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Active Sites of a [B]-ZSM-5 Zeolite Catalyst for the Beckmann Rearrangement of Cyclohexanone Oxime to Caprolactam

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[B]-ZSM-5 is a very active and selective catalyst for the vapor-phase Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam with high selectivities of up to 95% at 300°C and 100 mbar at complete initial conversion. The nature of the catalytically active sites on [B]-ZSM-5 was determined by investigating the influence of postsynthesis modifications, e.g., calcination under air, acid/base treatment, and hydrothermal treatment on the selectivity. Using FT-IR various hydroxyl groups and silanol nests on the surface of the [B]-ZSM-5 zeolites were found to be the active sites for the Beckmann rearrangement. Further investigations concerned the negative effect of adsorbed water on [B]-ZSM-5, which led to a decrease of its catalytic activity. This effect was shown to be reversible and could be explained with the hydration of boron oxide species on the surface. Experiments with as-synthesized and already calcined [B]-ZSM-5 showed the influence of the boron oxide species, which enhanced the conversion compared to the material without extraframework boron from 70% to 98%. © 2000 Academic Press

Key Words: **cyclohexanone oxime; ε-caprolactam; [B]-ZSM-5 zeolite; FT-IR; postsynthesis modification; hydroxyl groups; water adsorption.**

INTRODUCTION

As an intermediate for nylon-6, caprolactam is of high industrial importance. For the industrial bulk production of ε-caprolactam, concentrated sulfuric acid or oleum is used as a catalyst, resulting in the production of large quantities of ammonium sulfate. To avoid these well-known problems of this homogeneously catalyzed Beckmann rearrangement, research is ongoing to produce the lactam over heterogeneous catalysts. Thus far, results on the use of silica–alumina (1), boron oxide on various carriers (2–5), tantalum oxide (6), and several different zeolites including faujasites (7, 8), ZSM-5 (9), and Beta (10) have been published. Hölderich (11–14) presented several surveys on the heterogeneously catalyzed Beckmann rearrangement.

Recently, our group reported on the excellent catalytic performance of [B]-ZSM-5 in this reaction (15). Vapor-phase experiments were carried out in a fixed bed reactor using ethanol as the solvent for the oxime. Whereas in the literature typical reaction conditions are 350°C and 1 bar, it could be shown that especially a reduction of the reaction pressure led to a significant increase of the selectivity to caprolactam. At 300°C and 0.1 bar, selectivities of up to 95% were obtained. The addition of up to 6 mol of water/mol of oxime to the reaction mixture increased the conversion rate and increased the catalyst service time.

From FT-IR measurements it can be concluded that on siliceous catalysts like amorphous silica and crystalline silicalites hydroxyl groups are responsible for the Beckmann rearrangement (16). Especially silanol nests on the external surface of a silicalite-1 are most favorable, mainly due to their comparably weak acidity and their particular arrangement on the MFI structure. [B]-ZSM-5 is also likely to have these hydroxyls on defect sites. With respect to catalytically active sites, it could be shown by temperature-programmed desorption (TPD) (17) that [B]-ZSM-5 contains a large amount of weak acidic sites. As the framework boron of the [B]-ZSM-5 is not strongly incorporated (18–20), these sites are formed upon extraction of the boron from the lattice. Calcination under air is an effective tool for this boron removal, but other postsynthesis modifications, like acid/base or hydrothermal treatments, can also be applied. The deboronation procedure can be compared with the well-investigated dealumination of zeolites. To avoid extraction of framework boron, Kuehl (21) suggested the complete removal of water as well as oxygen from the calcination atmosphere and recommended the use of ammonia instead. De Ruiter (22) proposed a calcination route, which minimized the boron extraction during the removal of the template after the synthesis of [B]-ZSM-5. This method combines the positive effect of the calcination under an ammonia atmosphere with an ion exchange of the zeolite with sodium followed by a final calcination under oxygen (23–25). Here, we would like to report on the nature of the active sites when using [B]-ZSM-5 in the Beckmann rearrangement and the influence of several different postsynthesis treatments on these sites.

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METHODS

Catalyst

Preparation of [B]-ZSM-5. Boric acid (12.2 g) was added to 800 g of a 50 wt% aqueous solution of hexamethylenediamine while stirring, after which 64 g of SiO_2 (Aerosil-200) was added. The gel was autoclaved at 170°C at autogeneous pressure (stirring rate, 50 rpm). After 14 days, the crystals were separated, washed with distilled water, and dried at 110°C for 12 h. This initial material of [B]-ZSM-5 will be referred to as BZSM and was modified with several different methods.

The influence of the calcination temperature was investigated by calcining for 12 h under air at 300, 400, 550, and 600°C (heating rate, 2°C/min; for dehydration 120°C was kept for 1 h). The samples were denoted BZSM(300), BZSM(400), BZSM(550), and BZSM(600), respectively.

Acid treatments were done for 24 h by refluxing as-synthesized BZSM with aqueous hydrochloric acid solutions with concentrations of 2, 1, 0.1, and 0.01 M, thus obtaining BZSM(2 M), BZSM(1 M), BZSM(0.1 M), and BZSM(0.01 M). After the treatment, the zeolites were filtered, dried at 110°C for 4 h, and calcined in an air atmosphere at 550°C for 12 h (heating rate, 2°C/min).

For the basic treatments, 5 g of the as-synthesized zeolite was stirred in 20 g of a mixture of a 25 wt% aqueous ammonia solution and a 20 wt% aqueous ammonium nitrate solution. The ammonia concentration was varied by using three different weight ratios for the mixture of the ammonia solution and the ammonium nitrate solution. Therefore, according to the weight ratio *w*, the following modifications of the [B]-ZSM-5 zeolite were obtained: BZSM(3), BZSM(1), and BZSM(0.33). The procedure was carried out for 1 h in a stainless steel autoclave at 90°C under autogeneous pressure followed by a final treatment as described above.

Prior to hydrothermal treatment, the [B]-ZSM-5 was calcined at 550°C for 12 h in air (heating rate, 2°C/min). Subsequently, 3 g of the zeolite powder was treated with a water-saturated nitrogen flow (partial pressure, 4.7 kNm^{-2}) at 400, 500, and 600°C, obtaining the samples BZSM(H_2O-400), BZSM(H_2O-500), and BZSM(H_2O-600).

For the adsorption of water, calcined [B]-ZSM-5 pellets (0.5–1 mm) were evacuated over an oversaturated aqueous solution of ammonium nitrate for 6 weeks at room temperature obtaining BZSM(H_2O). A part of this BZSM(H_2O) was calcined at 550°C under air prior to its use as a catalyst in the rearrangement reaction and marked as reference material.

Additionally, the catalytic performance of silicalite-1, prepared according to Kitamura *et al.* (26), treated with triethyl borate was investigated. Silicalite-1 (5 g) was added to 5 g of an aqueous ammonia solution (25 wt%) and 15 g of an aqueous ammonium nitrate solution (20 wt%). The mixture was stirred at autogeneous pressure for 1 h at 90°C in a stainless steel autoclave. Subsequently, the material was washed, filtered, and dried at 110°C for 4 h. The chemical vapor deposition (CVD) with triethyl borate $B(OEt)_3$ was done according to Sato *et al.* (4, 27). Three grams of catalyst pellets (0.5–1 mm) was placed in the same fixed bed reactor used for catalytic experiments. Triethyl borate was dissolved in toluene (10 wt%) and a mass flow of 5 $g\,h^{-1}$ of this mixture was vaporized and fed through the reactor for 4 h, using air (5 $l\,h^{-1}$) as the carrier gas and oxidizing agent. The reaction temperature was varied between 250 and 400°C, yielding four catalysts: Sil(B-250), Sil(B-300), Sil(B-350), and Sil(B-400).

All materials were extrudated (without binder) to obtain tablets, which were subsequently crushed. The sieve fraction of 0.5–1 mm was used for the catalytic experiments.

Catalytic Experiments

The vapor-phase Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam was investigated in a fixed bed reactor with 10-mm inner diameter. The catalyst charge was 1.5 g, resulting in a catalyst bed length of approximately 40 mm. A solution of cyclohexanone oxime and ethanol (weight ratio 1 : 9) was vaporized and fed through the reactor using nitrogen as the carrier gas. Typical reaction conditions were 300°C, 0.1 bar, and a weight hourly space velocity (WHSV) of 0.33 $g_{oxime}\, g_{catalyst}{}^{-1}\, h^{-1}$.

The products were obtained by cooling in liquefied nitrogen and analyzed with gas chromatography using methyl undecanoate as an internal standard (50-m FS-SE 54 column).

Characterization

Fourier-transformed infrared (FTIR) spectra were recorded on a Nicolet Protégé 460 spectrometer. Samples were pressed into self-supported wafers (5 and 10 $mg\,cm^{-2}$) with a diameter of 13 mm, which were placed in a self-developed, heatable cell equipped with KBr windows. For dehydration, the cell was evacuated to 1.33 Nm^{-2} and heated to 400°C. Spectra were recorded at 150°C.

For pyridine adsorption measurements pyridine was adsorbed at 150°C for 5 min on dehydrated wafers followed by desorption of the physisorbed pyridine at the same temperature and 1.33 $N\,m^{-2}$ for 1 h. The spectra in the region of 1800–1300 cm^{-1} were recorded at 150°C. Although the FT-IR spectra suffer from scattering, the exact preparation method made them comparable.

Diffuse reflectance infrared (DRIFT) measurements of the powders were recorded in the same spectrometer equipped with a Praying Mantiss unit (Model HVC-DRP (Harrick)). The *in situ* cell was equipped with KBr windows. The samples were dried under nitrogen at 500°C (heating rate, 5°C/min) or at the maximum temperature of the applied thermal treatment to be investigated. The spectra were recorded at 150°C.

RESULTS AND DISCUSSION

Influence of Calcination Procedure of [B]-ZSM-5

In comparison to other materials, [B]-ZSM-5 proved to be an excellent catalyst for the vapor-phase Beckmann rearrangement. Besides high conversion rates and selectivities, this zeolite has a high thermal stability during the removal of deactivating hydrocarbons in a regeneration process (15), which is of great importance for possible industrial application. This good catalytic performance was a result of the high concentration of comparably weak acidic sites on its external surface. These active sites were very likely silanol nests, similar to those found on base-treated silicalite-1 (16).

The boron in ZSM-5 is rather weakly bonded to the lattice, causing a removal of framework boron upon calcination under air (18–20). This effect probably creates the above-mentioned silanol nests at the defect sites left behind by the extracted boron. Their acidity in combination with their arrangement in the MFI structure results in high caprolactam yields in the rearrangement reaction. The calcination of BZSM at temperatures between 300 and 600°C did not affect the Si/B ratio, which remained at 20.

The influence of the calcination on the catalytic performance is presented in Table 1.

The activity of the [B]-ZSM-5 zeolite increased with the calcination temperature. The highest conversion rate of around 90% after 2 h time on stream (TOS) was achieved with the catalyst calcined at 600°C. Even with a clearly visible deactivation of all catalysts, this trend in conversion is constant for over more than 6 h TOS.

In contrast to the activity, no clear dependency of the selectivity on the calcination temperature could be found. However, the highest selectivity of 93% is achieved with the BZSM(600).

To obtain further insight in the nature of the active sites, DRIFT measurements in the 4000 to 2800-cm^{-1} region were performed (see Fig. 1).

TABLE 1

Influence of the Calcination Temperature of [B]-ZSM-5 on the Catalytic Performance

	2 h TOS		6 h TOS	
Catalyst	Conv. [%]	Select. [%]	Conv. [%]	Select. [%]
BZSM(300)	42.5	88.6	25.4	94.4
BZSM(400)	57.2	88.9	35.0	90.2
BZSM(550)	71.5	84.1	46.1	90.4
BZSM(600)	96.1	93.1	72.2	94.3

Note. Reaction conditions: $T = 300°C$; $p = 0.1$ bar; WHSV = 0.33 h^{-1}; solvent, ethanol (9 : 1 w/w with respect to the reactant); carrier, nitrogen; TOS = time on stream.

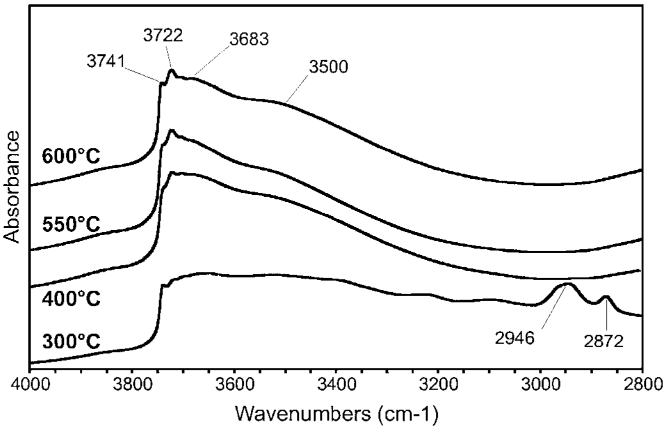

FIG. 1. DRIFT spectra of [B]-ZSM-5 zeolite calcined at different temperatures.

The lowest temperature of 300°C was not sufficient to decompose the template hexamethylenediamine completely, as was clear from the bands in the region 3000–2800 cm^{-1}, which are attributed to C–H bonds of organic residues. It is very likely that these template residues partially block the pore system of the MFI structure. Nevertheless, this should not affect the catalytic performance of the [B]-ZSM-5 zeolite, as the Beckmann rearrangement is thought to take place on the outer surface of MFI-type zeolites (12). Therefore, the low activity of the BZSM(300) could be explained rather by a lack of surface hydroxyls than by effects caused by the remaining template. It seems that a temperature of 300°C is not high enough to remove boron in large quantities from the lattice so the necessary hydroxyl groups are not available. However, all materials calcined at temperatures higher than 300°C performed better and did not show any bands of remaining organic material.

All materials revealed a very broad band around 3500 cm^{-1}. If this absorption is assigned to the hydrogen-bonded hydroxyl groups of the silanol nests (22), it could be concluded from the catalytic results that these nests are highly favorable for the Beckmann rearrangement.

Datka and Kawalek (28) however ascribed the bands at 3500 and 3680 cm^{-1} to Si–OH···O and B–OH groups, which are arranged as neighbors and are hydrogen bonded.

A comparison of the catalytic results and the DRIFT spectra leads to the conclusion that an increase of the activity could be obtained by increasing the amount of hydroxyl groups on the surface. However, it did not permit an exact assignment of certain hydroxyl groups being solely responsible for the activity and selectivity in the Beckmann rearrangement.

The formation of hydroxyl groups was investigated during an *in situ* calcination of the [B]-ZSM-5 zeolite under flowing air. A sample was heated to 550°C (heating rate, 2 K min^{-1}) inside the DRIFT cell and spectra were recorded

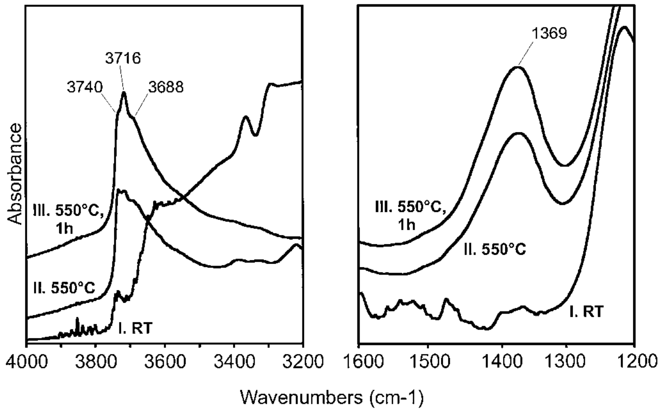

FIG. 2. DRIFT spectra of *in situ* template decomposition of [B]-ZSM-5 zeolite.

at different temperatures. In Fig. 2 the spectra at room temperature, 550°C, and 550°C after 1 h are shown.

The left spectra clearly show the formation of hydroxyl groups, as can be seen from the appearance of the bands at 3740 and 3500 cm^{-1}. After 1 h at 550°C (III), the majority of the template seems to be decomposed, which could be concluded from the annealing of the bands for N–H bonds at ca. 3300 cm^{-1}.

At room temperature no band could be found at 1380 cm^{-1}. After the sample was heated to 550°C and especially after 1 h at this temperature, a band in this region of the spectra emerged. This absorption around 1360 cm^{-1} is unlikely to originate from trigonal framework boron, which should be positioned at 1385 cm^{-1} (22, 29–31). This band could possibly be assigned to different kinds of extraframework boron oxide or hydrated boron oxide species, which reveal bands in the region 1340–1370 cm^{-1} (32). Its existence gives a hint of the removal of framework boron, which led to the creation of numerous boron oxide species.

Acid Treatment with Hydrochloric Acid of [B]-ZSM-5 Zeolite

In addition to calcination under an air atmosphere, the influence of acid treatment on the catalytic performance of the [B]-ZSM-5 zeolite was investigated. The aim of this modification was a controlled deboronation of the surface of the catalyst, thus creating surface hydroxyl groups. The main difference between these methods was that the deboronation by acid treatment also removed most of the extraframework boron species from the calcined material.

Acid treatment of as-synthesized [B]-ZSM-5 did not have a significant impact on the boron content of the material, as is to be expected since the template blocks the pore entrances. Acid treatment of the calcined crystals resulted in materials with Si/B ratios of 67–75.

The catalytic performance of the acid-treated [B]-ZSM-5 is shown in Fig. 3.

Acid treatment led to a substantial activity increase. The BZSM(0.1M) reached an initial conversion rate of 86% compared to that of 72% for the untreated BZSM. It is remarkable that this maximum conversion was obtained with the catalyst which was only mildly acid treated (0.1M). Stronger as well as weaker treatments yielded only lower activities. The selectivity to caprolactam was not significantly influenced by the acid treatment and remained at the same high level of up to 95% for all modifications of the [B]-ZSM-5.

Upon modification of calcined [B]-ZSM-5 with hydrochloric acid, the conversion rates obtained were significantly lower, but again the selectivity to caprolactam did not change. The difference between these two modification methods is that the treatment of the uncalcined material showing better performance leaves boron in the pore openings, supporting the thesis of Hölderich *et al.* (16) that the reaction mainly takes place at these openings. As in both cases the selectivities were the same, we conclude that the boron of a [B]-ZSM-5 is not the most important catalytic component in the Beckmann rearrangement concerning the selectivity, but its presence enhances the catalytic activity of the zeolite. Our observations indicate that silanol groups or nests are responsible for high yields of caprolactam.

A comparison of the FT-IR spectra of the untreated BZSM and the acid-treated BZSM(0.1M) is presented in Fig. 4.

There hardly seems to be an effect for the bands at around 3600 cm^{-1} but there could be a slight broadening of the band below 3700 cm^{-1}, which could be caused by an increase of hydrogen-bonded hydroxyl groups with low acidity. The band at 1380 cm^{-1}, which is assigned to trigonal boron, was still present in the case of the acid-treated zeolite, showing that not all of the framework boron was removed from the zeolite. Nevertheless, the infrared measurements do not allow any comment on the place of the boron species in the zeolite. Thus, we cannot conclude whether the boron remains inaccessible inside the pores or whether there are still species to be found on the surface.

The ratio of Brönsted and Lewis acidic sites on the [B]-ZSM-5 was investigated with pyridine adsorption (Fig. 5).

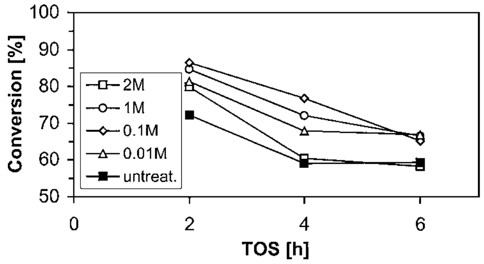

FIG. 3. Variation of hydrochloric acid treatment of [B]-ZSM-5 zeolite. Reaction conditions: $T = 300°\mathrm{C}$; $p = 0.1$ bar; WHSV $= 0.33\ \mathrm{h}^{-1}$; solvent, ethanol; carrier, nitrogen. Catalysts: BZSM; BZSM(2M); BZSM(1M); BZSM(0.1M); BZSM(0.01M).

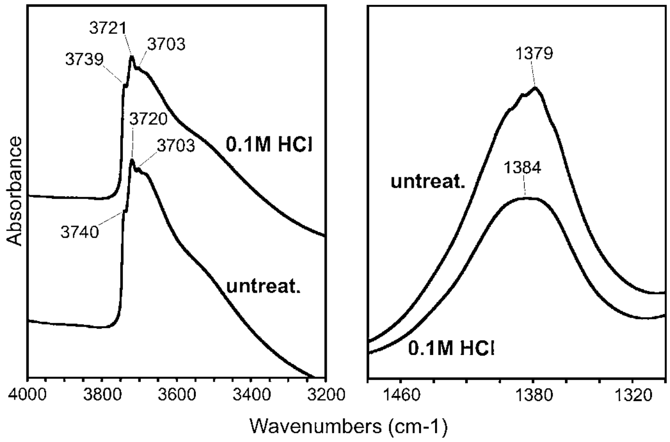

FIG. 4. FT-IR spectra of untreated and acid-treated [B]-ZSM-5 zeolites.

The bands at 1636 and 1545 cm^{-1} could be assigned to Brönsted acid sites, whereas the bands at 1624 and 1458 cm^{-1} resulted from Lewis acid sites. The sharp absorption at 1490 cm^{-1} was a result of both kinds of acidic sites (33). The Lewis acid sites were very likely a result of the calcination in air, which causes the formation of extraframework boron species.

Basic Treatment with Aqueous Ammonia of [B]-ZSM-5

According to Hölderich *et al.* (16) and Kitamura *et al.* (26), there is an increase in the activity of silicalite-1 in the Beckmann rearrangement upon treatment of the catalyst with aqueous ammonia. We have therefore also treated as-synthesized [B]-ZSM-5 with aqueous solutions of different concentrations of ammonia and NH_4NO_3, after which the materials were calcined at 550°C under air.

The conversion rates obtained with these treated materials are presented in Fig. 6.

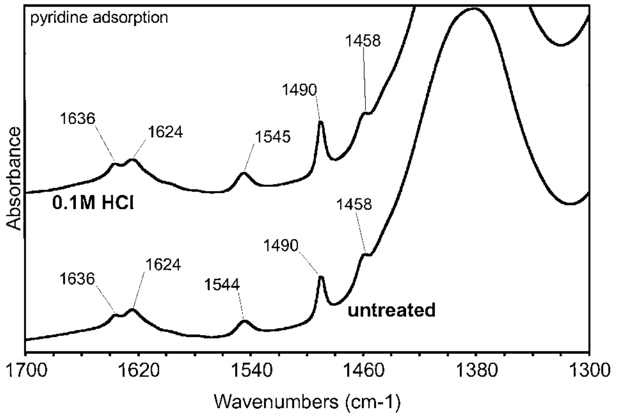

FIG. 5. FT-IR spectra after pyridine adsorption of untreated and acid-treated [B]-ZSM-5 zeolites.

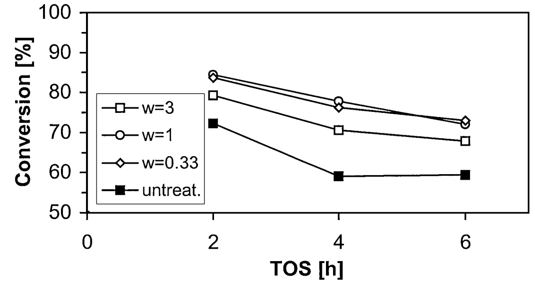

FIG. 6. Variation of basic treatment with aqueous ammonia of [B]-ZSM-5 zeolite. Reaction conditions: $T = 300°C$; $p = 0.1$ bar; WHSV = 0.33 h^{-1}; solvent, ethanol; carrier, nitrogen. Catalysts: BZSM; BZSM(3); BZSM(1); BZSM(0.33).

As was the case with a treatment with hydrochloric acid, the ammonia treatment also increases the activity of the [B]-ZSM-5 compared to that of the untreated initial material. The highest conversion rate of 84% after 2 h TOS was achieved with the mildly treated catalysts BZSM(0.33) and BZSM(1). Analogous to the acid treatment, the selectivities were not affected by the modification. All catalysts revealed selectivities to caprolactam of up to 93%. Although we did not investigate these catalysts with FT-IR, we assume that their better catalytic performance was also caused by a higher amount of hydroxyl groups that were formed by this basic treatment. Such a treatment resulted in a minor loss of boron. The Si/B ratio of BZSM(3), for example, increased to 25, compared to a ratio of 16 for the starting material. We conclude that the acid as well as the base treatment are equivalent means for improving the catalytic activity of a [B]-ZSM-5 zeolite in the Beckmann rearrangement.

Steaming of [B]-ZSM-5. The calcination of BZSM under air and the acid/base treatment resulted in an increase of the amount of surface hydroxyl groups. To obtain information on whether or not the hydroxyl groups are the active sites in the Beckmann rearrangement, BZSM was also subjected to a steaming treatment to destroy these SiOH groups.

It is well known that a hydrothermal treatment can be used for the dealumination of zeolites, causing the formation of silanol nests (34). These defect sites tend to be annealed simultaneously by a reinsertion of silicon atoms, as was reported by Kerr (35). Steamed zeolites have an ameliorated framework and are usually thermally more stable than their untreated counterparts.

Here, calcined BZSM was steamed at three different temperatures. The influence of the treatment on the activity is presented in Fig. 7.

As expected, there was a severe loss of activity after the hydrothermal treatment of the [B]-ZSM-5 compared to that of the usual calcined material. The initial conversion of the modified catalysts was lower and the zeolites steamed at 400 and 500°C deactivated faster compared to the calcined but

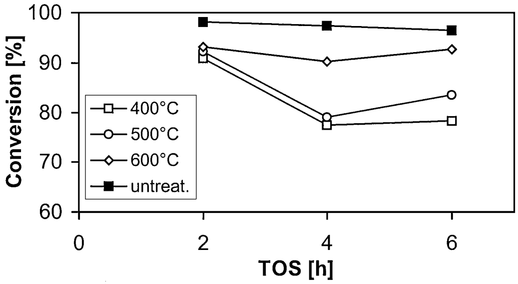

FIG. 7. Variation of hydrothermal treatment of [B]-ZSM-5 zeolite. Reaction conditions: $T = 300^\circ C$; $p = 0.1$ bar; WHSV = 0.33 h^{-1}; solvent, ethanol; carrier, nitrogen. Catalysts: BZSM; BZSM(H_2O-400); BZSM(H_2O-500); BZSM(H_2O-600).

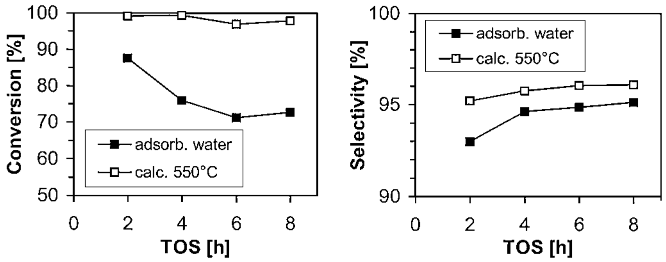

FIG. 8. Influence of adsorbed water on [B]-ZSM-5 zeolite (reaction conditions: 300°C; 0.1 bar). Reaction conditions: $T = 300^\circ C$; $p = 0.1$ bar; WHSV = 0.33 h^{-1}; solvent, ethanol; carrier, nitrogen. Catalysts: BZSM(H_2O); BZSM(H_2O) calcined at 550°C under an air atmosphere.

untreated material. Again, modification did not influence the selectivity to caprolactam, which was up to 95% for all catalysts.

Although we did not investigate these materials with FT-IR, it is likely that the amount of hydroxyl groups, especially of silanol nests, was reduced upon steaming. As the selectivity of the catalysts remained unaltered, the nature of the active sites as well as their arrangement on the outer surface of the zeolite did not change significantly. The annealing of the hydroxyl groups only resulted in the observed loss of activity.

Unexpectedly, the lowest conversion rates were obtained with the catalyst, which was steamed at the lowest temperature of 400°C. It was expected that the most severe loss of activity would occur with BZSM(H_2O-600). This could be explained by the influence of the temperature on the migration of the silica into the defect sites. This migration process needs a comparably high initial energy so it will show the best results at the higher temperature. At lower temperatures this migration process leads to higher amounts of terminal silanols, causing a faster deactivation according to Heitmann *et al.* (36).

Adsorption of Water on [B]-ZSM-5 Zeolite

The addition of water to the reactants has a positive influence on the catalyst activity in the vapor-phase Beckmann rearrangement. Kajikuri *et al.* (37) for example reported that the addition of up to 2.5 mol of water/mol of cyclohexanone oxime resulted in an increase of the catalyst service time as well as the selectivity to caprolactam, whereas Röseler *et al.* (15) reported on the addition of up to 6 mol of water/mol of oxime using [B]-ZSM-5 as the catalyst.

Adsorbed water has, in contrast to the addition of water to the reaction mixture, a negative effect on the catalytic performance of [B]-ZSM-5. Especially long contact times with water seemed to induce an alteration of the active sites on the zeolite. This alteration proceeded rather slow since no negative effect could be observed within a reaction time of 8 h TOS when water was added to the reaction mixture.

For a more precise examination of this effect, water was adsorbed on a [B]-ZSM-5 for 6 weeks at room temperature. One part of this modified material was directly used in the rearrangement reaction, and the other part was calcined at 550°C under air prior to its use as a catalyst.

Figure 8 clearly shows the loss of activity of the [B]-ZSM-5 zeolite at a reaction temperature of 300°C and 0.1 bar upon the adsorption of water. On the other hand, if the material was first calcined, the high activity of the catalyst was restored. With respect to the selectivity to caprolactam, only minor effects were observed.

However, at 350°C and 1 bar (Fig. 9) no differences between the two catalysts were found in activity nor selectivity to caprolactam. Over both zeolite catalysts, almost complete conversion was achieved, and the selectivity increased from 82% to a maximum of 93% within 8 h TOS.

Apparently, the reaction temperature of 300°C was not sufficient to reverse the changes on the surface of the [B]-ZSM-5 zeolite, which were a result of the adsorption of water. At the higher temperature of 350°C, however, the catalytic sites regained their normal high activity and selectivity.

Greater insight on this effect was obtained with temperature-dependent DRIFT measurements of water-loaded [B]-ZSM-5. The cell was heated to 300°C and kept at this temperature for 1 h, after which the catalyst was heated

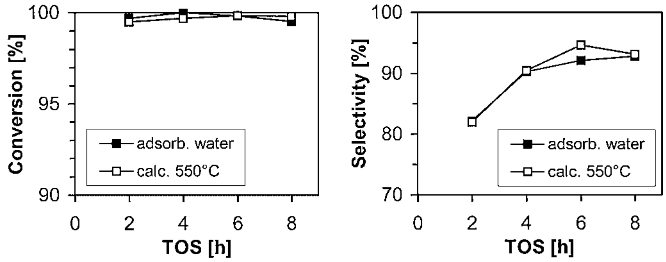

FIG. 9. Influence of adsorbed water on [B]-ZSM-5 zeolite (reaction conditions: 350°C; 1 bar). Reaction conditions: $T = 350^\circ C$; $p = 1$ bar; WHSV = 0.33 h^{-1}; solvent, ethanol; carrier, nitrogen. Catalysts: BZSM(H_2O); BZSM(H_2O) calcined at 550°C under an air atmosphere.

to 550°C. Finally, the cell was cooled down to 300°C again. The four spectra recorded are depicted in Fig. 10.

At 300°C the spectrum revealed a band at 3740 cm^{-1} attributable to terminal silanol groups. Additionally, a very broad band appeared around 3700–3400 cm^{-1}, whose intensity did not change after 1 h at 300°C. After the cell temperature was increased to 550°C, the broad adsorption band was reduced significantly in intensity and did not reappear after the temperature was cooled to 300°C, possibly due to an irreversible condensation of OH groups. This band could possibly be attributed to hydrogen-bonded vicinal hydroxyl groups on silicon and boron. A subtraction of spectrum IV from spectrum I results in a band with a clear maximum around 3520 cm^{-1}, which could possibly be attributed to hydrated boron oxide species (38), which confirms the hypothesis that the boron oxide species are necessary for high conversion. However, even if the amount of boron oxide was reduced, conversion rates above 70% were obtained. On the silanol nests and the vicinal silanol groups of the MFI structure, conversions of ca. 70% could be obtained. It seems that the presence of boron oxide species is responsible for the increase of the conversion up to 100%.

CVD of Boron on Silicalite-1

Boron oxide has a positive effect on the heterogeneously catalyzed Beckmann rearrangement, more specifically, boron oxide on amorphous carriers (2–5). Takahashi *et al.* (39, 40), impregnated a crystalline carrier, a highly siliceous ZSM-5, with boric acid and obtained higher caprolactam yields over this catalyst.

Here, silicalite-1 was subjected to a CVD treatment with triethyl borate ($B(OEt)_3$), which was reported by Sato *et al.* (4), to obtain very finely dispersed boron oxide species on the catalyst surface, partially by the interaction between the boron species and the surface hydroxyl groups. To create a high amount of silanol groups and nests, the silicalite was first treated with aqueous ammonia prior to the CVD treatment. Such a modification of silicalite-1 has proven to be very effective for high caprolactam yields (16). The aim of this modification was to imitate a [B]-ZSM-5 zeolite calcined under air. This material also contained high amounts of defect sites and the boron extracted from the framework was present as surface boron oxide species. The results are presented in Table 2.

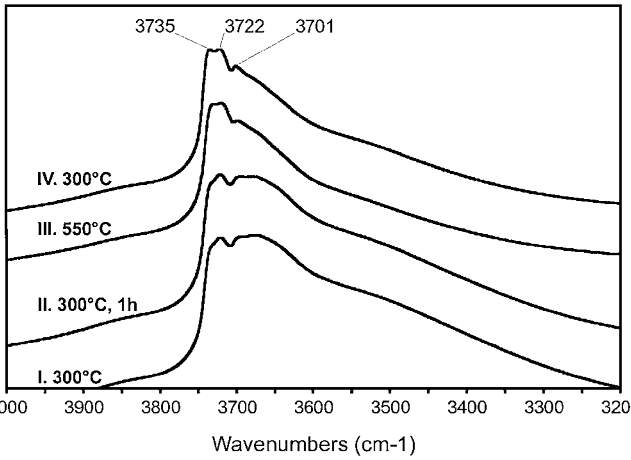

FIG. 10. DRIFT investigation of adsorbed water on [B]-ZSM-5 zeolite.

TABLE 2

Influence of Boron CVD on Silicalite

	2 h TOS		8 h TOS	
Catalyst	Conv. [%]	Select. [%]	Conv. [%]	Select. [%]
Sil	97.4	98.3	90.2	99.0
Sil(B-250)	95.2	95.7	96.5	99.5
Sil(B-300)	98.1	97.9	98.4	98.8
Sil(B-350)	96.0	98.1	97.8	99.5
Sil(B-400)	95.7	98.8	96.7	99.9

Note. Reaction conditions: $T = 300°C$; $p = 0.1$ bar; WHSV = 0.33 h^{-1}; solvent, ethanol; carrier, nitrogen.

Over the boron free silicalite-1 (Sil) high initial conversions were found after 2 h TOS. However, within 8 h TOS the catalyst deactivated, resulting in a lower conversion rate of up to 90%. There were no significant improvements of the initial activity by the boron-loaded catalysts but the deactivation after 8 h TOS was avoided. The highest conversion of 98% was achieved with the Sil(B-300), which was treated with $B(OEt)_3$ at 300°C, a temperature where clustering of the boron oxide could probably be avoided. The selectivity to caprolactam was essentially not affected.

Apparently, the CVD method caused interactions between the surface sites of the silicalite-1 and the boron species present on the surface. As the deactivation rate of the boron-loaded catalysts was lower, it was assumed that the acidity of the active sites was reduced by this CVD treatment, resulting in a decrease in the deposition of deactivating compounds on the catalysts during the reaction.

CONCLUSIONS

The influence of different treatments on the performance of [B]-ZSM-5 in the Beckmann rearrangement was investigated. An as-synthesized material was subjected to calcinations at different temperatures, acidic treatments with HCl solutions, basic treatments with ammonia solutions, steaming at different temperatures, water absorption, and boron CVD. The materials were investigated with FT-IR to obtain information on the nature of the active sites.

Calcination at high temperature (600°C), a mild acidic treatment with 0.1 M HCl, and a mild basic treatment with a 0.33 wt% solution of aqueous ammonia (25 wt%) and aqueous ammonia nitrate (20 wt%) resulted in materials showing the best results in catalytic performance. The steaming and water absorption experiments demonstrated the importance of hxdroxyl groups arranged in silanol nests or as bridged vicinal silanols as the active sites. Their presence could be shown with FT-IR revealing a band between 3700 and 3400 cm^{-1} with a maximum at 3500 cm^{-1}. The broadness of the band, especially in the deboronated samples, could be explained by the stronger delocalisation of hydrogen-bonded sites because of the relative proximity of the silanol groups in a silanol nest.

The influence of boron oxide species could be demonstrated by comparing the FT-IR spectra of the dehydrated material with the one where water was absorbed. Subtraction of the spectra resulted in a clear band at 3520 cm^{-1}, which might very well originate from hydrated boron oxide species.

As a result of these experiments, we propose that silanol nests and vicinal-bridged hydroxyl groups are most important in catalytic performance of the catalyst. Furthermore, strong evidence was found for a positive influence of boron oxide species on both conversion and service time of the catalyst, as upon removal of the boron oxide by either acidic or basic treatment or deactivated by hydration, the conversion decreased to around 70%. If the boron oxide species are left at the surface or reactivated as in the case of the water absorption, an increase of the conversions to 98–100% was obtained.

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