolyzed to at least 99.8%. The use of such a two step procedure allows an increased reaction time for the first 90% conversion and a shorter reaction time for the completion of the reaction to 99.8% or higher (a larger amount of active material, e.g. a thicker ZrO$_2$ shell). As the catalyst shell thickness was restricted due to diffusion limitation in the initial part of the ACN hydrolysis, the shell thickness can be increased for the reactor designed for high conversion ACN hydrolysis. The shell thickness is again directly proportional to the reduction in catalytic bed size required. However, to make a reliable quantification of this reactor volume reduction, a much more detailed description of the reaction kinetics and the mass transport phenomena are required.

**Conclusions**

The design of a viable process for the production of nylon 6 out of ACN is based on two major steps: the ZrO$_2$ catalyzed hydrolysis of ACN and the complete acylation of the hydrolysis product leading to nylon-6. The two consecutive process steps consist of a batch-wise operated fixed bed loop reactor for the complete hydrolysis of the nitrile
functionality of ACN and a continuously operated plug flow reactor for ultimate nylon-6 formation. As the second process step closely resembles the process for the current nylon-6 production from the partially hydrolyzed ε-caprolactam, the process analysis is completely focused on the first process step: the hydrolysis of ACN.

Due to a limited amount of accurate kinetic and physicochemical data only a preliminary kinetic model can be used for the description of the ACN hydrolysis. However, even using very rough values, it is clearly shown that, for spherical catalyst particles, intraparticle diffusion limitation limits the hydrolysis rate. Therefore a bed packing consisting of solid spherical particles with a thin porous shell of ZrO$_2$ shell has been proposed. For this catalyst morphology inter- and intraparticle mass transport limitation is negligible.

For an annual production of 50·10$^6$ kg nylon 6 (corresponding with 22.7·10$^7$ kg of ACN to be hydrolyzed) a reactor volume of about 67$\text{m}^3$ is necessary when a batch-wise operated catalytic fixed bed loop reactor is applied. The reactor should contain 4.15$\text{m}^3$ porous zirconium oxide catalyst material. The large reactor size can probably be reduced by performing the hydrolysis in two steps, allowing the reduction of the required catalytic fixed bed volume.

**Nomenclature**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x_i$</td>
<td>Conversion</td>
<td>[-]</td>
</tr>
<tr>
<td>$\overline{P}_n$</td>
<td>Average Degree of polymerization</td>
<td>[-]</td>
</tr>
<tr>
<td>$k^{V,0}_{\text{ACN}}$</td>
<td>Zero-order volumetric rate coefficient</td>
<td>[mol·m$_{\text{cat}}^{-3}$·s$^{-1}$]</td>
</tr>
<tr>
<td>$k^{V,1}_{\text{ACN}}$</td>
<td>First order volumetric rate coefficient</td>
<td>[m$<em>i^3$·m$</em>{\text{cat}}^{-3}$·s$^{-1}$]</td>
</tr>
<tr>
<td>$D_{E,i}$</td>
<td>Effective diffusion coefficient of component $i$</td>
<td>[m$^2$·s$^{-1}$]</td>
</tr>
<tr>
<td>$D_i$</td>
<td>Molecular diffusion coefficient of component $i$</td>
<td>[m$^2$·s$^{-1}$]</td>
</tr>
<tr>
<td>$d_p$</td>
<td>Particle diameter</td>
<td>[m]</td>
</tr>
<tr>
<td>$\delta_{p,\text{cat}}$</td>
<td>Zirconia shell thickness</td>
<td>[m]</td>
</tr>
<tr>
<td>$V_l$</td>
<td>Liquid volume of the reaction mixture</td>
<td>[m$^3$]</td>
</tr>
<tr>
<td>$V_{\text{cat}}$</td>
<td>Volume catalyst bed</td>
<td>[m$^3$]</td>
</tr>
<tr>
<td>$u$</td>
<td>Superficial flow velocity</td>
<td>[m·s$^{-1}$]</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Dynamic viscosity</td>
<td>[Pa·s]</td>
</tr>
<tr>
<td>$r_i^{v}$</td>
<td>Volumetric reaction rate</td>
<td>[mol·m$_{\text{cat}}^{-3}$·s$^{-1}$]</td>
</tr>
<tr>
<td>$\Delta P$</td>
<td>Pressure drop over the reactor</td>
<td>[bar]</td>
</tr>
<tr>
<td>$C_i$</td>
<td>Bulk concentration of component $i$</td>
<td>[mol·m$_i^{-3}$]</td>
</tr>
</tbody>
</table>
Preliminary process design for the polymerization of 6-aminocapronitrile

| $C^i_i$ | Concentration of component i at the outer catalyst surface | [mol·m$^{-3}$] |
| $C_{i,0}$ | Initial bulk concentration of component i | [mol·m$^{-3}$] |
| $k_{c,i}$ | Mass transfer coefficient of component i | [m·s$^{-1}$] |
| $f_i$ | Mole fraction of hydrolysis product with degree of polymerization i ($= P_n$) | [-] |
| $\Phi_{WP}$ | Weisz modulus | [-] |
| $A_{cat}/V_{cat}$ | Specific outer surface per unit volume of the particles | [m] |
| i | Number of monomer residues | [-] |
| n | Order of the reaction | [-] |

**Greek letters**

| $\varepsilon$ | Bed porosity | [-] |
| $\rho$ | Density | [kg·m$^{-3}$] |

**Subscripts**

| i | Component i |
| E | Effective |
| cat | catalyst |
| liq | Liquid reaction mixture |

**Reference List**

Summary

Although nylon-6 is a versatile polymer, its production out of the raw material benzene is notably environmentally unfriendly. The high environmental impact results from some serious polluting organic reactions required for the synthesis of the monomer ε-caprolactam. New developments for the nylon-6 production are therefore mainly aimed at improving the synthesis of ε-caprolactam. A promising alternative route starts from the raw material butadiene with 6-aminocapronitrile as an intermediate product. 6-aminocapronitrile is not only important as a starting material for an alternative ε-caprolactam synthesis, but also has good prospects as an alternative monomer directly used for the nylon-6 production. A prerequisite to obtain a high molar mass, linear nylon-6, is the complete nitrile hydrolysis of 6-aminocapronitrile, which still requires the conquer of a lot of hurdles.

The work described in this thesis addresses the fundamental aspects of the nylon-6 synthesis out of 6-aminocapronitrile. The gained insight is translated into a preliminary process design.

To evaluate potential methods for the complete hydrolysis of 6-aminocapronitrile, a model reaction was applied. The model reaction was aimed at the N-hexyl pentaneamide synthesis out of pentanenitrile and n-hexylamine. This model reaction clearly represents the chemistry for the polymerization of 6-aminocapronitrile. First, the behavior of the model reaction was analyzed, only using an elevated temperature as the activation method for the required nitrile hydrolysis. pentanenitrile was hardly hydrolyzed in the absence of the n-hexylamine even at a temperature of 230°C. However, with n-hexylamine present, more than 80% of the nitrile was selectively hydrolyzed after 18 hours at 230°C. The development of the composition fo the reaction mixture with time demonstrated that the nitrile was first transformed into the primary amide. Subsequently the N-alkyl amide was formed by reaction of the primary amide with n-hexylamine. For high nitrile conversions the N-alkyl amide is the primary product. A further improvement of the nitrile hydrolysis is required, as the nitrile hydrolysis is still incomplete after 18 hours at 230°C. Therefore, we applied a catalyst to improve the conversion and the rate of
the nitrile hydrolysis. The well-known homogeneous catalyst RuH₂(PPh₃)₄ tremendously increases the initial nitrile hydrolysis rate: after 4 hours reaction at 140°C more than 60% nitrile conversion is already reached with only 0.5 mol% of RuH₂(PPh₃)₄. Although the N-hexyl pentaneamide is eventually the main product, initially the terminal amide is the only product up to 60% nitrile conversion. Although the ruthenium causes a high hydrolysis rate, a strong decline in rate was observed after reaching a nitrile conversion of approximately 70%. This decline was due to catalyst inhibition by the product. Higher conversions could only be obtained by increasing the temperature or by increasing the amount of catalyst. However, an increased reaction temperature results in side reactions of the primary amine. In addition, ruthenium is a too expensive catalyst for the application at relatively high concentrations for the production of a bulk product. Although a homogeneous ruthenium catalyst remains a proper choice for nitrile hydrolysis in organic synthesis, it can not be used for the polymerization of 6-aminocapronitrile, for which at least a nitrile conversion of >99% is a strict condition. Consequently, another method of nitrile hydrolysis is required.

Inspired by a number of patents, metal oxides were screened with respect to their potential as heterogeneous catalysts for the hydrolysis of 6-aminocapronitrile, again using the model reaction of n-hexylamine with pentanenitrile. Zeolites did not show a good performance. However, the metal oxides Nb₂O₅, TiO₂ and ZrO₂ convert more than 80% of the nitrile within only 2 hours at 230°C. The comparison of the conversion-time histories for these three metal oxides at 180°C demonstrated that the ZrO₂ has by far the best performance. For TiO₂ and ZrO₂ the N-alkyl amide is initially the only product. Only for conversions higher than 50% distinct amounts of terminal amide are formed due to equilibria. The comparison of Nb₂O₅ with TiO₂ and ZrO₂ shows a distinct difference in the development of the composition of the reaction mixture with pentanenitrile. Contrary to TiO₂ and ZrO₂, Nb₂O₅ does not strongly enhance the terminal amide hydrolysis. Although the hydrolysis rate declines strongly after reaching 90% nitrile conversion, the required nitrile conversion larger than 99% can readily be reached within 6 hours at 230°C.

To obtain a better insight into the strong decline of the hydrolysis rate at high conversions, the surface chemistry of acetonitrile on ZrO₂ was studied using infrared spectroscopy. Infrared characterization of the ZrO₂ surface with acetonitrile as a probe molecule, demonstrated that even at room temperature the zirconia surface hydrolyzes adsorbed nitriles. However, the products formed were rather converted into partially hydrolyzed, ionic acetamide species than completely into molecular acetamide. Our observations show that although zirconia has a high tendency to hydrolyze nitrile
functionaities, the abundant formation of ionic acetamide species on the zirconia surface points to strong product inhibition. Removal of the ammonia formed will prevent the formation of terminal amide and consequently prevent product inhibition.

As the required nitrile conversions higher than 99% can be obtained using the heterogeneous zirconia catalyst, zirconia was used for the polymerization of 6-aminocapronitrile. In a blank reaction without catalyst, 6-aminocapronitrile only forms oligomers after reacting at 230°C. The use of ZrO₂ considerably increases the molar mass, although, the desired molecular weight is still not reached. The limited molecular weight is not due to residual nitrile functionalities, side reactions or amide functionalized chain ends. However, the limited molar mass is clearly due to the dilemma between the water required to hydrolyze the nitrile functionality and the required water removal to build-up the molar mass. Therefore, the product was subjected to a successive condensation reaction using either solid state or melt postcondensation, resulting in an increase of the molar mass, up to a weight average molar mass exceeding 1.200 g·mol⁻¹.

To evaluate the scope and limitations of the current state of the art, a preliminary process design was made based on the promising results for the nitrile hydrolysis using zirconia. Based on the chemistry requirements, a two step process is necessary. In the first step the complete hydrolysis of the nitrile functionality in the presence of an excess of water is performed. In the second step the amine amidation is carried out, resulting in the required molar mass. A high molar mass product demands for an effective and complete removal of the water. For the hydrolysis step a fixed bed, batchwise operated recycle reactor was chosen. Mass transport effects limit the catalyst morphology to a shell-type catalyst, as an efficient use of the catalytic material is desired. The analysis of the reactor design results in the suggestion to use particle diameters of 5 mm with a 100 µm thick shell of catalytic material. For an annual production of 50·10³ kg nylon-6, the calculation result in a reactor size of 70 m³ of which 35 m³ is occupied by the reaction mixture itself and 35 m³ is occupied by the catalyst particles.

In conclusion, porous ZrO₂ offers good perspectives as a heterogeneous catalyst for the polymerization of 6-aminocapronitrile into nylon-6. During the polymerization the ZrO₂ will be used as a shell-type catalyst in the first process-step directed towards the complete hydrolysis of the nitrile functionality. In the second process-step the intended molar mass of 16.000 g·mol⁻¹ is achieved by the complete removal of water.
**Samenvatting**

Nylon-6 is een veelzijdig polymer, maar de productie ervan uit de grondstof benzeen is buitengewoon milieu-onvriendelijk. De hoge milieu impact komt voort uit de vervuilende synthese van het monomeer ε-caprolactam. Nieuwe ontwikkelingen met betrekking tot de nylon-6 productie zijn daarom met name gericht op het verbeteren van de ε-caprolactam synthese, waarbij de veelbelovende alternatieve route vanuit de grondstof butadien met 6-aminocapronitril als tussenproduct sterk in de belangstelling staat. 6-aminocapronitril is echter niet alleen belangrijk als tussenprodukt voor de ε-caprolactam synthese, maar is ook veelbelovend als alternatief monomeer voor de nylon-6 synthese. Een eis voor het gebruik van 6-aminocapronitril als monomeer is helaas dat de nitril functionaliteit volledig gehydrolyseerd moet worden nylon-6 met een hoog molekulair gewicht te kunnen produceren. Hiervoor moeten nog steeds flinke hordes genomen worden.

Het werk beschreven in dit proefschrift behandelt een aantal fundamentele aspecten van de nylon-6 synthese uit 6-aminocapronitril en vertaalt het verkregen inzicht in een initieel procesontwerp.

Voor de evaluatie van de verschillende methoden voor de volledige hydrolyse van de nitril groep in 6-aminocapronitril is een modelreactie gebruikt. De modelreactie is de N-hexyl pentanamide synthese uit pentaannitril en n-hexylamine. Deze modelreactie geeft veel inzicht in de sleutelfactoren bij de vorming van nylon-6 uit 6-aminocapronitril. Om te beginnen is het gedrag van de modelreactie bestudeerd gebruik makend van hoge temperaturen als activeringsmethode voor de nitril hydrolyse. Ondanks dat de nitril hydrolyse nauwelijks verliep zonder toevoeging van het amine, werd in aanwezigheid van een stochiometrische hoeveelheid n-hexylamine na 18 uur op 230°C een nitrile hydrolyse conversie van meer dan 80% bereikt met volledige selectiviteit. Het samenstellingsverloop toont aan dat het nitril eerst gehydrolyseerd wordt tot het primair amide, dat vervolgens het gesubstitueerd N-alkyl amide vormt door reactie met n-hexylamine. Het N-gesubstitueerd amide vormt het hoofdproduct bij hoge conversies. Aangezien de conversie voor de nitril hydrolyse nog steeds niet volledig is na 18 uur bij 230°C, moet er een oplossing gezocht worden om de conversie te verhogen. Daarom is er
Samenvatting

Gekozen voor het gebruik van een katalysator. De bekende homogene katalysator, RuH\(_2\)(PPh\(_3\))\(_4\), verhoogt de initiele hydrolyse snelheid enorm. Na 4 uur reactie bij 140°C is bijvoorbeeld al meer dan 60% van het nitril omgezet met slechts 0.5 mol% ruthenium. Hoewel N-alkyl amide uiteindelijk het hoofdprodukt is, is het eindstandig amide het enige produkt tot 60% nitril conversie. Ondanks dat de ruthenium katalysator leidt tot een hoge initiele hydrolysesnelheid, wordt een sterke afname van de reactie-snelheid waargenomen na het bereiken van een nitril conversie van ongeveer 70%. Deze snelheidsafname is het gevolg van katalysator inhibitie door het product. Hogere conversies kunnen alleen behaald worden door de reactie temperatuur te verhogen of door de hoeveelheid katalysator te verhogen. Het verhogen van de reactietemperatuur leidt echter tot nevenreacties van de amine functionaliteit en de ruthenium katalysator is duur voor toepassing bij relatief hoge concentraties bij de productie van een bulkprodukt. RuH\(_2\)(PPh\(_3\))\(_4\) kan dus niet gebruikt worden voor de polymerisatie van 6-aminocapronitril, maar blijft desondanks een goede keuze voor de nitril hydrolyse in de organische chemie. Een andere methode om het nitril te hydrolyseren is daarom nodig.

Geïnspireerd door de patentliteratuur zijn een aantal metaal oxides getest als heterogene katalysator voor de hydrolyse van 6-aminocapronitril, gebruikmakend van de model reactie van n-hexylamine met pentaannitril. Hoewel zeolieten geen goede prestatie leverden, werd bij 230°C in 2 uur een omzetting bereikt van 80% met Nb\(_2\)O\(_5\), TiO\(_2\) en ZrO\(_2\) als katalysator. De vergelijking van het conversieverloop bij toepassing van deze drie metaal oxiden bij 180°C toont aan dat ZrO\(_2\) verreweg het meest kansrijk is. Voor zowel ZrO\(_2\) en TiO\(_2\) is het N-alkyl amide initieel het enige product en wordt het eindstandig amide alleen maar gevormd voor conversies hoger dan 50%. Voor Nb\(_2\)O\(_5\) vertoont de model reactie een ander samenstellingsverloop dan voor TiO\(_2\) en ZrO\(_2\). Nb\(_2\)O\(_5\) versnelt in tegenstelling tot TiO\(_2\) en ZrO\(_2\) de hydrolyse van het eindstandig amide niet sterk. Ondanks dat de reactiesnelheid van de nitril hydrolyse sterk afneemt bij conversies hoger dan 90%, kan de vereiste 99% conversie van de nitril hydrolyse nog steeds vrij eenvoudig bij 230°C binnen 6 uur bereikt worden.

Om een beter begrip in de sterke afname van de hydrolysesnelheid te krijgen, is de opervlaktechemie van acetonitril op zirconia bestudeerd met infrarood spectroscopie. Infrarood karakterisatie van het ZrO\(_2\) oppervlak met acetonitril als een indicator molekuul toont aan dat het zirconia oppervlak zelfs bij kamertemperatuur het geadsorbeerde acetonitril hydrolyseert, maar dat de gevormde producten voornamelijk ionisch acetamide zijn in plaats van moleculair acetamide. De resultaten van de nitril adsorptie op ZrO\(_2\) laten zien dat het zirconia oppervlak een sterke neiging heeft om nitril groepen te hydrolyzeren. De vorming van ionische acetamide produkten aan het zirconia oppervlak
Samenvatting

suggereert dat produktinhibitie een belangrijke rol speelt tijdens de katalytische hydrolyse van de nitril groepen.

Aangezien de benodigde conversie van de nitril hydrolyse boven de 99% nitril hydrolyse verkregen kan worden met de heterogene zirconia katalysator, is dit zirconia gebruikt voor de polymerisatie van 6-aminocapronitril. In een blanko reactie zonder katalysator vormt het 6-aminocapronitril alleen oligomeren na reactie bij 230°C. Het gebruik van ZrO₂ verhoogt het molekuulgewicht aanzienlijk, maar het gewenste molekuulgewicht van 15.000 g⋅mol⁻¹ kan nog steeds niet bereikt worden. Het beperkte molf gewicht wordt niet veroorzaakt door resterende nitril functionaliteiten of door eindstandig amide gefunctionaliseerde keteneinden. Het beperkte molekuulgewicht moet daarom het gevolg zijn van de tegenstrijdigheid dat water nodig is voor de hydrolyse, maar dat water moet worden verwijderd bij de polymerisatiereactie. Het product is vervolgens onderworpen aan een verdere condensatie door middel van vaste stof nacondensatie om de molmassa te verhogen, resulterend in een toename van de molmassa.

Om de vooruitzichten en beperkingen van de huidige kennis te evalueren, is een initiële procesontwerp gemaakt. Dit procesontwerp is gebaseerd op de veelbelovende resultaten voor de nitril hydrolyse en maakt gebruik van de heterogene zirconia katalysator. Gebaseerd op de vereisten van de chemie is een twee staps proces nodig. De eerste stap is gericht op de complete hydrolyse van de nitril functie in de aanwezigheid van een overmaat water. In de tweede stap volgt de polymerisatie. Het hydrolyse proces in de eerste stap is verder geëvalueerd, omdat dit proces nog de meeste aandacht vraagt. Er wordt gekozen voor een vast-bed recycle reactor die batchgewijs wordt bedreven. Massatransport overwegingen resulteren in de keuze voor een dunne katalytische laag op een inert niet poreus materiaal, aangezien de effectieve benutting van het katalytisch materiaal is gewenst. De analyse van het reactor ontwerp resulteert in het gebruik van een bovormige schaalkatalysator (5 mm diameter, 100 μm ZrO₂ schil). Voor een jaarproductie van 50·10³ kg nylon-6 volgt hieruit een benodigd reactorvolume van 70 m³, waarvan 35 m³ in beslag genomen wordt door het katalysator materiaal.

Ter afsluiting, poreus ZrO₂ biedt een goed perspectief als heterogene katalysator voor de polymerisatie van 6-aminocapronitril tot nylon-6. Voor de polymerisatie zal het ZrO₂ gebruikt worden als schaalkatalysator in de eerste processtap gericht op de volledige hydrolyse van de nitril functie. In de tweede processtap wordt de gewenste molmassa van 16.000 g⋅mol⁻¹ bereikt door water volledig te verwijderen.
Dankwoord

Naast alles wat ik op chemisch gebied geleerd heb, zijn de afgelopen vier en een half jaar ook een belangrijke leerschool op persoonlijk vlak voor mij geweest. Ondanks dat het project een moeizaam verloop heeft gekend, zou ik deze tijd dan ook niet willen missen. Daarom wil ik langs deze weg mijn dank uitspreken, omdat zonder de hulp en het geduld van een hoop mensen dit werk niet had kunnen worden wat het nu is.

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Joep

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1 To help my SPC colleagues to improve their Dutch skills, I wrote this part in Dutch.
Curriculum Vitae

Adrianus Johannes Maria (Joep) van Dijk was born on the 14th of October 1976 in Tilburg, the Netherlands. After obtaining his high school degree at the Cobbenhagencollege in Tilburg, he started studying Chemistry and Chemical Engineering at the Eindhoven University of Technology. After a traineeship of four months at the University of Cambridge, the United Kingdom and a traineeship of three months at Raychem N.V., Belgium he obtained his master degree in 2001. The same year the author started his Ph.D. project at the Laboratory of Polymer Chemistry under the guidance of Prof. dr. C.E. Koning, Dr. R. Duchateau and Dr. J. Meuldijk. The most relevant results of the work are described in this thesis.