



# Beckmann-rearrangement of cyclododecanone oxime to $\omega$ -lauro lactam in the gas phase

W. Eickelberg, W.F. Hoelderich \*

Chemical Technology and Heterogeneous Catalysis, University of Technology RWTH Aachen, Worringerweg 1, 52074 Aachen, Germany

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## ABSTRACT

The classical route for the industrial production of  $\omega$ -lauro lactam is the homogeneously catalyzed Beckmann-rearrangement of cyclododecanone oxime in the liquid state using fuming sulfuric acid catalyst. Contrary to that, a completely different way is shown in the present work. In addition to the use of a solid acid catalyst, the vapor phase was chosen. From a process technical point of view it is a superior route compared with the classical one. Following intensive investigations of the vapor phase behavior of substrate, product and the main by-products, a catalyst screening of the most promising materials was performed. In addition, a modification of the most active catalysts was carried out to get more information about reaction sites and to optimize the catalyst activity. Using an acid treated [Al,B]-BEA zeolite at a temperature of approx. 320 °C and reduced pressures, complete conversion combined with excellent selectivity of 98% were obtained. The accumulation of reactants in the fixed bed was less than 5 wt%. Furthermore, investigations of deactivation and regeneration behavior of the catalyst were done. It could be demonstrated that the catalytic material could be regenerated under oxidative atmosphere as well as under non-oxidative conditions through thermal desorption of the deactivating compounds without any measurable loss of catalytic performance.

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## 1. Introduction

The most well-known polyamide is Nylon 6. Its monomer  $\epsilon$ -caprolactam is one of the 50 most important bulk chemicals in the world, with an estimated annual production of 4.4 million tons worldwide [1,35]. Another very important polyamide is Nylon 12, which is characterized by superior mechanical, chemical and thermo-mechanical load capacities. The classical synthesis route for  $\omega$ -lauro lactam starts from 1,3-butadiene, through the intermediates 1,5,9-cyclododecatriene, cyclododecane, cyclododecanone and cyclododecanone oxime, which undergoes a Beckmann-rearrangement to form  $\omega$ -lauro lactam (Scheme 1).

The standard catalyst for industrial plants for the oximation and rearrangement is fuming sulfuric acid. Generally ammonia is used to neutralize the product mixture. The disadvantage of this procedure is the enormous production of ammonia sulfate, causing some ecological concerns in addition to an economical drawback. Starting with the optimization and reengineering of the old reaction pathways, important producers nowadays focus their efforts on new synthesis routes. A solution to the problem even for world scale plants could be the change from homogeneous to heteroge-

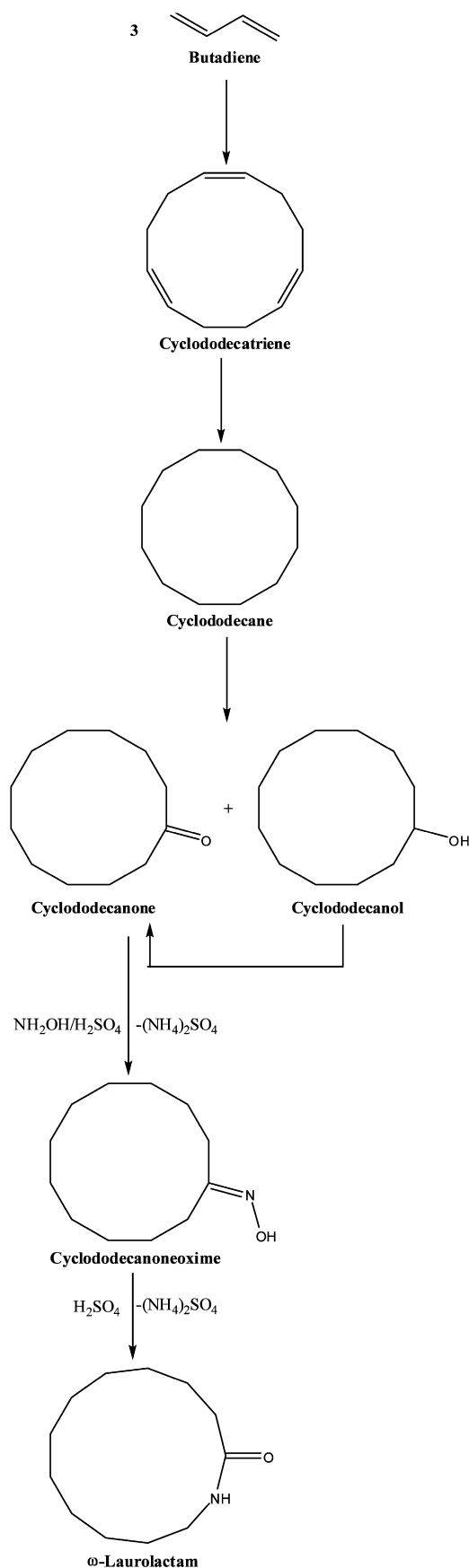
neous catalysis, wherein the catalytic material can be separated from the reaction mixture and reused again. In this work a closer look on zeolitic catalysts is given, since these led to good results for the Beckmann-rearrangement of cyclohexanone oxime to  $\epsilon$ -caprolactam [2–7].

Corma et al. [8] reported a heterogeneously catalyzed rearrangement of cyclododecanone oxime in the liquid state. They carried out the reaction batch-wise with chlorobenzene under reflux at 130 °C and ambient pressure during 24 h. The catalysts used were H-ZSM-5 and [Al]-BEA with molar Si/Al ratios of 31 to 10,000. A non-dealuminated [Al]-BEA (Si/Al-ratio = 34) turned out to be the most active material. The selectivity was approximately 98% and the conversion higher than 92%. The only by-product formed during the reaction was cyclododecanone. Later on, the same group published results where they used MCM-41 and ITQ-2 structures as catalysts for the reaction [9,10]. The drawback of these reaction routes was that the catalyst could be used only once and could not be regenerated due to very strong adsorption of heavier products.

Our research focused also first on solvents in the liquid and supercritical phase. The liquid phase was chosen because of the high boiling point of the feed and the product. Unfortunately, also in our case the catalyst could be used only once due to the fact that the deposits could not be removed. A paper concerning this research will be published separately. Due to the results obtained thereby, the research strategy was changed. The aim of this work was to

\* Corresponding author.

E-mail address: hoelderich@rwth-aachen.de (W.F. Hoelderich).



**Scheme 1.** Synthesis of  $\omega$ -lauro lactame.

**Table 1**

BEA zeolites prepared by the group of Mr. F. Fajula, CNRS, in Montpellier.

Catalyst	Treatment
BEA2	Dealuminated [Al]-BEA
BEA3	Dealuminated [Al]-BEA
BEA5	Dealuminated [Al]-BEA
BEA7	Dealuminated [Al,B]-BEA
PT262	Dealuminated [Al]-BEA
PT271	Dealuminated [Al]-BEA
PT313	Dealuminated [Al,B]-BEA
PT349	Dealuminated [Al]-BEA
PT326/328	Dealuminated [Al]-BEA

carry out the Beckmann rearrangement in the gas phase, which originally was thought not to be possible. An important step to build up such a reactor system is the observation of the thermodynamical properties of the substrate, the product and the main by-products of the rearrangement reaction. The vapor pressures of the compounds involved in the reaction were investigated in detail. Theoretical calculations were done using different incremental methods and the results were compared with the experimental results.

For the presented reaction, a broad range of zeolitic and non-zeolitic catalysts was applied under different conditions. Even high temperatures of above 300 °C could be used without any thermal decomposition of the unstable starting material cyclododecanone oxime. The deactivation and regeneration behavior of the catalyst was investigated as well as the nature the catalytically active sites.

## 2. Experimental

### 2.1. Catalysts

For the catalyst pre-selection some standard catalysts were tested. Degussa provided Aerosil and H-ZSM-5 material, Grace provided Z-alumina and USY catalysts. The [B]-MFI zeolite was synthesized according to the patent of BASF [US 6884743].

In addition, some catalytically interesting materials such as MCM-41 (all silica) [Catalyst A], TS-1 [Catalyst B], [Al] MCM-41 [Catalyst C] and the [B]-BEA [Catalyst D] were prepared in our group and applied.

*Si-MCM-41 (all silica) [Catalyst A]:* In the first step, 350 g (35%) TEAOH, 659.5 g H<sub>2</sub>O and 70.3 g tetradecyltrimethyl ammonia bromide were stirred for one hour under argon atmosphere and at room temperature. Then 30.59 g Aerosil-200 SiO<sub>2</sub> was added and the mixture stirred again for three hours. In the next hour 83.7 g Aerosil-200 and 175.8 g H<sub>2</sub>O were added continuously and stirred for three more hours, before the mixture was put in a steel autoclave for one week at 130 °C. Finally the obtained material was washed with deionized water, filtered, dried and calcined.

The synthesis of the TS-1 [Catalyst B] material was performed based on a route developed by Serrano et al. [11,12].

[B]-BEA [Catalyst D] was synthesized and calcined according to the method of De Ruiter et al. [13,14]. For a slight deboronation, the raw material was treated for 60 min with HCl-solution (pH 6) at room temperature. The resulting material has a Si/B-ratio of approx. 32. For a stronger deboronation, the raw material was treated for 24 h with HCl-solution (pH 5) at room temperature. After this treatment, the catalyst showed a Si/B-ratio of approx. 700 [Catalyst D deb.].

A broad range of dealuminated and/or deboronated BEA zeolites were synthesized by the group of F. Fajula, CNRS in Montpellier (Table 1).

For the dealumination treatment, a route developed by Des Courieres et al. [15] was used.

For the use in the gas phase reactor system all catalysts were pressed with a weight of 4 tons, crushed again and sieved. The

fraction with a grain size distribution of 1.0–1.4 was used in the tubular reactor.

## 2.2. Characterization

X-ray powder diffraction (XRD) was carried out using a Siemens D5000 ( $\text{CuK}\alpha_{1,2}$ , secondary monochromator, variable diaphragm V20, angular velocity of  $1, 2^\circ \text{min}^{-1}$ ). Elemental analysis (ICP-AES) was performed using a Spectroflame D (Spectro). BET and nitrogen sorption isotherms were measured (at  $-196^\circ\text{C}$ ) using a ASAP 2000 (Micrometrics). NMR measurements were conducted on Bruker DSX 500. For thermogravimetric analysis a Netsch 209/2/E equipped with a STA 409 controller was used (heating rate  $2^\circ\text{Cmin}^{-1}$ ,  $\text{Al}_2\text{O}_3$  crucibles were used with  $\alpha\text{-Al}_2\text{O}_3$  as reference).

$\text{NH}_3$ -TPD was performed on a Porotec, TPDRO 1100. The already calcined material was heated to  $550^\circ\text{C}$  for 24 h under helium atmosphere. Then the ammonia was adsorbed at room temperature for 3 h (atmosphere: 3 vol%  $\text{NH}_3$  in Helium, flow: 0.02 l/min). To remove the physisorbed water, the catalyst was heated to up to  $150^\circ\text{C}$  under helium. During the measurement the system was heated up with  $15^\circ\text{Cmin}^{-1}$  up to  $1000^\circ\text{C}$  (helium flow: 0.02 l/min).

The IR-spectra were taken with the system of Nicolte (Protégé 460), but with a modification of the cell to measure also crystalline substances. For that, a special carrier was installed inside the cell, where a wafer with a diameter of 13 mm could be fixed. The wafer with a material density of  $5\text{--}10 \text{ mg/cm}^2$  was prepared in a press by Gasby Specac. The wafer was heated with a heating coil fixed in a ceramic casing, wherein the temperature measurement was located. The wafer temperature was regulated by a Eurotherm-PID-controller. The cell windows were made of KBr. Furthermore, a high-vacuum-pump (Fa. Edwards E2M12) was connected to the measuring cell to evacuate the cell to a pressure of  $10^{-3}$  mbar.

The analysis of the product mixture was generally performed using gas chromatography. For these measurements, a system of Hewlett-Packard (HP 6890 Series, Chem Station) was used.

## 2.3. Vapor pressure measurement

To measure the vapor pressure of the substrate cyclododecanone oxime, the product  $\omega$ -laurolactam and the main by-product cyclododecanone, a pressure cell was built as shown in Fig. 1. The cell (stainless steel, material: 1.4571) was installed in a temperature-controlled oven. The pressure indicator (Edwards, APG/NPMW/16 ST/ST) was attached to the top of the steel cell. A second capillary was passed out of the oven and was connected to a vacuum pump (Edwards, Model E2M-12).

For the measurements, a certain amount of material was filled into the steel cell and set to the system. The oven was heated to up to  $80^\circ\text{C}$  and evacuated for one hour to remove impurities. Before the measurement was started, the valve was closed and the system was heated stepwise ( $10^\circ\text{C}$ ) up to  $200^\circ\text{C}$ . In each temperature step, the system was held at constant temperature until the equilibrium was reached and no more pressure increase could be detected. At the end the cell was cooled down again to  $80^\circ\text{C}$  to compare the starting pressure with the one after the measurement. A sample of the test substance was analyzed.

## 2.4. Catalytic experiments

The reactor system for the gas phase rearrangement was installed in a single temperature-controlled oven (Fig. 2). The feed solution was cyclododecanone oxime dissolved in isopropanol with a concentration of 3 g oxime per 100 g solvent, which is the upper solubility limit at room temperature. While using catalysts with a

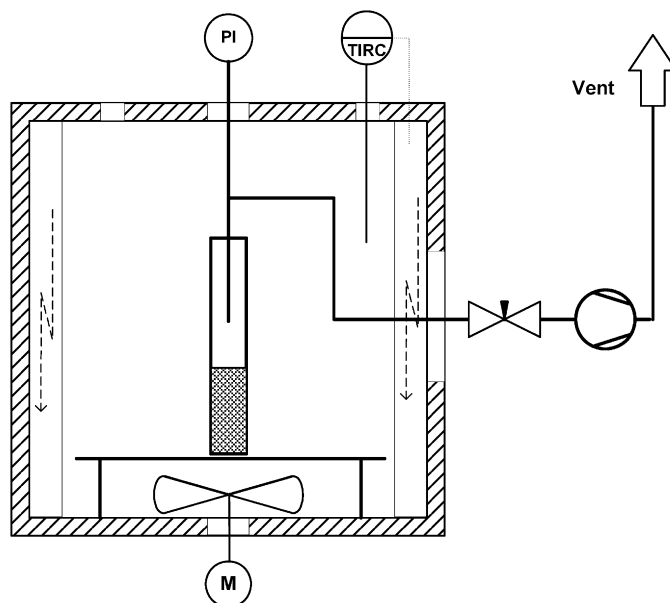


Fig. 1. System for vapor pressure measurements.

low Si/Al-ratio, cyclohexane was used as solvent, because the preferred solvent isopropanol reacts on the alumina sites. The feed solution was pumped through a capillary (inner diameter of 0.5 mm) into the vaporization system, where the preheated carrier gas was purged to vaporize the substrate solution immediately. Then the reaction mixture was heated in the preheating zone to the reaction temperature and fed into the fixed bed with a diameter of 6 mm and a length of approx. 250 mm where the catalyst was packed. To quench the reaction mixture together with the solvent, after the reactor a cooling trap (liquid nitrogen) was connected at the outlet of the tubular reactor. Behind the cooling trap a vacuum pump with an air needle valve was installed to control the system pressure. To create a homogeneous temperature distribution, the heated air was circulated in the oven by a propeller.

The standard reaction conditions were: reaction temperature:  $325^\circ\text{C}$ , system pressure: 50 mbar, amount of catalyst: 1.0 g, feed flow: approx. 10 g/h, substrate concentration in the feed solution: 3.0 wt%, WHSV: approx.  $0.3 \text{ g}_{\text{oxime}}/(\text{g}_{\text{cat}} \text{ h})$ , carrier gas: approx. 3.5  $\text{Nl/h N}_2$

After 120 min TOS (time on stream) a sample of the product mixture from the cooling trap and a sample of the catalyst were taken and analyzed. For the long-term reaction study the cooling trap was changed every 60 min and the content was analyzed.

## 2.5. Regeneration

For regeneration, the same reaction system as described was taken. After the reaction the deactivated catalyst was regenerated under the following regeneration conditions:  $550^\circ\text{C}$ , 1013 mbar, ca. 3.5  $\text{Nl/h}$  air or nitrogen as regeneration gas. Duration of regeneration: approx. 12 h.

## 3. Results and discussion

### 3.1. Vapor pressure

The determination of the vapor pressures of substrate, product and the main by-product cyclododecanone is an essential key value for the process of the gas phase rearrangement of cyclododecanone oxime to laurolactam.

Fig. 3 shows the results of the theoretical calculation of the vapor pressure. The boiling point was determined using the method

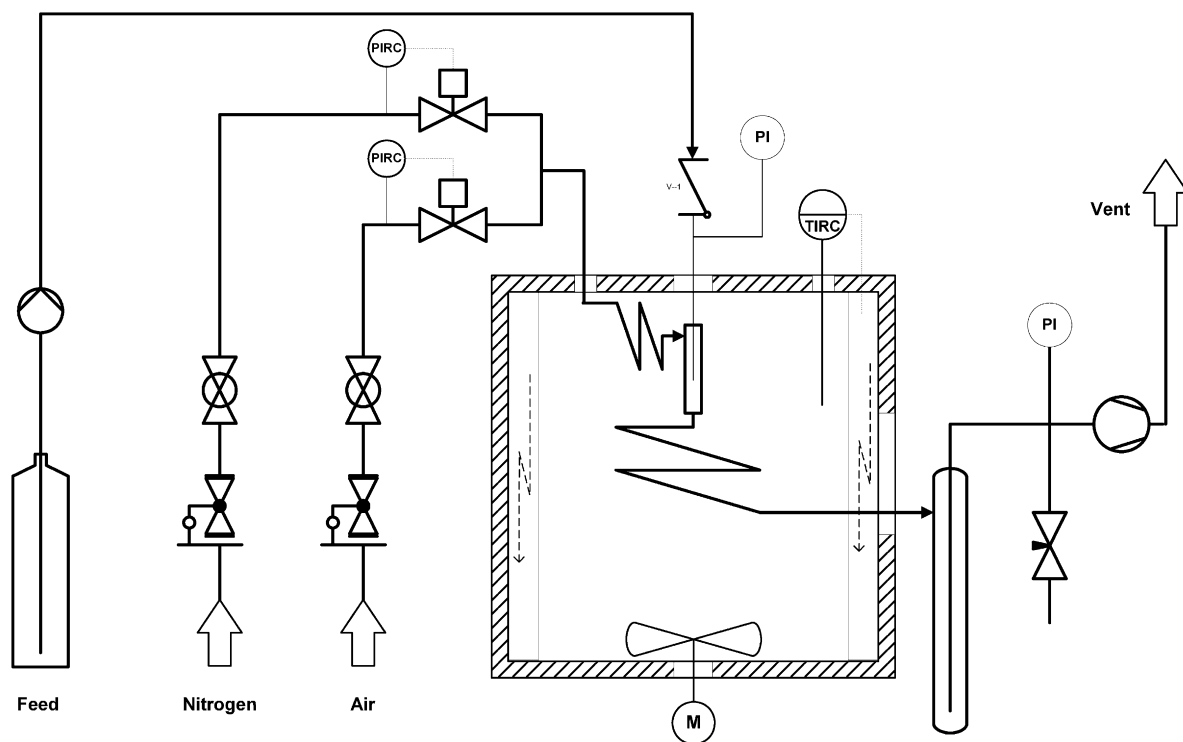


Fig. 2. Gas phase reactor system.

of Miller et al. [16–18], the critical data analogous to the method of Joback et al. [19,20] and finally the vapor pressure was calculated based on the considerations of Gomez-Nieto and Thodos [21–23].

The vapor pressure of cyclododecanone oxime is shown in Fig. 3A. At standard reaction conditions ( $T = 325\text{ }^{\circ}\text{C}$ ) this substrate has a calculated vapor pressure of approx. 130 kPa or 1.3 bar, and at the minimum reaction temperature ( $T = 200\text{ }^{\circ}\text{C}$ ) a vapor pressure of 6.7 mbar. Laurolactam shows comparable values (see Fig. 3B). At standard reaction conditions ( $T = 325\text{ }^{\circ}\text{C}$ ) laurolactam has a calculated vapor pressure of approx. 115 kPa or 1.15 bar, and at the minimum reaction temperature ( $T = 200\text{ }^{\circ}\text{C}$ ) a vapor pressure of 7.2 mbar.

In the case of cyclododecanone, some additional Antoine-data, determined by DuPont [24], were used to determine its vapor pressure. Fig. 4 shows these values together with the results of the theoretical calculation. At lower temperatures the curves show a difference. The vapor pressure between 120 and  $280\text{ }^{\circ}\text{C}$ , determined by the incremental method, is lower than the one from DuPont. However, both curves are in the uncritical area, where condensation of cyclododecanone could not take place during the reaction.

To prove the accuracy of the chosen method, the vapor pressure of the chemically similar reaction system cyclohexanone oxime to  $\epsilon$ -caprolactam was studied. The well-known vapor pressure data of cyclohexanone oxime,  $\epsilon$ -caprolactam and cyclohexanone were compared with the vapor pressure investigated via incremental calculations (see Fig. 4). In the case of cyclohexanone oxime (see Fig. 4A), the vapor pressure determined via incremental methods between 120 and  $240\text{ }^{\circ}\text{C}$  is lower than that taken from the database. At temperatures of above  $240\text{ }^{\circ}\text{C}$  the curves are almost congruent.

For caprolactam the vapor pressure data determined by incremental method, are in the whole temperature interval higher than the base data (see Fig. 4B). For lactames a better fitting method could not be found, but in the scope of the present work this error is acceptable.

For the cyclic ketone cyclohexanone the selected method fits very well to the base data. Both curves are congruent (see Fig. 4).

The measured vapor pressure of cyclododecanone oxime of up to  $200\text{ }^{\circ}\text{C}$  and the already discussed data from the incremental calculation are shown in Fig. 5A. Two very important facts are responsible for the deviation between measurement and theoretic data: first the error of the incremental method. Especially at low temperatures the error of the method is comparatively high. The error between these curves is in the same range as the error of the analog reaction system (see Fig. 4A) at low temperatures. The second and main influencing factor on the error is the instability of the cyclic keto oxime. Even at low temperatures of 130 to  $150\text{ }^{\circ}\text{C}$  the oxime decomposes to ammonia and cyclododecanone. This decomposition is generally greater at higher temperatures. Between 150 and  $200\text{ }^{\circ}\text{C}$  it was not possible to adjust the equilibrium between gas and liquid state of cyclododecanone oxime. The cell pressure increased constantly, due to the decomposition and the built up of ammonia. After cooling down the system again, the starting pressure was not reached, which is a sign of the formation of gaseous substances. By opening the measurement system, the characteristic smell of ammonia was noticed and the GC-analysis showed the production of cyclododecanone during the measurement.

However, laurolactam showed a stable chemical behavior. During the measurement no decomposition was observed and a stable equilibrium could be adjusted to the system at each temperature. Nevertheless, the measured vapor pressure is higher than the theoretical values. Thereby the error of the incremental method is responsible for this deviation, too.

Section 3.2 will show that these data are sufficient for the present investigation.

### 3.2. Partial pressure distribution of the feed gas

To ensure that all compounds, particularly the substrate and the products, are in the gas phase, the partial pressure of each reaction partner had to be checked. If the partial pressure is lower than the

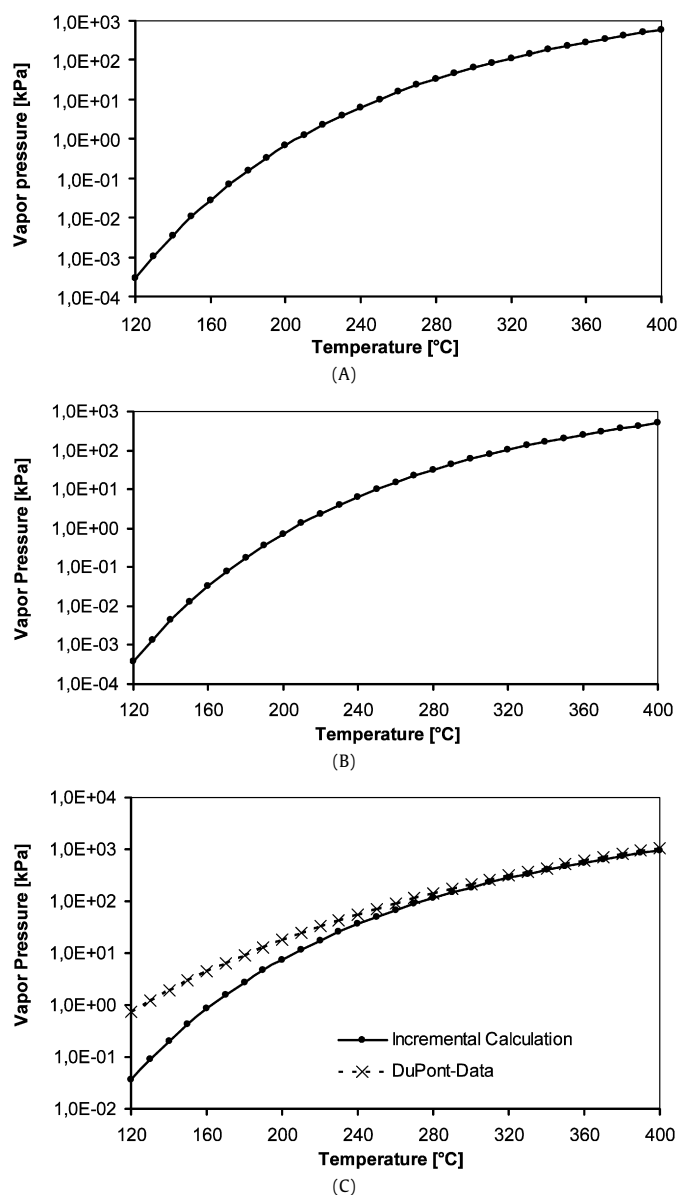


Fig. 3. Theoretical vapor pressure as function of temperature determination via incremental methods. (A) Cyclododecanone oxime, (B) laurolactam, (C) cyclododecanone.

vapor pressure, which was investigated in Section 3.1, this compound is in the gaseous state.

The partial pressure distribution was determined using the data of Table 2. For the given standard reaction mixture of a carrier gas flow of 3.5 Nl/h  $N_2$  and a feed flow of approx. 10 g/h with an concentration of 3.0 wt%, the fraction of cyclododecanone oxime or laurolactam of the partial pressure is only 0.056% of the system pressure. Even at high system pressures of around 1000 mbar the partial pressure of substrate or product is far below the vapor pressure (refer to Section 3.1) at minimum reaction temperatures. This means that all compounds are gaseous under each reaction condition adjustment and no condensation takes place, even with the error of the vapor pressure calculation determined in Section 3.1.

### 3.3. Investigation of the reaction parameters

#### 3.3.1. Temperature effect

The temperature has an important influence on the conversion of cyclododecanone oxime and the selectivity of laurolactam. For

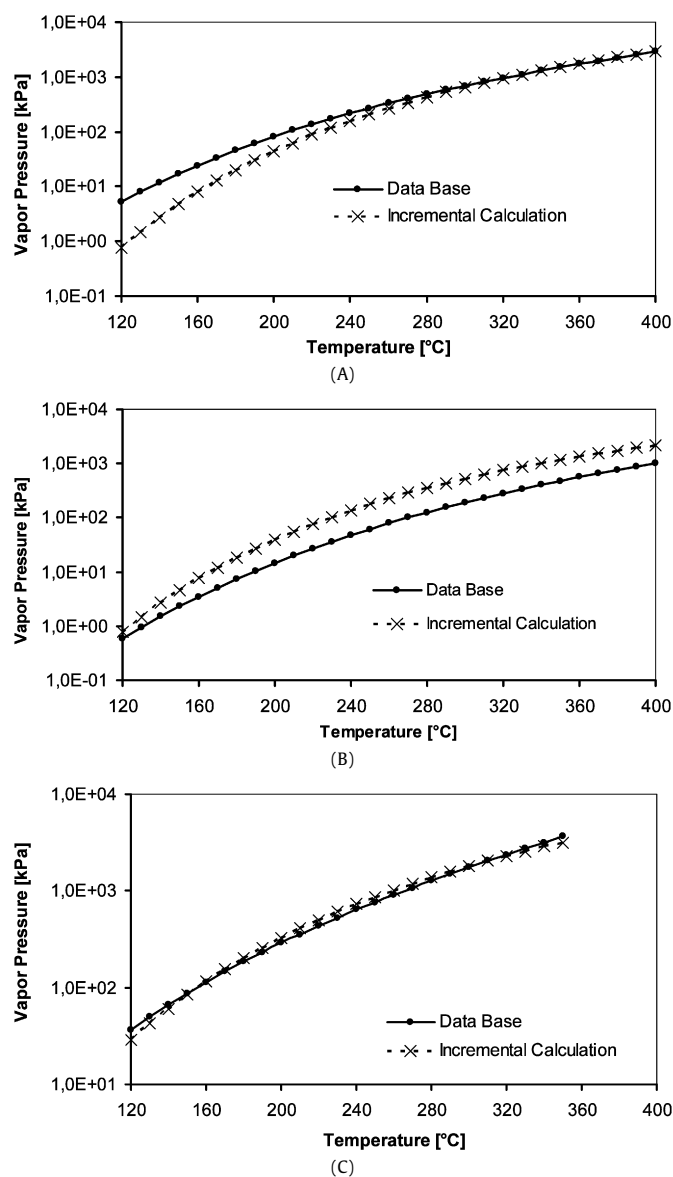


Fig. 4. Comparison of the used incremental methods with the reaction system of cyclohexanone oxime (A)/caprolactam (B)/cyclohexanone (C).

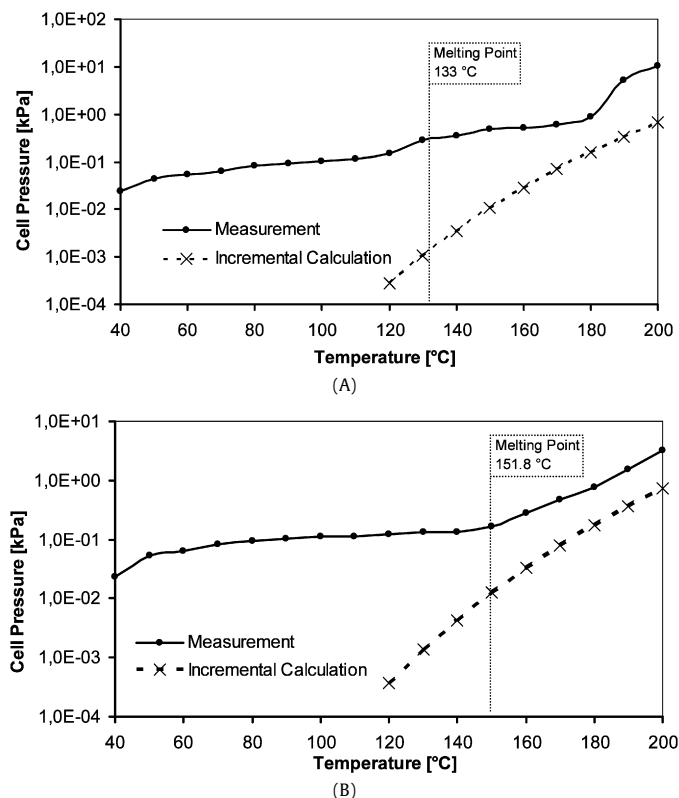
the test reaction a dealuminated [Al]-BEA (BEA5) with a high catalytic activity for the rearrangement was used. For a significant result the catalyst mass in the reactor system was increased to 3.0 g instead of 1.0 g as for the standard reaction.

For the reactions at different temperatures the dealuminated [Al]-BEA (BEA5) treated with  $HNO_3$  (Si/Al-ratio: 557) from CNRS was used. The reactions were carried out at 200, 250, 300 and 350 °C. The other parameters remained constant.

Fig. 6 illustrates how the temperature influenced the conversion. The initial conversion for all temperatures was at a high level of 100%. At a low reaction temperature of 200 °C the conversion decreased rapidly to 60% after 360 min TOS. At higher temperatures, the catalyst kept its high activity. At 250 °C after 360 min TOS, 93% of the oxime were still converted. After increasing the reaction temperature to 300 or 350 °C, no decrease in conversion was observed anymore during the reaction time of 6 hours. That means that higher temperatures help to facilitate the desorption of the products and the deactivation by self-inhibition is reduced.

Cyclododecanone oxime is a very unstable molecule, which decomposes easily to cyclododecanone. Especially at temperatures higher than 130 °C the thermal decomposition rate increases. In





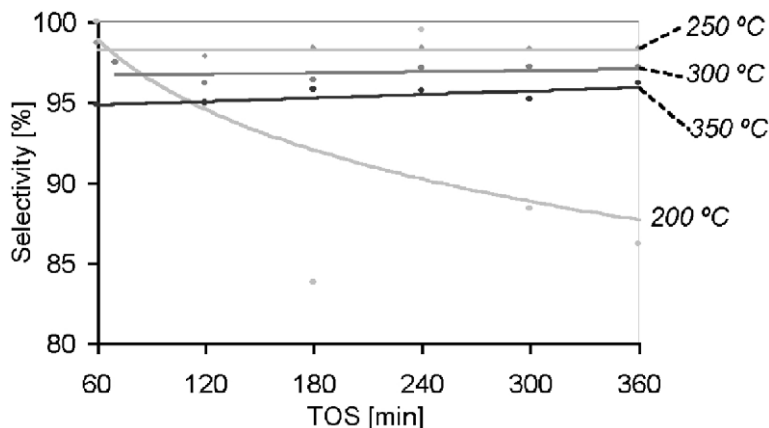
**Fig. 5.** Comparison of the theoretical determined data to the measurement. (A) Cyclododecanone oxime, (B) lauro lactam.

**Table 2**

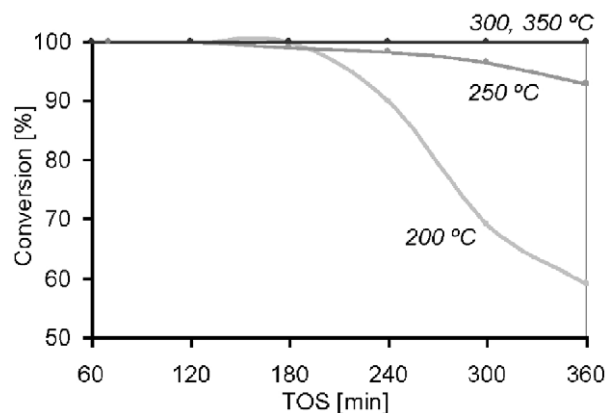
Real gas data of the reaction mixture compounds.

	Critical pressure [Pa]	Critical temperature [K]	"Van der Waals" constant $a$ [Pa m <sup>6</sup> /mol <sup>2</sup> ]	"Van der Waals" constant $b$ [m <sup>3</sup> /mol]
Nitrogen	3.40E+06	126,2	1.37E-01 [25]	3.87E-05 [16]
Isopropanol			1.58E+00 [16]	1.11E-04 [16]
Cyclododecanone oxime	3.20E+06 [26]	823 [17]	6.17E+00	2.67E-04
Lauro lactam	2.80E+06 [17]	920 [17]	8.82E+00	3.41E-04

view of this property it was expected that at higher reaction temperatures the selectivity should decrease. Fig. 7 shows the selectivity as function of the TOS at different temperatures. Surprisingly, higher temperatures did result in a deterioration of the selectivity.



**Fig. 7.** Selectivity as function of TOS at different temperatures. Catalyst: 3.0 g dealuminated [Al]-BEA (BEA5), system pressure: 50 mbar, WHSV: approx. 0.1 g<sub>oxime</sub> g<sub>catalyst</sub><sup>-1</sup> h<sup>-1</sup>, carrier gas: 3.5 Nl/h N<sub>2</sub>.



**Fig. 6.** Conversion as function of TOS (time on stream) at different temperatures. Catalyst: 3.0 g dealuminated [Al]-BEA (BEA5), system pressure: 50 mbar, WHSV: approx. 0.1 g<sub>oxime</sub> g<sub>catalyst</sub><sup>-1</sup> h<sup>-1</sup>, carrier gas: 3.5 Nl/h N<sub>2</sub>.

ity. On the contrary, the selectivity improved at a temperature of 250 °C. Even at 300 and 350 °C, selectivities of more than 98% could be obtained. The reason for this is the very short residence time of less than a second in the reactor system. After the flash evaporation of the oxime, the reaction gas entered the catalyst fixed bed immediately, where the substrate was rearranged to lauro lactam. Without any catalytic influence, the thermodynamically preferred decomposition would take place.

The most important advantage of high temperatures is the much better desorption of the products from the active sites. Fig. 8 shows the material accumulation curves at different temperatures. The strongest hold-up was clearly at temperature around 200 °C. During the first 180 min TOS almost 100 wt% of the fed material remained in the system. When the temperature was increased to 250 °C, only 45 wt% were held up within the first hour, and from 180 to 360 min TOS approx. 20 wt% remained in the fixed bed. At 300 °C, 10–15 wt% were accumulated and this value is in the error range of the measurement. At a temperature of 350 °C the hold-up increased again slightly to approx. 20 wt%. At this state probably compounds of a high molecular weight were formed on the surface, which could not be removed easily anymore.

An interesting issue was the by-product composition at different reaction temperatures (Fig. 9). At 200 °C cyclododecanone was formed. The long residence times favored the formation of the ketone. When the temperature was increased to 250 °C, no more cyclododecanone formation could be detected, and only a small amount of new unknown compounds were found. Higher reaction temperatures again favored the formation of cyclododecanone

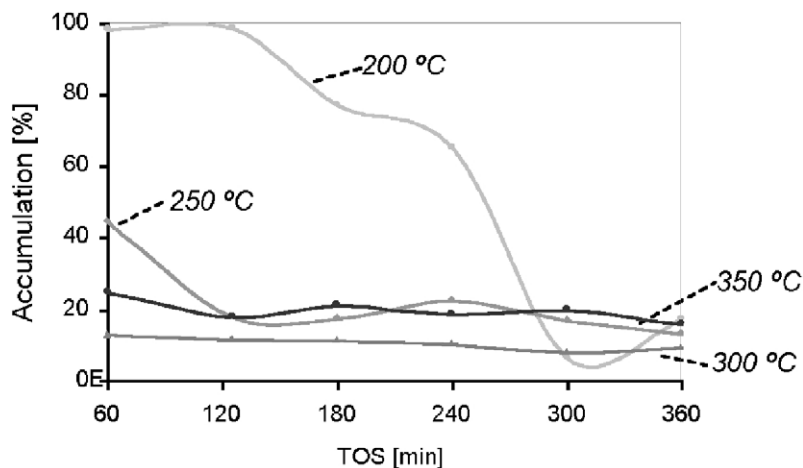


Fig. 8. Material accumulation as function of TOS at different temperatures. Catalyst: 3.0 g dealuminated [Al]-BEA (BEA5), system pressure: 50 mbar, WHSV: approx.  $0.1 \text{ g}_{\text{oxime}} \text{ g}_{\text{catalyst}}^{-1} \text{ h}^{-1}$ , carrier gas: 3.5 Nl/h  $\text{N}_2$ .

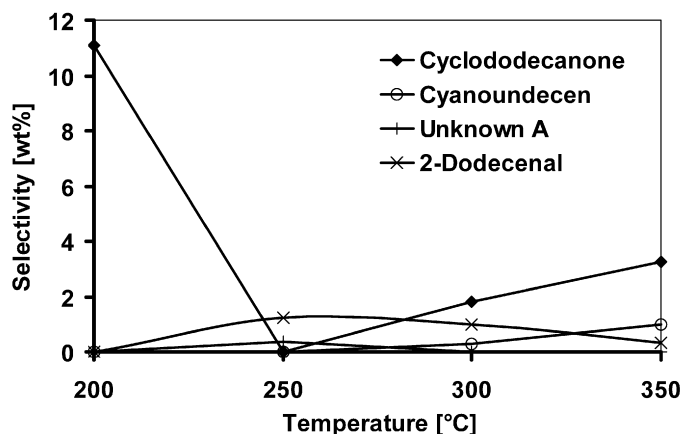


Fig. 9. By-product composition at different reaction temperatures. Catalyst: 3.0 g dealuminated [Al]-BEA (BEA5), system pressure: 50 mbar, WHSV: approx.  $0.1 \text{ g}_{\text{oxime}} \text{ g}_{\text{catalyst}}^{-1} \text{ h}^{-1}$ , carrier gas: 3.5 Nl/h  $\text{N}_2$ .

and the consecutive reaction of cyclododecanone to 2-dodecenal. In addition the ring opening to cyanoundecene was increasingly detected at temperatures of 300 °C and higher. This olefin has the tendency to polymerize easily.

### 3.3.2. Pressure effect

A dealuminated [Al]-BEA (BEA2) material treated with  $\text{HNO}_3$  and a Si/Al-ratio of 434 (after the regeneration tests) was used to study the influence of the pressure. Fig. 10 shows the conversion and the selectivity as function of the system pressure and corresponding partial pressure of cyclododecanone oxime and lauro lactam.

The selectivity to lauro lactam is strongly influenced by the pressure. At a partial pressure lower than 0.1 mbar lauro lactam is formed almost exclusively. With increasing system pressure, and with it partial pressure, the selectivity decreased to approx. 30% at about 1000 mbar. Low pressure facilitates desorption of the formed products from the active sites, resulting in higher selectivity. Another sign of a better desorption is the high production of ring-opening products and faster deactivation of the catalyst at higher system pressures, which is characteristic for long residence times on the acid sites and polymerization of the ring opening products such as cycloundecene.

### 3.4. Catalyst screening

For the screening tests quite a number of catalysts were chosen in addition to the very active zeolites with BEA structure. Since it

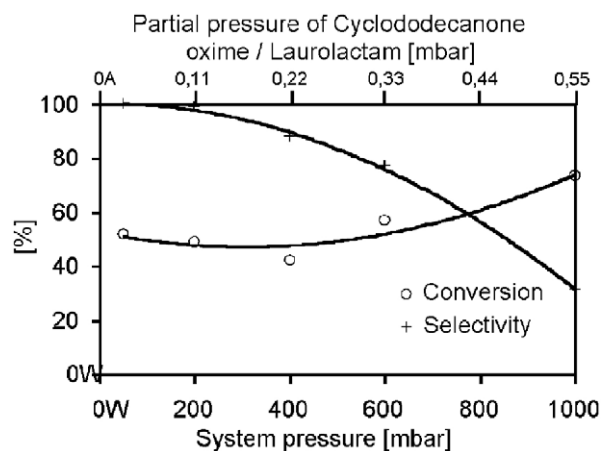
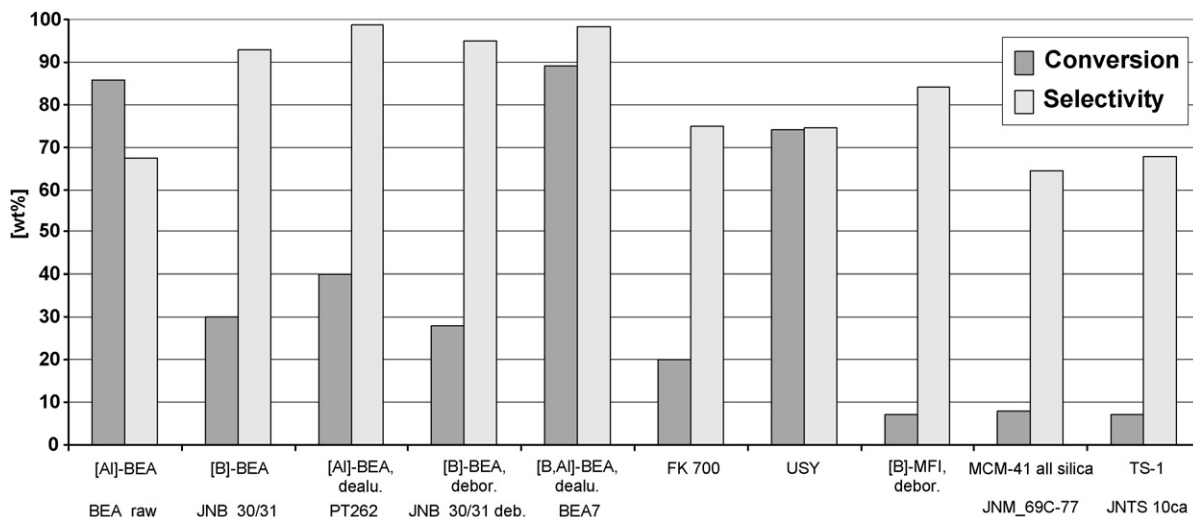


Fig. 10. Influence of the pressure on the conversion and the selectivity. Catalyst: 1.0 g dealuminated [Al]-BEA (BEA2). Reaction temperature: 300 °C, WHSV: approx.  $0.3 \text{ g}_{\text{oxime}} / (\text{g}_{\text{cat}} \text{ h})$ , carrier gas: 3.5 Nl/h  $\text{N}_2$ .

was known that in the gas phase rearrangement of cyclohexanone oxime to caprolactam delocalized silanol groups, especially silanol nests, are the catalytically active sites that catalyze the reaction very well, particular focus on silanol rich materials was taken [7]. Fig. 11 shows some selected results of the screening test.

The material providing highest selectivity for the rearrangement of cyclododecanone oxime to lauro lactam in the gas phase is



**Fig. 11.** Activity of different types of zeolitic and non-zeolitic catalysts under standard conditions. Reaction temperature: 325 °C, system pressure: 50 mbar, WHSV: approx. 0.3 g<sub>oxime</sub>/(g<sub>cat</sub> h), carrier gas: approx. 3.5 NI/h N<sub>2</sub>.

the dealuminated [Al]-BEA zeolite (Si/Al-ratio: 260) [PT262]. Even though the non-dealuminated BEA (Si/Al-ratio: 13.4) [BEA\_raw] led to higher conversion, the acid treated variation is much more interesting due to its excellent selectivity (see Fig. 11, PT262). The Brønsted acid sites of the [Al]-BEA [BEA\_raw] are so strong at standard reaction conditions (325 °C), thus side reactions occur. The main by-product formed during the reaction was the ring-opening product cyanoundecene. Weaker acid sites are much more selective, and with the right setup the highest yield could be achieved. Surprisingly, deboronated [B]-BEA zeolite (Si/B-ratio: approx. 700) [JNB\_30/31 deb. =Catalyst D deb.] is not that selective, although it carries a similar silanol structure on the surface and the same pore structure.

The Brønsted acid sites of USY with a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>-modul of 28 are too strong. As for the non-dealuminated [Al]-BEA [BEA\_raw], the selectivity is lower than in the case of dealuminated [Al]-BEA [PT262] and the formation of cyanoundecene is observed.

Of interest was the behavior of the [B]-MFI in the rearrangement reaction of cyclododecanone oxime, as this zeolitic catalyst results in excellent performance for the reaction of cyclohexanone oxime to caprolactam [6,7]. However, the reaction tests have shown only a weak activity of this zeolite catalyst in the lauro lactam formation. Only 8% of cyclohexanone oxime was converted with a moderate selectivity of 85% to ω-lauro lactam. In case of the bulkier cyclododecanone oxime, the pore opening could not be entered and furthermore, no pore mouth selectivity as in the case of ε-caprolactam [7] could take place. Therefore, only some reaction occurred on the outer crystal surface.

The simplest catalyst is amorphous silica (FK700) without any zeolitic pore structure, but with a huge amount of silanol groups on the surface. The activity is comparatively weak. Only 20% of the oxime was converted and a selectivity of only 75% was observed even though terminal and geminal silanol groups were present, but those do not catalyze the rearrangement very well, as is also known for the ε-caprolactam production.

MCM-41 is characterized by a distinctive mesopore system. The substrate can therefore enter the pore system easily. Nevertheless, the catalytic performance of Catalyst A (=JNM\_69C-77) is poor. Only 8% of the oxime were converted with a low selectivity of just 65%. The silanol configuration on the surface is similar to the one of amorphous silica, because the MCM-41 (all silica) was not treated after the synthesis like the active [Al]-BEA, and hence none of the catalytically highly active defect sites were introduced into the framework.

The titanium-silicalite 1 (TS-1, Catalyst B), which contains Lewis-acid sites on its surface was also tested. At standard conditions the activity was poor. The conversion was lower than 10% and the selectivity was less than 70%. Remarkable in this context is the increasing activity at higher reaction temperatures. Not only the conversion could be improved, but the selectivity increased as well. At a reaction temperature of 375 °C the conversion increased to 25% and a selectivity of 90% was obtained.

In summary it can be said that BEA zeolite is the most promising catalyst due to its excellent selectivity for the rearrangement of cyclododecanone oxime to lauro lactam. Therefore, several modifications of BEA zeolite have been carried out and the catalytic performance of those modified materials was investigated.

### 3.5. Catalyst modification

#### 3.5.1. Post synthesis treatment of [Al]-BEA zeolite

The dealumination treatment significantly influenced the catalytic activity of BEA zeolite catalysts in the Beckmann-rearrangement of cyclododecanone oxime to ω-lauro lactam. Several structural analyses were carried out to get more information about the active sites. Fig. 12 shows the IR bands in the range between 3800 and 3600 cm<sup>-1</sup>. The starting [Al]-BEA zeolite has two intensive bands at 3741 and 3734 cm<sup>-1</sup> and two weak signals at 3615 and 3781 cm<sup>-1</sup>. Kirisci et al. reported that the small peak at 3615 cm<sup>-1</sup> is the result of bridged hydroxyl groups of framework alumina [25, 26]. The species were assumed to have a very strong acidity. The same group gives an explanation for the intensive bands at 3741 and 3734 cm<sup>-1</sup> with the shoulder up to 3741 cm<sup>-1</sup>. This area is related to internal and external terminal silanol groups with comparatively weak Brønsted acidity. The band at 3781 cm<sup>-1</sup> is called the “very high frequency”-band. Löffler et al. [27] and Kustov et al. [28] report that these species are terminal Al-OH groups with medium acidity.

Due to the acid treatment using HNO<sub>3</sub>, framework and extra framework alumina species were removed. This work was carried out by the group of F. Jajula. The variations PT271 and PT262 are [Al]-BEA zeolites treated to a different extent, by leaving the catalyst twice the time in the HNO<sub>3</sub>-solution. Their spectra are also shown in Fig. 12. The bands at 3615, 3781 and 3673 cm<sup>-1</sup> are removed completely or alternatively covered by the broad band between 3300 and 3700 cm<sup>-1</sup>. According to Jia et al. and our own results [7,29], this expanded peak is the result of a high concentration of silanol nests, formed during the acid treatment, when



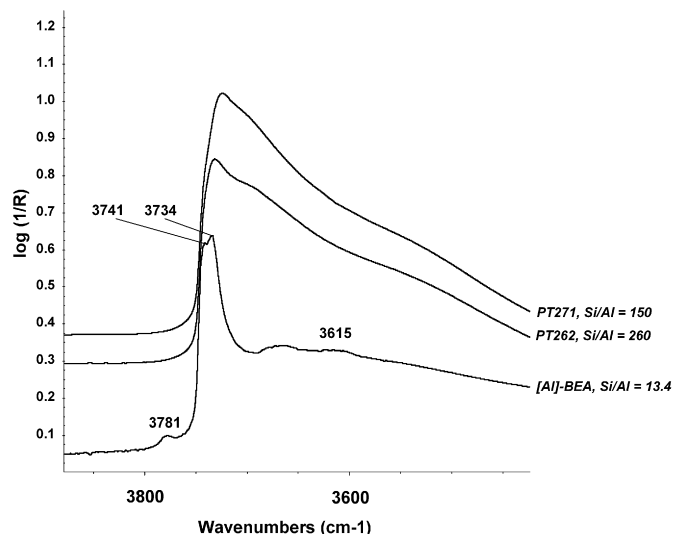


Fig. 12. FTIR-spectra of the non-dealuminated [Al]-BEA and two dealuminated (PT271, PT262) BEA zeolites.

Table 3  
Band allocation of the adsorbed pyridine.

Band position [cm <sup>-1</sup> ]	Adsorbed species	Acid site character
1635	Pyridine ion	Brønsted
1621	Pyridine	Lewis
1576	Pyridine	Lewis
1545	Pyridine ion	Brønsted
1490	Pyridine and pyridine ion	Lewis and Brønsted
1455	Pyridine	Lewis
1397	Pyridine ion	Brønsted

T-atoms were removed from the framework and defects have been created.

With the help of pyridine adsorption during the FTIR measurement, it is possible to get detailed information about the character of the acid sites. The method is discussed intensely in the Literature. The report of Creighton et al. [30] provides a good overview of the acid character of the adsorbed pyridine species. The respective band positions are specified in Table 3.

The results of the FTIR measurements with pyridine adsorption for the already mentioned BEA zeolites [Al]-BEA, PT271 and PT262 are shown in Fig. 13. The peak at 1545 cm<sup>-1</sup> is a characteristic signal for the type of acidity. It represents the pyridine ion attached to strong Brønsted acid sites. The disappearance of this peak gives evidence that the newly created material lost strong Brønsted acidity during the acid treatment. However, next to the Lewis acid sites weak Brønsted acidity is still left, as can be seen by the slight band at 1635 cm<sup>-1</sup>.

With the help of NH<sub>3</sub>-TPD measurements, the acidic strength and the density of the acid sites on the zeolite can be determined. Therefore the non-dealuminated [Al]-BEA and the differently HNO<sub>3</sub> treated e.g. dealuminated PT271 and PT262 were investigated with this method (see Fig. 14). All three catalysts revealed a distinctive peak at approx. 280 °C, indicating weak acidic sites. Additionally, the starting [Al]-BEA shows a second NH<sub>3</sub>-desorption at 450 °C, indicating that this material has also strong acid sites in addition to weaker ones. At temperatures of 280 °C the ammonia was desorbed from the weakly acidic silanol groups [31,32] and at higher temperatures of approx. 450 °C the ammonia desorbed from the stronger acidic hydroxyl groups of the Brønsted acid alumina species. In the case of PT271 and PT262 the high temperature peak disappeared completely. That means that only weakly acidic sites remained.

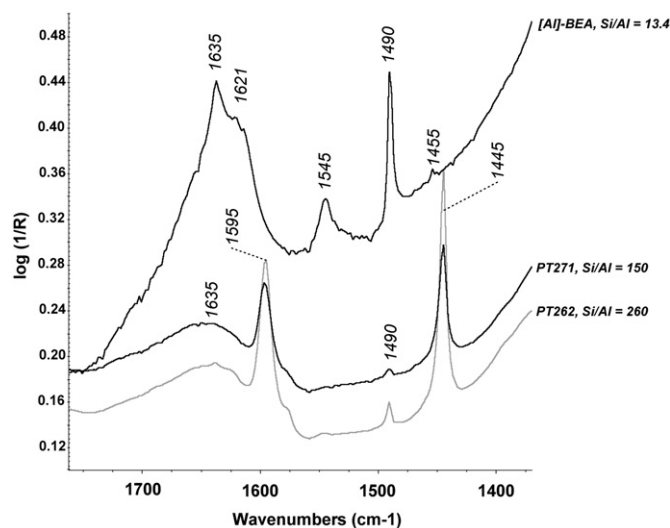


Fig. 13. FTIR spectra after pyridine adsorption and 60 min desorption at 150 °C and 10<sup>-2</sup> mbar.

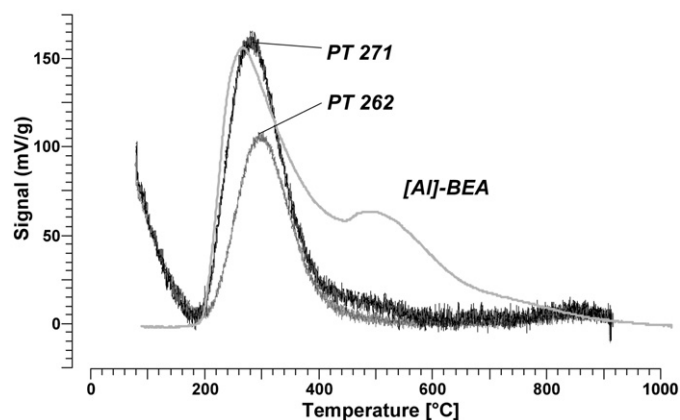


Fig. 14. Temperature programmed desorption of ammonia of the raw material and the two dealuminated variations.

The peak area is a direct indicator for the density of acid sites. By integrating this peak area, the amount of adsorbed ammonia can be determined. In the case of the raw material BEA<sub>raw</sub>, 670 μmol/g<sub>cat</sub> at 280 °C and 414 μmol/g<sub>cat</sub> were desorbed at 450 °C. For the material PT262 402 μmol/g<sub>cat</sub> and for PT271 690 μmol/g<sub>cat</sub> were desorbed at 280 °C and no further NH<sub>3</sub> desorption was detected at higher temperatures.

Finally, these materials were tested for their catalytic activity. Fig. 15 illustrates conversion, selectivity and accumulation of reactants in the fixed bed as function of Si/Al-ratio of the tested catalysts. Furthermore, the amount of adsorbed ammonia in TPD-measurements is shown. For the reaction the standard conditions at 325 °C and 50 mbar were used.

As previously discussed, the dealumination treatment has a crucial influence on catalyst performance. Even if the conversion of cyclododecanone oxime drops with increasing Si/Al-ratio, the selectivity increased to an excellent level of almost 100%. The second crucial advantage is the reduced reactant accumulation of the catalyst, which is associated to a faster deactivation of the catalyst. Strong Brønsted acidic sites of alumina species are responsible for the formation of by-products, especially the ring opening to cyanoundecene, which has high polymerization tendency.

When T-bonded alumina sites were removed from the BEA framework, highly selective silanol nests remained on the surface, which were of only extremely weak Brønsted acidity. Such sites

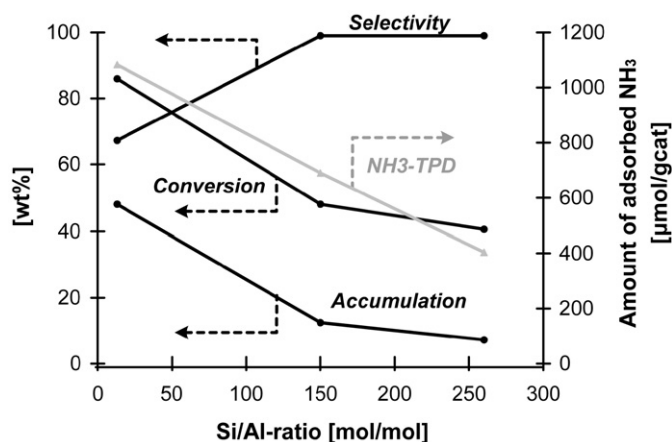


Fig. 15. Conversion, selectivity and reactant accumulation in catalyst bed as function of the Si/Al-ratio and the amount of adsorbed ammonia (TPD-measurement) at standard reaction conditions.

Table 4

Results of the ICP- and NH<sub>3</sub>-TPD-measurement of the zeolites PT262, PT313, BEA7 and [B]-BEA (Catalyst D).

Catalyst	Si/Al-ratio, Si/B-ratio [mol/mol]	Amount of adsorbed NH <sub>3</sub> [μmol/g <sub>cat</sub> ]
[Al]-BEA (PT 262)	260, –	402
[Al,B]-BEA (PT 313)	320, 45	351
[Al,B]-BEA (BEA7)	260, 37	437
[B]-BEA (Catalyst D)	Approx. 1500, 32	915

catalyzed the rearrangement in a superb manner. Due to the acid treatment, the hard accumulation of reactants was reduced to a minimum level.

### 3.5.2. Boron containing BEA zeolites

Other interesting catalysts in this context were boron-containing BEA zeolites. Instead of alumina, boron oxide was incorporated into the framework. To remove the T-sites, less aggressive treatment was sufficient compared with the treatment in the case of [Al]-BEA zeolites. During the deboronation procedure silanol nests were created in the framework, as it was found by the Hoelderich et al. for the [B]-MFI Zeolite used in the Beckmann rearrangement of cyclohexanone oxime to  $\epsilon$ -caprolactam [7].

For the experiments three types of BEA zeolites were prepared and applied. These materials have different fractions of boron oxide and alumina introduced into the framework. Zeolites were slightly dealuminated, or rather deboronated, and analyzed by ICP, pyridine-FTIR, NH<sub>3</sub>-TPD. In the case of the pyridine-FTIR of these samples no signal at 1545 cm<sup>-1</sup> was detected. That means that the strong Brønsted acidity of the strong active hydroxyl groups from the alumina species was lowered to an insignificant level. The results of the ICP and NH<sub>3</sub>-TPD-measurement are shown in Table 4.

The dealuminated [Al]-BEA PT 262, which was already discussed in Section 3.5.1, is compared with the boron-containing materials. The PT 313 and the BEA7 were [Al,B]-BEA zeolites differently treated with HNO<sub>3</sub> according to the method of Des Courieres et al. [15]. The longer the residence time in the treatment solution, the less alumina and boron oxide species remain in the structures. The [B]-BEA is almost alumina free.

PT262, PT313 and BEA7 desorbed during the NH<sub>3</sub>-measurement 402, 352 and 437 μmol/g<sub>cat</sub>, respectively. The [B]-BEA has a significantly higher amount of desorbed ammonia indicating a higher density of active sites. Thus, this BEA was supposed to show the best catalytic performance.

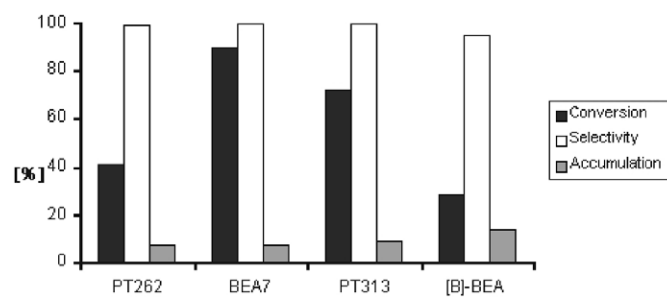


Fig. 16. Activity of boron containing BEA zeolites at standard conditions.

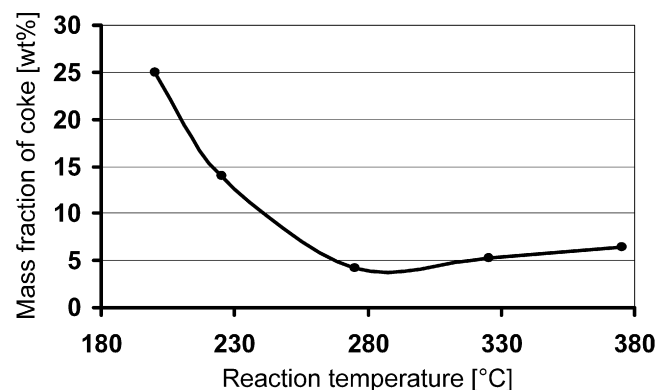


Fig. 17. Mass fraction of coke to catalyst after 8 h TOS at different reaction temperatures and under standard conditions.

In Fig. 16 the results of the reaction tests are shown. Surprisingly, the [B]-BEA showed the poorest catalytic performance among these 4 boron containing BEA zeolites with a selectivity of approximately 95%, a conversion of less than 25% and the highest accumulation of the reactants and products.

The performance of the other three catalysts was much better. The selectivities are at a high level of almost 100%. The most remarkable attribute is the sharply increased conversion of PT313 and especially of BEA7. Using these BEA zeolites the conversion more than doubled without any influence on selectivity and on the accumulation of the reactants and products. The reason for the excellent performance could not be determined yet, but the catalytic effect on the rearrangement was remarkable.

### 3.6. Deactivation/regeneration

Long-term reaction test have shown that the catalysts are strongly deactivated after approx. 8 h time on stream under standard reaction conditions. After these 8 h the amount of organic compounds were measured with thermogravimetric analysis. Fig. 17 shows the mass fraction of organic compounds adsorbed on the catalyst or polymer compounds or coke blocking the active sites of the zeolitic catalyst at different reaction temperatures.

At lower reaction temperatures the catalyst adsorbed high amounts of organic substances. Desorption test have shown that these residues were mainly substrate and product adsorbed on the catalyst. At approx. 300 to 320 °C a minimum of less than 5 wt% material hold up was detected and due to this the highest yield of lauro lactam could be obtained. At this point the optimum conditions for the gas phase reaction were achieved and the formation of so-called white coke, oligomers of lauro lactam was reduced due to depolymerization.

For the regeneration of the catalyst two pathways are possible: oxidative and non-oxidative removal of the deactivating compounds.

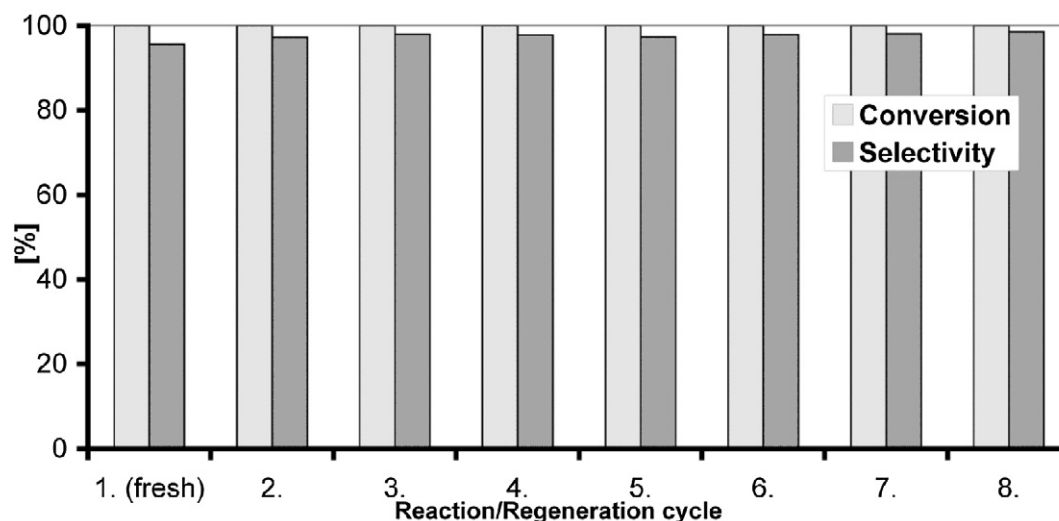


Fig. 18. Activity of a dealuminated [Al]-BEA (PT326/328) during 8 reaction cycles (standard reaction conditions) with intermediate oxidative regeneration.

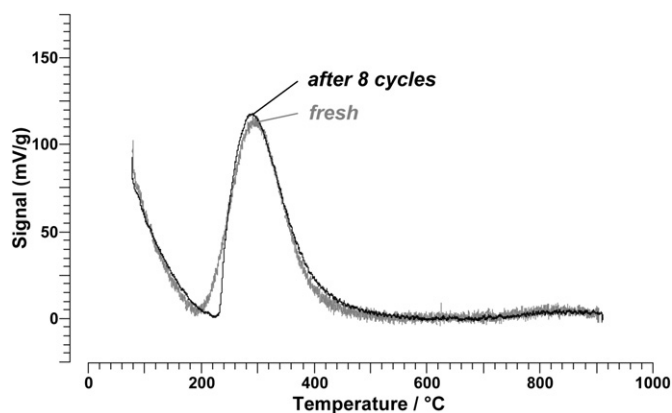


Fig. 19.  $\text{NH}_3$ -TPD measurements of fresh BEA and after 8 reaction/regeneration cycles.

The standard regeneration with air was carried out at below  $550^\circ\text{C}$  for approx. 12 h. After this treatment all catalysts used recovered their complete initial activity. To observe the regenerability of the dealuminated [Al]-BEA rich in silanol groups with a Si/Al-ratio of approx. 531, eight cycles of reaction with intermediate regeneration under oxidative conditions were carried out (Fig. 18).

These reaction tests have shown that the activity of the catalyst did not drop through the stress of this treatment. Selectivity and conversion stay on the high level of almost 100%.

Before and after this treatment the catalyst was investigated with ICP-AES, BET, XRD and  $\text{NH}_3$ -TPD to determine the physical structure and the surface morphology of the zeolite.

The ICP AES analysis showed the same Si/Al-ratio of approx. 531 for both samples. Therefore, a further dealumination of the catalyst could not be observed. This assumption is supported by the  $\text{NH}_3$ -TPD (Fig. 19) measurement. Both catalysts have shown the same signal at  $280^\circ\text{C}$  with the same amount of adsorbed ammonia (approx.  $420 \mu\text{mol}/g_{\text{cat}}$ ), confirming that the kind and the number of acid sites did not change during the tests.

Also the zeolitic structure was stable. The XRD analysis (Fig. 20) showed that the characteristic signal of BEA-structures [33] at  $2\theta = 7.8^\circ$  and  $22.4^\circ$  did not change. Especially the signal at  $22.4^\circ$  is a typical sign of the crystallinity of the zeolite [34]. Another structural analysis was carried out via  $\text{N}_2$ -BET-surface measurement of the fresh and the used BEA (Fig. 21). The distribution of

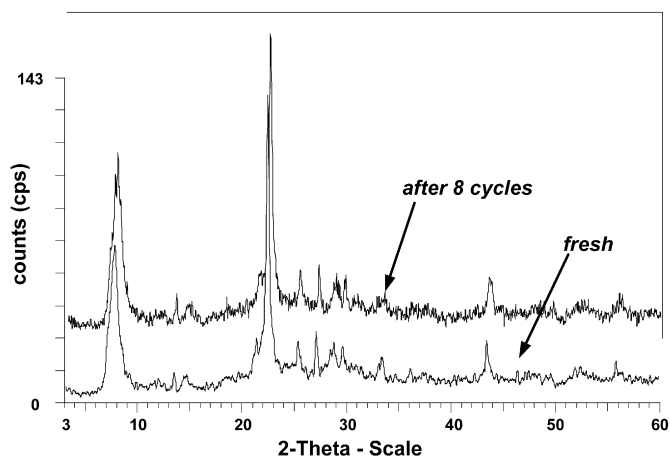


Fig. 20. XRD measurements of fresh BEA and after 8 reaction/regeneration cycles.

the micro- and the mesopores did not change and the BET-surface stayed at  $520 \text{ m}^2/\text{g}$ .

Within the scope of these investigations, the dealuminated BEA is stable over the regeneration treatments under oxidative conditions. No loss of activity, no changes of the surface morphology and zeolitic structure were observed.

The second regeneration pathway is the regeneration under inert conditions (here under  $\text{N}_2$ -atmosphere). The advantage could be a smoother regeneration, without “burning” of the organic compounds from the catalyst, to avoid hot spots and a possible long-time deactivation due to silanol condensation. Because of the limited number of reaction/regeneration cycles, a weak silanol condensation was not detected. Hence the same test series as for air-regeneration was done under nitrogen atmosphere, where the deactivating compounds were removed through thermal desorption from the catalyst surface.

Fig. 22 shows the results of the activity test. Conversion and selectivity remained high even after the eighth regeneration cycle under nitrogen.

To make sure that all deactivating compounds were removed from the surface, the regenerated BEA was analyzed by TG (Fig. 23). Up to a temperature of  $150^\circ\text{C}$  large amounts of water, which were adsorbed during the preparation for the measurement, were desorbed. In the interesting temperature interval between  $200$  and  $600^\circ\text{C}$  no significant loss of mass was detected. The loss of mass at temperatures higher than  $600^\circ\text{C}$  was caused by the

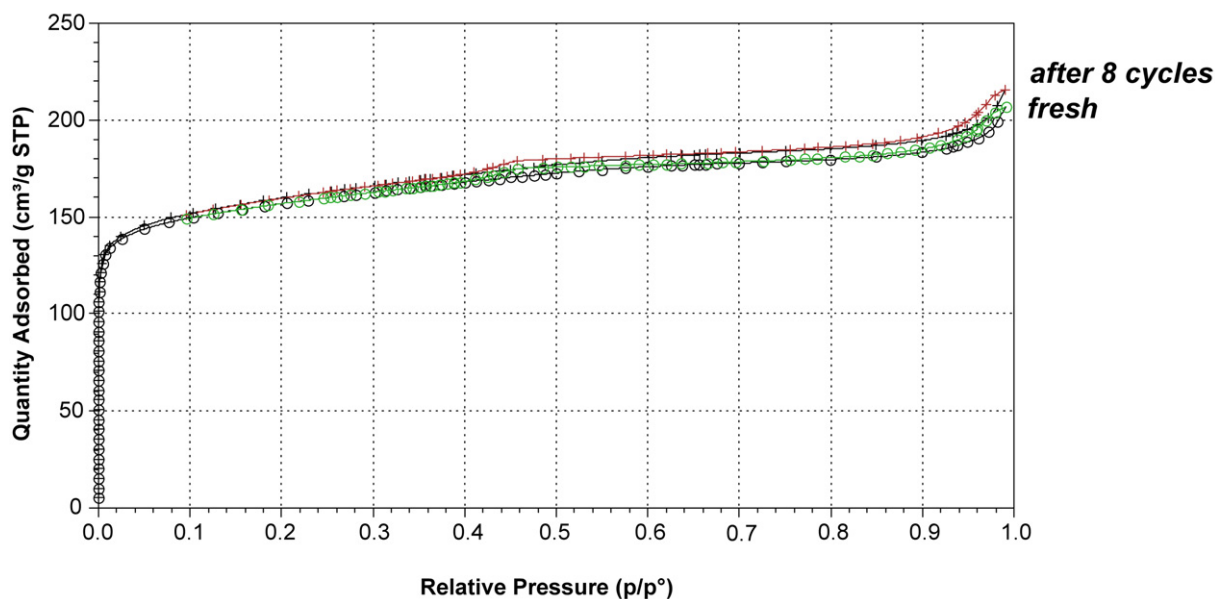


Fig. 21. BET measurements of fresh BEA and after 8 reaction/regeneration cycles.

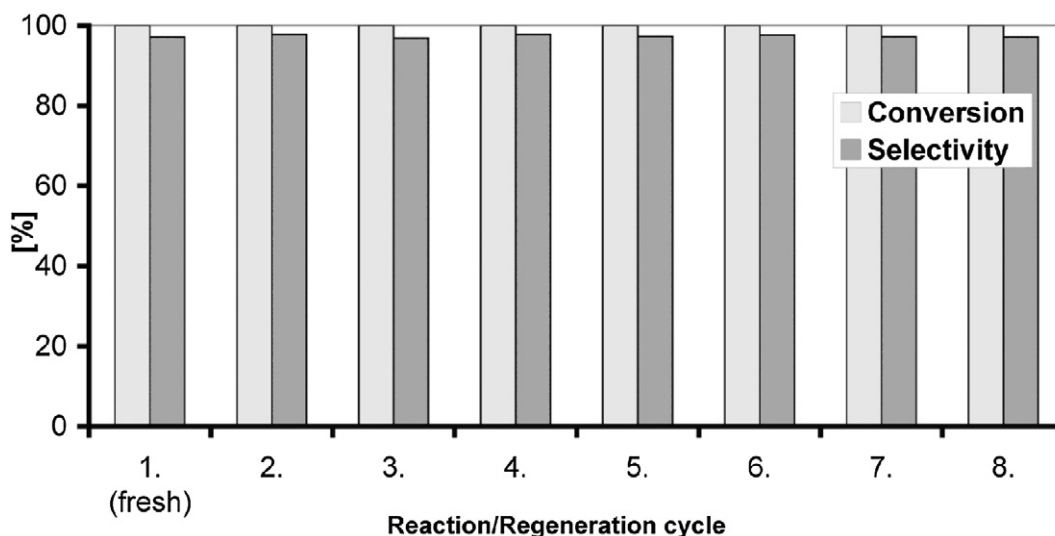


Fig. 22. Activity of a dealuminated [Al]-BEA (PT326/328) during 8 reaction cycles (standard reaction conditions) with intermediate non-oxidative regeneration.

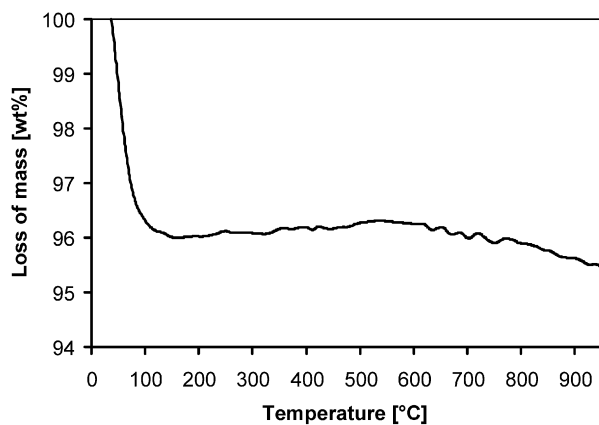


Fig. 23. TG analysis of a catalyst regenerated under nitrogen atmosphere.

typical condensation of silanol groups of the BEA zeolite. The evidence was that through nitrogen regeneration the catalyst could

be reactivated in the same way as with the standard oxidative regeneration.

In addition to the different load of deactivating compounds at various reaction temperatures, Fig. 24 shows the influence of the regeneration gas. A catalyst used in the reaction at 200 °C is mainly blocked due to the product formed. As already mentioned, these substances could be removed through oxidation or desorption at high temperatures.

No significant difference of both 325 °C-curves between nitrogen and air regeneration can be seen.

#### 4. Conclusions

The aim of the present work was the investigation of the possibility of gas phase rearrangement of cyclododecanone oxime to lauro lactam over solid acid catalysts. To prove that all reactants were in the gaseous state, vapor pressure measurements and theoretical calculations using incremental methods were carried out.

To study the catalytic performance a fixed bed reactor system was chosen to screen different types of solid acids. The reaction



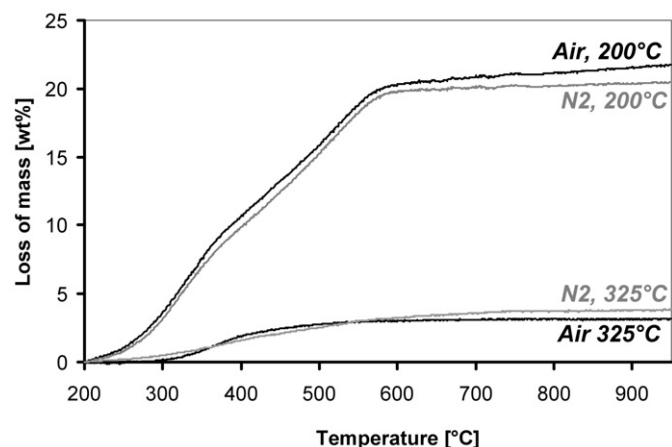


Fig. 24. Thermogravimetric analysis under air and nitrogen atmosphere of two catalysts used at different reaction temperatures (200 and 325 °C).

tests have shown that BEA zeolite has the most promising structure. Thus, the investigations focused on this material. The starting material [Al]-BEA showed strong catalytic activity, but due to the strong Brønsted acidity, the formation of ring opening products such as cyanoundecene was preferred. Consequently the selectivity was low. By modifying the BEA zeolite with post-synthesis acid treatment, the alumina T-sites were removed from the BEA framework, defects have been created and less Brønsted acidic sites remained on the catalyst surface. Structural analysis with the help of ICP,  $\text{NH}_3$ -TPD and pyridine-FTIR have shown that delocalized silanol groups were generated. Modified BEA zeolite catalysts yielded far better performance. The conversion decreased slightly, but the selectivity increased to an excellent level of almost 100% in combination with a minimized accumulation of reactants and products on the catalyst.

Remarkable are the results with boron containing BEA zeolites. Using a dealuminated [Al,B]-BEA the conversion was more than doubled with the same excellent selectivity and a minimum accumulation. The BEA zeolite named BEA7 in the present work showed the best catalytic activity.

In addition to the catalyst, the reaction conditions were investigated. The reaction temperature has a crucial influence on the adsorption and desorption process of the catalyst. At low reaction temperatures of less than 250 °C, the formed products could not be desorbed and the catalyst deactivated very fast. Consequently the yield decreased rapidly after short reaction times. At higher reaction temperatures this phenomenon disappeared. 325 °C turned out to be the optimum reaction temperature. At this point excellent selectivities with a minimum accumulation in the fixed bed were detected. It should be mentioned that the reactor setup is quite important. Due to instable behavior of the cyclododecanone oxime at temperatures higher than 130 °C, the residence time of the substrate in the hot reaction zone had to be minimized. The solution is a flash evaporation of the dissolved substrate in the reactor system. Thereby residence times of less than 1 s could be achieved and the thermal decomposition to cyclododecanone, which is thermodynamically preferred, was prevented.

Furthermore, a closer look was taken at the influence of the partial pressure on the reaction. Low pressures are of advantage. Using substrate partial pressures lower than 0.1 mbar, which corresponds to 200 mbar system pressure at standard reaction conditions, supported the desorption of the formed lauro lactam and the selectivity increased.

Finally, the deactivation and regeneration behavior was investigated. At lower reaction temperatures of less than 200–250 °C the formed product is mainly responsible for the deactivation, due to its strong adsorption on the surface of the catalyst. At temper-

atures above 250 °C more and more lauro lactam polymerized to oligomers—the so-called “white coke”—which is additionally blocking the active sites. Both compounds could be removed with an oxidative regeneration at 550 °C. Eight reaction cycles with intermediate regeneration have shown that the BEA zeolite is completely regenerable without any loss of its catalytic activity. Another interesting pathway is the non-oxidative regeneration under nitrogen atmosphere at 550 °C, where the deactivating compounds are removed through thermal desorption, which is the more gentle treatment due to the prevention of hot-spots. Even here the catalyst could be reactivated completely. Thermogravimetric analyses have shown that no residues were left on the catalyst surface after regeneration with nitrogen.

For the Beckmann rearrangement of cyclododecanone oxime to  $\omega$ -lauro lactam zeolite catalysts have been used only in liquid reaction systems so far. The disadvantages of this process are the strong deactivation of the catalyst, the comparatively difficult regeneration of the catalytic material and the high technical effort caused by this. From a process technical point of view, a gas phase rearrangement is the far better solution. A broad range of different reactor systems is available. The results have shown that the catalytic performance in the gas phase is excellent. Even in the standard fixed bed reactor, selectivity and conversion of almost 100% in combination with a minimum reactant accumulation were achieved. Thus, for a large-scale use, the route of a gas phase reaction system should be chosen.

#### Acknowledgments

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