DOI: 10.1002/chem.200601898

Polyamide Synthesis from 6-Aminocapronitrile, Part 2: Heterogeneously Catalyzed Nitrile Hydrolysis with Consecutive Amine Amidation

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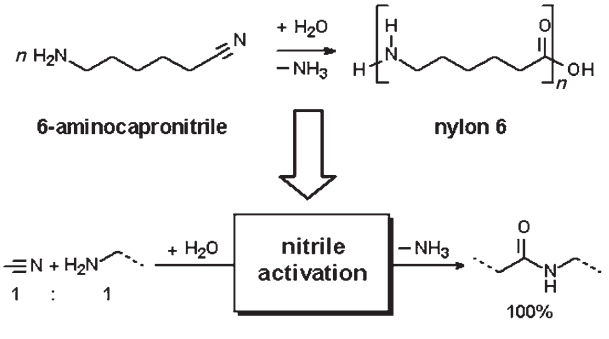
Abstract: To test the potential of heterogeneous catalysts for the nylon-6 synthesis from 6-aminocapronitrile, a number of zeolites, aluminum silicate, and metal oxides were tested as catalysts for the model reaction of pentanenitrile with water and hexylamine to *N*-hexylpentanamide. All zeolitic and aluminum silicate systems showed an insufficient performance, while the metal oxides (TiO_2, ZrO_2, Nb_2O_5) showed very promising results. The kinetic behavior of the metal oxides was further investigated. First the nitrile was catalytically hydrolyzed to the terminal amide and subsequently the amidation of the hexylamine occurred. To polymerize 6-aminocapronitrile into nylon-6, more than 99% nitrile conversion was required to obtain a high-molecular-weight polymer. Pentanenitrile conversions larger than 99% can be obtained within six hours, at 230 °C, by using ZrO_2 as the catalyst. A kinetic study (by using IR spectroscopy) on the behavior of the metal oxides demonstrated that the adsorbed nitrile was catalytically hydrolyzed at the surface, but remained tightly bound to the surface. Zirconia-catalyzed polymerizations of 6-amino-capronitrile demonstrated that high-molecular-weight nylon-6 is feasible by using this route.

Keywords: amides · heterogeneous catalysis · hydrolysis · metal oxides · nitriles · zirconium

Introduction

From an economic point of view, 6-aminocapronitrile (ACN) is an attractive alternative for ε-caprolactam as a monomer for nylon-6 formation (Scheme 1).[1] ACN can be prepared starting from butadiene by consecutive hydrocyanation and hydrogenation. The bottleneck for the polymerization of 6-aminocapronitrile into high-molecular-weight nylon-6 is the requirement of *complete* conversion of the nitrile functionality into an amide functionality. Unreacted nitriles or, for example, imine side products will function as chain stoppers that will dramatically affect the polymer molecular weight. Furthermore, side reactions such as disproportionation of the primary amine are also very undesirable as they will lead to branching of the polymer. In an attempt to reach the requirement of complete nitrile conversion, we recently reported a comparative study of two methods to improve the performance of the nitrile hydrolysis.[2] One



Scheme 1. Essential chemistry of the nylon-6 synthesis from 6-aminocapronitrile.

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method comprised the use of a mild hydrothermal process and the other method was based on the use of a homogeneous ruthenium catalyst. Although high conversions were obtained, neither of the systems resulted in complete nitrile hydrolysis. Nevertheless, the study yielded insight into the mechanism of the nitrile hydrolysis reaction, which is beneficial for studying nitrile hydrolysis in the presence of heterogeneous catalysts.

Changing from homogeneous to heterogeneous catalysis would be very advantageous. It dramatically simplifies the process operation and allows a high catalyst to reactant ratio that might reduce the reaction time of the hydrolysis step.

Except for patent literature on the nylon-6 synthesis out of ACN, there has not been much attention for the heterogeneously catalyzed formation of N-substituted amides from nitrile and amine functionalities (Scheme 1). The only relevant study available in the open literature deals with the heterogeneously catalyzed nitrile hydrolysis and subsequent esterification by using benzonitrile, water, and ethanol as substrates and several zeolites as catalysts.[3a] Contrary to the heterogeneously catalyzed formation of N-substituted amides by using nitrile hydrolysis, the use of heterogeneous catalysis for nitrile conversion into its corresponding terminal amide is receiving more and more attention.[4] The best heterogeneous systems for this reaction described so far are ruthenium hydroxide on alumina[4a] and magnesia-supported copper systems.[4b] Although these catalysts also seem very attractive for the polymerization of 6-aminocapronitrile, the presence of the amine functionality in this system dramatically affects 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_2O_3 surface.[5] During the course of our study, a BASF patent appeared describing the polymerization of 6-aminocapronitrile by using TiO_2 as the heterogeneous catalyst.[1e,h] Unfortunately, nothing was disclosed about the mechanisms involved and information about the characteristics of the catalyst and catalyst activity was very limited.

Herein we describe a study aimed at identifying heterogeneous catalysts that catalyze the consecutive nitrile hydrolysis and amine amidation. Furthermore, IR spectroscopy has been used to investigate the three steps of the catalytic cycle, being nitrile adsorption, nitrile hydrolysis on the oxide surface, and desorption of the hydrolysis products from the catalyst surface. The catalyst with the best performance in the model reaction was also tested in preliminary polycondensation reactions.

Results and Discussion

To simplify the catalyst screening for the hydrolysis and subsequent polymerization of 6-aminocapronitrile, a model system of monofunctional reactants (*n*-pentanenitrile and *n*-hexylamine) was investigated (Scheme 1). Furthermore, the use of a model system also facilitates the mechanistic studies. Clearly, it is desirable to remove NH_3 from the reaction mixture as its presence is expected to limit the conversion by chemical equilibrium.[2] However, for practical reasons the reactions were performed in a closed system. The results from the model reaction, obtained after 2 h at 230 °C, are collected in Table 1. The selectivity for the nitrile hydrolysis was determined by the combined yield of the terminal amide and *N*-hexylpentanamide that account for nearly all the nitrile conversion.[2] The small deviation from complete nitrile selectivity was caused by the formation of traces of pentanoic acid. Nitrile hydrolysis was not observed for a noncatalyzed reference experiment (entry 1, Table 1) and is therefore completely attributed to the catalytic activity of the oxide surfaces.

Table 1. Performance of the different catalyst systems for the reaction shown in Scheme 2.[a]

Entry	Catalyst	X_{PN}[b] [%]	X_{HA}[c] [%]	S_{PN}[d] [%]	S_{HA}[e] [%]
1	–	0	0	–	0
2	SiO_2/Al_2O_3	3	9	>99	44
3	zeolite HY	2	15	>99	13
4	zeolite NaY	11	10	99	90
5	zeolite Hβ	44	54	99	80
6	Cu^I–zeolite β	53	65	99	80
7	Cu^{II}–zeolite β	32	46	99	67
8	TiO_2	86	79	>99	100
9	ZrO_2	93	84	>99	100
10	Nb_2O_5	84	78	>99	100

[a] 2 h, 230 °C, in a closed system, 0.29 g PN, 0.35 g HA, 0.13 g H_2O and 0.2 g catalyst. [b] X_{PN} = The conversion of pentanenitrile. [c] X_{HA} = The conversions of hexylamine. [d] S_{PN} = The selectivity for the conversion of pentanenitrile into pentanamide and *N*-hexylpentanamide. [e] S_{HA} = The selectivity for the conversion of hexylamine into *N*-hexylpentanamide.

As zeolites show good performance for nitrile hydrolysis,[4e,h] as well as for nitrile hydrolysis combined with condensation of alcohols,[3a] we started by testing some zeolitic systems. Since the target application was the combined hydrolysis and polymerization of 6-aminocapronitrile and partial oligomerization during the hydrolysis step could not be avoided, the zeolites used were restricted to the large-pore-size forms faujasite and beta zeolite. In addition to zeolites, amorphous aluminum silicate was screened. Unfortunately, all silica-based systems (entries 2–5, Table 1) displayed a low activity towards nitrile hydrolysis, mostly in combination with a poor selectivity for the amine amidation. The low selectivity was mainly the result of dihexylamine formation.[6] The disproportionation of hexylamine was a posteriori not a big surprise for zeolitic systems. Note that, among others, zeolites are industrially used to catalyze the disproportionation of methylamine into dimethylamine and trimethylamine.[7] Despite the fact that amorphous aluminum silicate and sodium faujasite show much better selectivity with respect to the amine conversion into *N*-alkyl amide, their activities are very low. The Hβ zeolite (entry 5, Table 1) has a distinctly higher activity than the faujasite zeolite (entries 2 and 4, Table 1), but the observed conversion is still far from sufficient. In an attempt to improve the catalytic activity Hβ zeolite was impregnated with copper (entries 6 and 7, Table 1). Copper is known to catalyze the nitrile hydrolysis.[3d,4d] Although both Cu^I- and Cu^{II}-modified zeolites catalyze the model reaction, both systems showed similar, or even worse nitrile conversion and selectivity than Hβ. Besides the zeolites, three metal oxides, ZrO_2, TiO_2, and Nb_2O_5 (entries 8–10, Table 1), were tested. All three metal oxides showed a high conversion of the nitrile and showed excellent selectivity for the conversion of hexylamine into *N*-hexylpentanamide. Owing to their promising activity and selectivity, we decided to study these metal oxide systems in more detail.

ZrO_2 clearly showed the highest activity of the three metal oxides (Table 1). After 2 h, at 230 °C, already 93 % of nitrile had been converted against 86 and 84 % for TiO_2 and Nb_2O_5, respectively. The conversion-time history and the composition development of the metal oxide systems measured at a lower temperature (180 °C) indicate that ZrO_2 is by far the most active catalyst with more than 50 % nitrile conversion within 2 h (Figure 1 and Figure 2). For all three catalyst systems pentanamide, *N*-hexylpentanamide, and traces of pentanoic acid are the sole products.

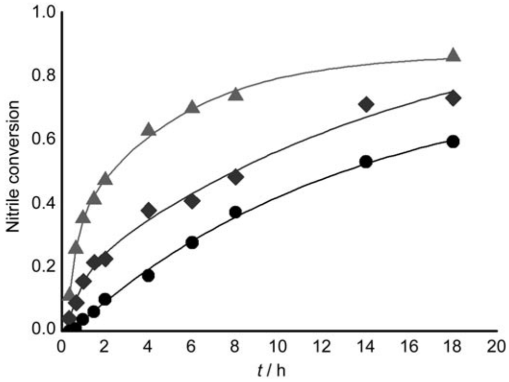


Figure 1. Conversion–time history for the reaction of *n*-pentanenitrile and *n*-hexylamine at 180 °C with ZrO_2 (▲), TiO_2 (◆), and Nb_2O_5 (●) in a closed system.

The Group 4 metal oxides (ZrO_2 and TiO_2) showed a very similar composition development, which surprisingly enough is completely different with respect to that obtained for Nb_2O_5. For ZrO_2 and TiO_2 *N*-hexylpentanamide was the main product from the start of the reaction. Only for nitrile conversions higher than 50 %, a small amount of the terminal amide was observed (Figure 2a). For a nitrile conversion of 85 %, 4 % of pentanamide and less than 1 % of carboxylic acid were formed as the only side products beside 95+ % of *N*-hexylpentanamide. On the other hand, in the Nb_2O_5-catalyzed reaction, pentanamide was initially the major product (Figure 2b). Extrapolation of the pentanamide selectivity to zero conversion according to the Delplot methodology identified the terminal amide as the initial product.[8] *N*-Hexylpentanamide was the major species with increasing conversion, comprising more than 90 % of the converted nitrile after 18 h. This implies that pentanenitrile was first hydrolyzed into pentanamide, which subsequently reacted with *n*-hexylamine to give *N*-hexylpentanamide (Scheme 2).

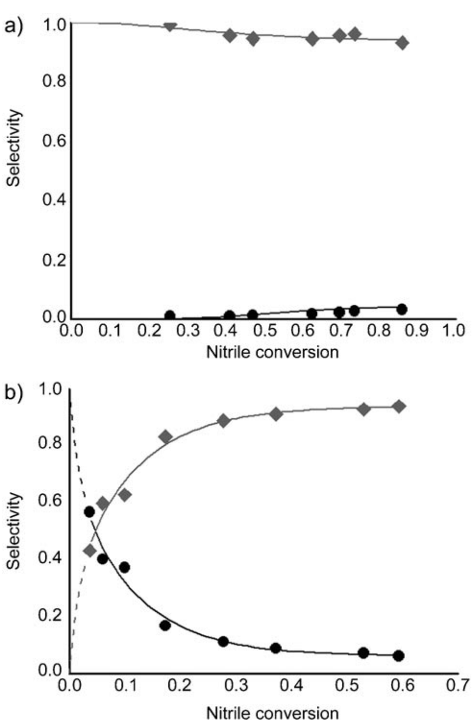
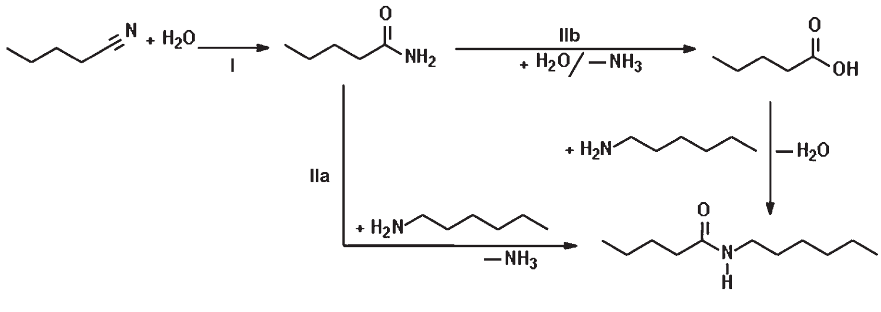


Figure 2. Selectivity development of pentanamide (●) and *N*-hexylpentanamide (◆) with nitrile conversion for the model reaction in a closed system with: a) ZrO_2 and; b) Nb_2O_5, at 180 °C.

Despite the initial absence of pentanamide in the ZrO_2- and TiO_2-catalyzed systems, their reaction mixture development can also be explained by Scheme 2. For the Nb_2O_5-cat-



Scheme 2. Reaction sequence for the formation of *N*-hexylpentanamide from *n*-pentanenitrile and *n*-hexylamine. All reactions are catalyzed by metal oxides.

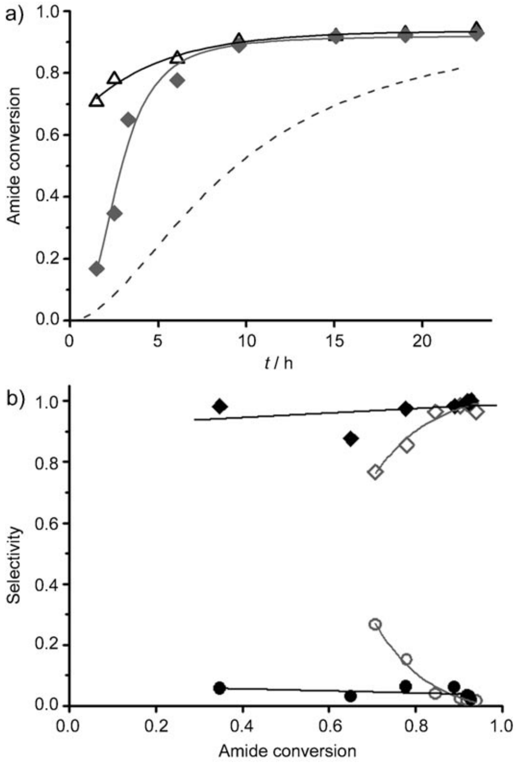


Figure 3. Conversion–time history (a) for the reaction of pentanamide with hexylamine in the presence of water and ZrO_2 (△) or Nb_2O_5 (◆) in a closed system. The uncatalyzed acylation reaction at 140 °C (-----) has been included as a reference. The selectivity development with the conversion (b) is shown for pentanoic acid (○: ZrO_2 and ●: Nb_2O_5) and *N*-hexylpentanamide (◇: ZrO_2 and ◆: Nb_2O_5).

alyzed reactions, the nitrile hydrolysis and the amidation proceed with time constants of the same order of magnitude. So, no rate determining step could be assigned. For Group 4 metal oxides, however, the nitrile hydrolysis was found to be rate limiting. These observations suggest that Group 4 metal oxides catalyze the amine amidation better than Nb_2O_5. To prove this hypothesis, the amidations of hexylamine with pentanoic amide in an aqueous environment with zirconia and niobia as catalysts were compared (route II, Scheme 2). In the hope of tracing possible reaction intermediates, the reaction was performed at 140 °C instead of 180 °C. As shown in Figure 3, both Nb_2O_5 and ZrO_2 increase the amide conversion compared to the reaction without an oxide. Taking into account that the reaction is performed in a closed system, which unavoidably leads to an equilibrium situation,[9] it is clear that ZrO_2 catalyzes the hexylamine amidation with pentanamide far more effectively than Nb_2O_5. Whereas with ZrO_2, most of the amide is already converted within 1.5 hour at 140 °C, the pentanamide consumption is then only 17 % for the Nb_2O_5 system and shows a gradual increase over more than 6 h. For both catalyst systems, after about 10 h a thermodynamic equilibrium ($K_{eq} \approx 30$, conversion $\approx 90\,\%$) is approximately reached with a product mixture consisting of 91 % *N*-hexylpentanamide, 7 % pentanamide, and 2 % of pentanoic acid. For the zirconia-catalyzed system, a significant amount (up to 19 %) of pentanoic acid is present at lower conversions than 90 %, which is gradually consumed with increasing conversion. In the niobium-oxide-catalyzed amidation reaction only a small amount of pentanoic acid was present and for the uncatalyzed amidation, no pentanoic acid was observed at all. This difference in pentanoic acid concentration is a strong indication that the difference between the two catalysts is that zirconia effectively catalyzes the hydrolysis of pentanamide to pentanoic acid whereas niobia only effectively catalyzes the nitrile hydrolysis to the amide.[10] Indeed, the zirconia-catalyzed hydrolysis of pentanamide in the absence of hexylamine afforded 30 % of pentanoic acid after 15 h at 140 °C, while pentanamide was hardly hydrolyzed without ZrO_2.[2] Although the subsequent amine acylation with a carboxylic acid was significantly faster than direct amine amidation and proceeded satisfactorily without the addition of a catalyst, also this reaction was found to be catalyzed by hydrated zirconia.[11] Therefore route IIb in Scheme 2 is clearly more important than route IIa and both steps of route IIb are catalyzed by zirconia. Niobia is significantly less efficient in hydrolyzing the pentanamide into pentanoic acid compared to zirconia and, at this point, it is not clear whether or not niobia catalyzed the subsequent amine acylation with pentanoic acid or whether the *N*-hexylpentanamide was formed mainly through the direct amine amidation route IIa.

So far, ZrO_2 turned out to be the most active and highly selective catalyst for the combined nitrile hydrolysis and amine amidation. Regardless of how promising this might seem, the 93 % nitrile conversion obtained within two hours, at 230 °C (see Table 1) is not sufficient for the target reaction, being the conversion of 6-aminocapronitrile into a high-molar-mass nylon-6. To find out whether the required 99+ % nitrile conversion can be obtained at all, the conversion–time history of the model reaction using ZrO_2 was followed at 180 °C, 210 °C, and 230 °C without NH_3 removal (Figure 4). At 230 °C, thermodynamic equilibrium was reached with a 99 % nitrile conversion and with complete selectivity of the amine conversion into *N*-hexylpentanamide. At 230 °C, the reaction was approximately irreversi-

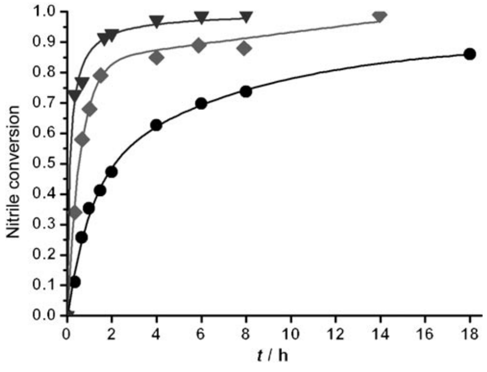


Figure 4. Conversion–time histories of the reaction of valeronitrile with hexylamine in an aqueous environment with ZrO_2, in a closed system. $T = 180$ °C (●), 210 °C (◆), and 230 °C (▼).

ble, even in a closed system. Clearly, these excellent results satisfy the requirement for the polymerization of 6-aminocapronitrile (see below).

At all temperatures, a high initial nitrile hydrolysis rate was observed that decreased strongly at higher conversion. The origin of the strongly decreasing nitrile hydrolysis rate at higher conversions might be due to product inhibition, as was also found in the homogeneous ruthenium catalyst system.[2] An IR spectroscopic study was performed to get more insight into the mechanism of the nitrile hydrolysis reaction. Acetonitrile, often used as a probe molecule for the surface site characterization of heterogeneous catalysts, was used as the nitrile.

The first step of the catalytic cycle for nitrile hydrolysis is believed to be the reversible adsorption of the nitrile onto the zirconia surface (Figure 5a). The difference between the hydroxide bands in vacuum (ν_1/ν_2) and under acetonitrile pressure (p) indicate that the adsorption of acetonitrile is reversible and that the hydroxy groups on the surface are not directly consumed upon nitrile adsorption on a hydrated surface. This is in contrast to the observations reported by Aboulayt and co-workers for a dehydrated oxide surface.[12] The molecular adsorption of CD_3CN on a zirconia surface gives rise to four adsorption bands in the IR spectrum, as shown in Figure 5b. The bands at 2299 and 2262 cm^{-1} originate from the stretch vibration of the acetonitrile nitrile group, ν(CN), bound to Lewis acidic zirconia sites[12,13] and physisorbed acetonitrile,[14] respectively. The symmetrical stretch vibration, $\nu_s(CD_3)$, and the asymmetrical stretch vibration, $\nu_{as}(CD_3)$, of the methyl group are observed at 2113 and 2250 cm^{-1}, respectively.[15] Both these methyl bands are characteristic for physisorbed acetonitrile.

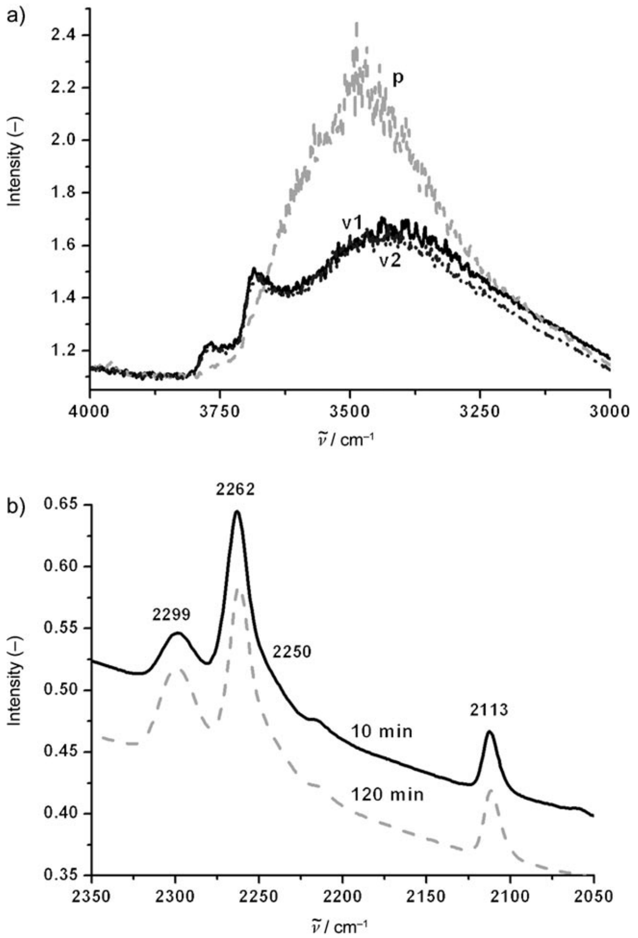


Figure 5. a) IR spectra (4000–3000 cm^{-1}) for the successive application of vacuum (ν_1) and acetonitrile pressure (p), and vacuum (ν_2). b) IR spectra (2350–2050 cm^{-1}) after introduction of CD_3CN on a zirconia surface calcined at 30 °C for 10 min and during 120 min.

While still highly hydroxylated after calcination at 30 °C for 120 min, the amount of zirconia-coordinated acetonitrile increases more than 65 % in comparison to the amount of coordinated acetonitrile on a zirconia surface only activated by evacuation for 10 min at 300 °C, as shown in Figure 5b ($\nu_{(C\equiv N)ads} = 2299\ cm^{-1}$). The amount of chemisorbed acetonitrile is strongly dependent on the degree of hydration of the surface, as an increased amount of physisorbed water is competing with physisorbed acetonitrile for Lewis acid coordination. Hence, a less hydrated surface results in a distinctly higher amount of chemisorbed acetonitrile and consequently affords a higher nitrile hydrolysis rate compared to a more hydrated surface, in agreement with Figure 5b. Furthermore, an increase of the acetonitrile pressure results accordingly in an increase of the absorption bands of both chemi- and physisorbed acetonitrile (Figure 6). The increase of the amount of coordinated acetonitrile can be rationalized by ligand displacement of zirconia-bound water as proposed by Morterra and co-workers.[13]

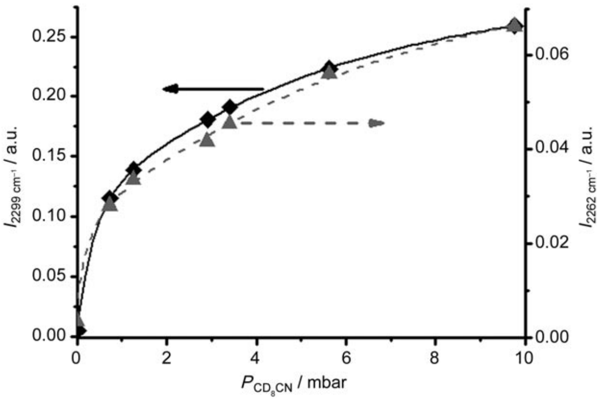


Figure 6. Adsorption isotherm for chemisorbed (◆) and physisorbed acetonitrile (▲).

The zirconia surface used for the catalytic nitrile hydrolysis will always be highly hydrated, as at least stoichiometric amounts of water are required to completely convert the nitrile. As discussed above, this limits the amount of absorbed acetonitrile activated for hydrolysis, and consequently decreases the hydrolysis rate. The surface reaction of adsorbed acetonitrile at 30 °C is evidenced by a decrease of the intensity of the $\nu_{(C\equiv N)ads}$ band at 2299 cm^{-1} during nitrile hydroly-

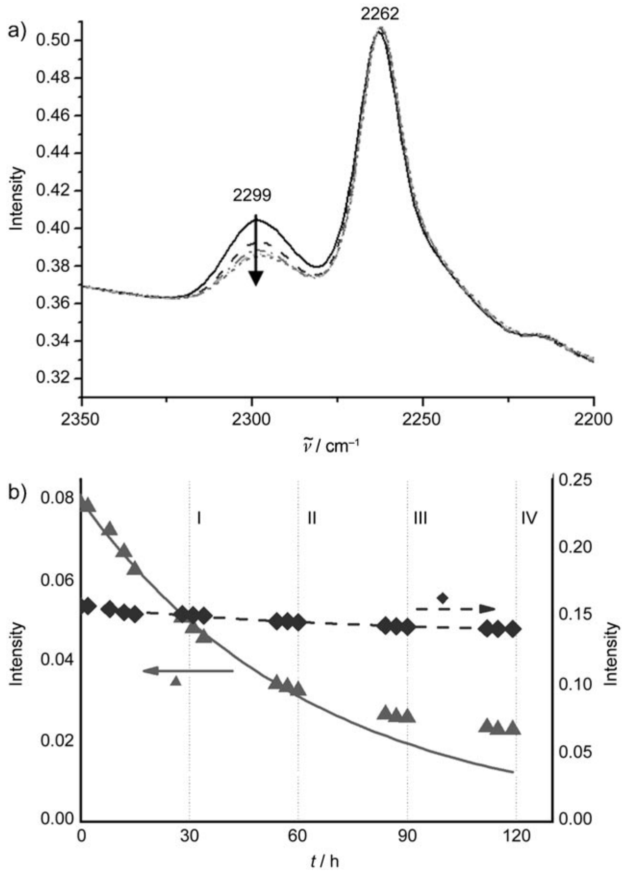


Figure 7. Effect of time (0.5 h increments) on the intensity of the nitrile $\nu_{(C\equiv N)ads}$ signals at 2299 cm^{-1} (▲) and 2262 cm^{-1} (◆). Zirconia surface evacuated for 120 minutes. The solid line represents a first-order decay of the $\nu_{(C\equiv N)ads}$ absorption band.

sis (Figure 7a). Remarkably, the amount of physisorbed nitrile remains constant, while both the physisorbed and chemisorbed acetonitrile are in equilibrium with gaseous acetonitrile, according to the adsorption isotherm shown in Figure 6. The change in chemisorbed acetonitrile coverage is therefore ascribed to the consumption of surface sites due to nitrile hydrolysis. Proton abstraction from acetonitrile, observed for highly dehydroxylated metal oxides,[12,13,16] is unlikely to occur at a highly hydroxylated surface. Indeed, signals corresponding to [CD_2CN^-] and the formation of a broad OD band at 2170 cm^{-1} are not observed.[12,16] Up to about 60 % conversion, the nitrile hydrolysis obeys first order kinetics. At higher nitrile conversion the hydrolysis rate starts to deviate from first-order kinetics (Figure 7b).

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 8a.[12,17] An important observation is that although the adsorbed acetonitrile is hydrolyzed on a zirconia surface, most of the products are only converted into acetamide anions. Only the signal at 1651 cm^{-1} can be assigned to molecularly adsorbed acetamide, which shows a good resemblance to the bands of acetamide absorbed on TiO_2.[17a] The other bands show a

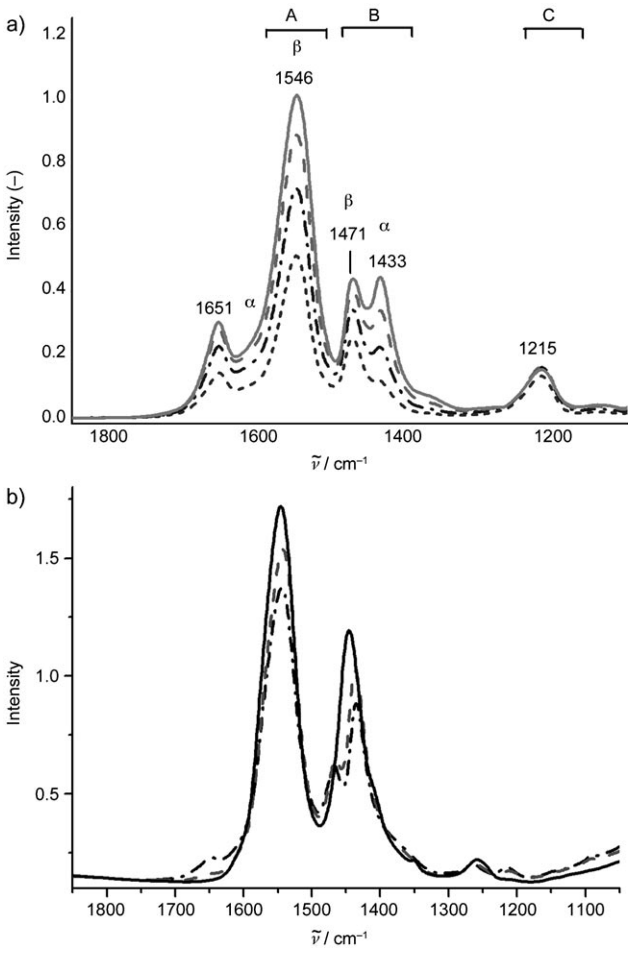


Figure 8. a) Effect of time (0.5 h time increments) on the intensity of the absorption bands of the nitrile hydrolysis products and. b) After gradual heating to 50 (–•–•), 150 (– – –), and 150 °C (——).

strong similarity with the bands in spectra reported by Aboulayt and co-workers. These authors assigned the bands α and β to two kinds of anion acetamide species, resulting from the nitrile hydrolysis on a zirconia surface.[12] Even though an excess of molecular water is present, acetamide ions are not fully converted into molecular amide, which obstructs the completion of the nitrile hydrolysis. This might suggest that hydrolysis and desorption of the surface-bound acetamide species are both governing the rate of the reaction. So product inhibition indeed plays a crucial role in the catalytic nitrile hydrolysis process.

Figure 8b shows the evolution of the infrared bands of the hydrolysis products upon stepwise heating. The gradual change in surface species is a result of the hydrolysis of the acetamide surface ions into surface acetate species.[12,17c] Despite the fact that there are still surface hydroxyls present to complete the catalytic cycle, the ionic products remain strongly bound to the zirconia surface. The ionic products are not readily transformed into molecular acetamide or acetic acid and will simply not desorb upon heating. The presence of the primary amine might facilitate the completion of the catalytic cycle of the nitrile hydrolysis.

Polymerization of 6-aminocapronitrile (ACN): To study whether the results obtained for the model system are also valid for making high-molecular-weight nylon-6, we performed the zirconium-catalyzed polymerization of 6-aminocapronitrile. Before synthesizing nylon-6 out of ACN by using ZrO_2, the uncatalyzed synthesis was performed as a reference first. Both time and amount of water were varied, as shown in Table 2.

Table 2. The molar mass distribution of the nylon-6 synthesized from 6-aminocapronitrile without a catalyst, at 230 °C.

Entry	ACN/H_2O	t [h]	M_n [$g\,mol^{-1}$]	PDI
1	1:2	8.5	1200	2.5
2	1:2	22.5	2100	1.6
3	1:10	8.5	1100	1.6
4	1:10	22.5	1300	1.4

Although some oligomeric material was obtained, no high-molecular-weight material was formed. The molecular weight was largely independent of the amount of water used and of the reaction time, although a smaller amount of water initially resulted in a higher polydispersity (entry 1, Table 2). After more than 22 hours with two equivalents of water (entry 2, Table 2) the polydispersity index (PDI) was similar to that obtained in the polymerizations with ten equivalents of water, but the number average molecular weight (M_n) is in this case about a factor of two higher. As the amount of water used seems to affect the polymerization of ACN, polymerization using the zirconia catalyst was also performed with varying amounts of water (Table 3). A distinct increase of the molecular weight was observed for all experiments compared to the polymerization without zirconia, demonstrating that zirconia indeed catalyzes the nitrile hydrolysis of ACN, as was earlier observed for the studied model compounds (see above). 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.

Table 3. The molar mass distribution of the nylon-6 synthesized from 6-aminocapronitrile, by using ZrO_2 as the catalyst.[a]

Entry	ACN/H_2O	M_n [$g\,mol^{-1}$]	PDI
1	1:2	4100	1.4
2[b]	1:2	4700	2.6
3	1:4	4000	1.4
4	1:8	4000	1.5
5	1:10	3900	1.4

[a] 230 °C, 8 h. [b] Nylon of entry 1 after 24 h 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 low with respect to the required molar mass of about $1.5 \times 10^4\,g\,mol^{-1}$. The most trivial origin for the formation of the low-molecular-weight nylon is that the product obtained after the ACN hydrolysis still contains some residual nitrile end-groups. The absence of nitrile absorption bands in the IR spectrum of the product excludes the presence of residual nitrile end-groups as the cause of the moderate molecular weight. The model reactions demonstrated that when 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. However, by performing the polycondensation of adipamide with 1,6-hexanediamine it was found that amide-functionalized monomers lower the polycondensation rate but do not affect the final molecular weight. The molecular weight is probably limited due to the presence of water required during the ACN hydrolysis. A successive further amidation under water-free conditions is therefore required to achieve the maximum molecular weight. Since the amount of polymer product obtained from the experiment (Table 3, entry 1) was too low to perform a controlled-melt polymerization, the semicrystalline product has been submitted to a solid-state post-condensation (SSP) step (Table 3, entry 2). Whereas the post-condensation only results in a minor increase of the number average molecular weight (M_n), the polydispersity is distinctively higher, and a weight average molar mass (M_w) of approximately $12\,000\,g\,mol^{-1}$ is reached. This value is already close to that of commercial low-M_w-grade nylons. The amidation during solid-state post-condensation was performed at 185 °C, which is well below the melting temperature of the nylon-6 prepolymer. At this temperature, the molecules present in the crystals do not participate in the post-condensation reaction. Only the chain ends present in the amorphous phase will undergo chain extension. This explains the broad PDI obtained after the SSP. Although not satisfactory yet, this build-up of molecular weight during the SSP step at 185 °C clearly shows the potential of increasing the molecular weight by post-condensation and it is very likely that a melt-polymerization step will result in the required molecular weight.

Conclusion

In an attempt to develop a catalytic system for the combined hydrolysis and subsequent polymerization of 6-aminocapronitrile to nylon-6, some zeolites, amorphous aluminum silicate, and metal oxides were tested as catalysts for the combined nitrile hydrolysis and amine amidation of *n*-pentanenitrile and *n*-hexylamine. All silicates proved unsuitable as they gave low nitrile conversion. Furthermore, the observed secondary amine formation is detrimental to the targeted polymerization process, since secondary amines lead to branched products and loss of stoichiometry. The metal oxides gave high nitrile conversions and excellent selectivity. Among the oxides zirconia was found to be by far the best catalyst system. With a nitrile conversion above 99 %, ZrO_2 is a truly interesting catalyst for the combined hydrolysis and polymerization of 6-aminocapronitrile. The composition development of the reaction mixture shows that the nitrile is first hydrolyzed into the amide that either directly, or after further hydrolysis to the corresponding carboxylic acid, acylates the amine to the corresponding *N*-hexylpentanamide. Group 4 metal oxides not only catalyze the nitrile hydrolysis but also prove to be highly active catalysts for the amine acylation. Consequently, whereas the Nb_2O_5 catalyzed nitrile hydrolysis and amine acylation proceeds with time constants of similar order of magnitude, for zirconia and titania, the nitrile hydrolysis is clearly rate determining.

IR spectroscopy clearly demonstrates that the catalytic cycle starts with reversible nitrile adsorption, followed by hydrolysis. The so formed surface-bound amide species are further hydrolyzed to surface-bound carboxylates instead of being protonated to form molecular amides. In fact both amides and acetates are strongly bonded to the metal oxide surface. The strong binding of the amides and carboxylates to the metal oxide predicts product inhibition and by that a drop in catalytic activity of the metal oxides at high nitrile conversions. However, the rate of *N*-hexylpentanamide production is strongly increased by the metal oxides, implying that the completion of the catalytic cycle is strongly improved by the presence of an amine. Tuning the amount of water present in the system is also crucial, as a low water concentration is beneficial for nitrile adsorption but results in low rates of hydrolysis and product desorption. Conversely, a high water concentration increases the rate of nitrile hydrolysis and desorption of the hydrolysis products but limits the nitrile adsorption.

ZrO_2 is a very promising catalyst for the complete and selective hydrolysis of 6-aminocapronitrile into nylon-6. In comparison with 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, presence of water required for the hydrolysis prevents build-up of the molecular weight. Preliminary results by using an SSP step clearly demonstrate that water removal leads to the desired build-up of molecular weight.

Experimental Section

General: Zeolite NaY was obtained from Akzo Nobel and had a silica-to-alumina ratio of 2.5 and a surface area of 500 m^2g^{-1}. Zeolite HY was synthesized through ion exchange of NaY with NH_4NO_3 followed by calcination to deammonate the formed NH_4Y into HY. Zeolite Hβ was obtained from Zeolist Int. and has a silica-to-alumina ratio of 37.5 and a surface area of 680 m^2g^{-1}. To avoid the formation of clustered copper species during the synthesis of Cu^Iβ and Cu^{II}β, the use of solid-state ion exchange and a high Si/Al ratio for the zeolite was chosen.[18] The complete ion-exchange procedure was 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 2 wt% of Cu^ICl or $Cu^{II}Cl_2$ to obtain Cu^I/β and Cu^{II}/β loaded with 2 wt% of metal, respectively. The obtained mixture was then heated for 2 h at 500 °C in a nitrogen flow. In this way the hydrogen was replaced by copper and the HCl formed was removed with the gas flow. Titanium oxide was prepared from a commercially available precursor (FinnTi S150, acquired from Kemira) by calcination at 300 °C in an air stream for 6 h. SEM images indicated an average particle size of 4–10 μm. The BET surface area was 201 m^2g^{-1} and the pore diameter was 5.8 nm. Zirconia was prepared from a commercially available precursor (MEL XZ01247/01, acquired from Mel Chemicals) by calcination at 300 °C in an air stream for 6 h. SEM images indicated an average particle size of 5–10 μm. The BET surface area was 288 m^2g^{-1} and the pore diameter was 4.9 nm. Niobium oxide (HY 340) was acquired from CBMM Ltd. (Araxá, Brazil) and was used after calcination at 200 °C in an air stream for 6 h. The BET surface area was 193 m^2g^{-1} and the pore diameter was 4.3 nm. 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 h. For the determination of the BET surface area, values 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. Pentanenitrile (99.5%, Aldrich), hexylamine (99%, Merck), pentanamide (99%, Acros), and *p*-xylene (99+ %, Aldrich) were used as received. 6-Aminocapronitrile was kindly donated by BASF AG The reaction products were identified by using ^{1}H NMR spectroscopy (Varian Mercury 400). The product mixtures were analyzed by gas chromatography by using a CP 9000 gas chromatograph (GC) equipped with a 30 m × 0.32 mm id, capillary CP volamine column, and a FID detector. *p*-Xylene was used as an internal standard. Samples were injected at 120 °C and after a stabilization time of 1 min the temperature was raised with 15 °C min^{-1} to 290 °C. All single-point experiments were performed in duplicate.

Nitrile hydrolysis with subsequent amine amidation: The hydrolysis experiments were performed in closed, stainless-steel 5 mL microreactors by using a solvent-free system consisting of equimolar amounts of pentanenitrile and hexylamine in aqueous environment.[2] Reaction mixtures consisting of *n*-pentanenitrile (8.6 mmol, 0.71 g), *n*-hexylamine (8.6 mmol, 0.87 g), water (17.2 mmol, 0.31 g), and 0.2 g of the heterogeneous catalyst were 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 previously applied.[2] Reaction mixtures were sufficiently stirred by using magnetic stirrer bars 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 duplicate. The results presented are the mean values of the conversion and selectivity results.

IR spectroscopy: The zirconia used was obtained by calcination of a commercially available precursor (MEL XZ01247/01, Mel Chemicals) at 30 °C, for 6 h, in an air stream. The zirconium oxide obtained was mainly amorphous and exhibited a specific surface area of 288 m^2g^{-1}. Infrared spectra were recorded by 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 lower than 1×10^{-6} mbar. All IR spectra were recorded at 30 °C with a resolution of 1 cm^{-1}. The zirconia material was pressed into self-supporting wafers ($\approx$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. Deuterated acetonitrile was used as a reactant for infrared studies. Due to the strong complication of the CN region for acetonitrile by Fermi resonances between the ν(CN) and the combination $\delta_s(CH_3)+\nu(CC)$ frequencies, deuterated acetonitrile (CD_3CN) was more appropriate for infrared studies than CH_3CN.[19] The CD_3CN (liquid, 99.9%, Aldrich) was purified by several freeze-pump-thaw cycles before use.

Nylon-6 synthesis from 6-aminocapronitrile: The polymerization of ACN was performed by using the same system as applied in the catalytic nitrile hydrolysis experiments.[2] A typical polymerization experiment was performed by using ACN (0.90 g, 1 mL, 8.0 mmol, 1 equiv), water (0.29 g, 16 mmol, 2 equiv), and ZrO_2 (0.40 g, 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 h at 40000 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 h, under a nitrogen flow, by using the method described in literature.[20]

Polymer analysis: The molecular weight distribution of the synthesized nylon-6 was determined by 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-10 AD), an injector (Spark Holland, Midas), a two-column set (PSS, PFG Linear xl 7 μm 8×300 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^{-1}, 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 IR spectroscopy (Biorad, FTS 6000) on a thin polymer film, obtained by compression of a polymer particle with a diamond press.

Acknowledgements

The authors thank the Dutch Polymer Institute (DPI) for their financial support. This research forms part of the research program of the Dutch Polymer Institute (DPI), project #297.

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Received: December 30, 2006
Revised: March 6, 2007