Journal of Catalysis **186,** 12–19 (1999)
Article ID jcat.1999.2552, available online at http://www.idealibrary.com on IDEAL®

Catalytically Active Sites for the Beckmann Rearrangement of Cyclohexanone Oxime to ε-Caprolactam

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Received July 13, 1998; revised October 17, 1998; accepted May 10, 1999

The rearrangement of cyclohexanone oxime to ε-caprolactam was investigated over heterogeneous catalysts, especially over highly siliceous zeolites with a MFI structure. The aim of this work was to determine the active sites on these catalysts, rather than to optimize their catalytic performance. Amorphous silica and the silicalite-1 zeolite were chemically modified with aqueous acidic or basic solutions. Silicalite-1 was also treated hydrothermally at temperatures above 400°C. Catalytic reactions were carried out with the initial materials and their modifications in a fixed-bed reactor. Characterization of the catalyst with FT-IR, nitrogen sorption, and XRD revealed significant differences and gave important information about the active sites in the reaction. Silanol nests on the external surface of the highly siliceous ZSM-5 zeolite were most suitable for the Beckmann rearrangement. © 1999 Academic Press

INTRODUCTION

The intermediate for the production of nylon 6, ε-caprolactam, is of great industrial importance. Attempts have been made recently to produce the lactam in a heterogeneous Beckmann rearrangement of cyclohexanone oxime instead by means of a homogeneously catalyzed process, which is considered to be detrimental to the environment. Hölderich (1–3) made a survey of the research in this field.

In our earlier work, we found high yields of caprolactam in the vapor-phase Beckmann rearrangement over [B]-ZSM-5 zeolites (4). Apart from investigations of the catalytic performance, we determined the active sites that are beneficial for the rearrangement of the oxime (5, 6). Reports about the active sites are contradictory. Corma *et al.* (7, 8) suggested that the strong acid sites on crystalline silica–alumina are favorable. Curtin *et al.* (9–13) conducted TPD investigations of alumina-supported boron and showed that acid sites of intermediate strength give high yields of the lactam. Ushikubo and Wada (14) recently reported on high catalytic efficiencies using tantalum oxide on silica. A different assumption was made by Sato *et al.* (15–17) based on investigations of HZSM-5 zeolites with high Si/Al ratios. On one hand, the yield of caprolactam increased with decreasing aluminum content of the zeolite, while on the other hand blocking strong acid sites with basic compounds did not reduce the catalytic performance. These results imply that weak or even neutral acid sites, e.g., silanol groups, are effective for the Beckmann rearrangement, an assumption also made by Hölderich (1). Furthermore, basic treatment of a highly siliceous HZSM-5 zeolite led to enhanced conversions and selectivities, together with lower deactivation rates (18).

The purpose of our study was to examine the heterogeneously catalyzed Beckmann rearrangement as influenced by different kinds of hydroxyl groups on the surface of amorphous and crystalline catalysts. We compared the catalytic performances of silica and the silicalite-1 zeolite as well as modifications of these materials. Infrared measurements in the 4000- to 3200-cm^{-1} region were made to determine the nature of the hydroxyl groups on these catalysts; the crystalline silicalites were also characterized by nitrogen sorption and XRD measurements.

METHODS

Catalysts

Highly siliceous catalysts used in these investigations included amorphous silica, crystalline silicalite, and modifications of these materials. Amorphous silica (SiO_2), with the product name D 11-10, was kindly provided by BASF AG, Ludwigshafen, Germany. The starting material was modified by acid treatment: 5 g of silica was mixed with 100 g of an aqueous solution of hydrochloric acid. After this mixture was stirred for 24 h at 40 or 100°C with reflux cooling, the catalyst was filtered, washed with deionized water, and dried for 4 h at 110°C. In all, six alterations of the starting material were obtained by varying the acid concentration and the temperature during treatment (Table 1).

To determine the impurities in this industrial material, elemental analysis (ICP-AES) of all modifications of the silica was made. Additionally, the different solutions of

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0021-9517/99 $30.00

TABLE 1

Alterations in the Acid Treatment of Silica

Silica	HCl (aq)	Treatment temp. (°C)
SiO_2(40-1 M)	1 M	40
SiO_2(40-0.1 M)	0.1 M	40
SiO_2(40-0.01 M)	0.01 M	40
SiO_2(100-1 M)	1 M	100
SiO_2(100-0.1 M)	0.1 M	100
SiO_2(100-0.01 M)	0.01 M	100

hydrochloric acid were also investigated after use in the treatment process. Finally, we investigated the acidic solution (1 M HCl), which was stirred in a glass flask at 100°C without adding the catalyst. The aim was to find out whether metal ions were extracted from the glass walls, which might form catalytically active sites on the silica. The results of the elemental analysis are shown in Table 2.

Synthesis of crystalline silicalite-1 was carried out according to Kitamura *et al.* (18): 500 g of tetraethylorthosilicate, 1070 g of ethanol, and 1120 g of an aqueous solution (10 wt%) of tetrapropylammonium hydroxide were fed into a stainless steel autoclave and thoroughly mixed for 2 h. The autoclave was subsequently heated to 105°C, and crystallization occurred under autogeneous pressure and vigorous stirring for 96 h. Finally, the zeolite powder was washed with deionized water, filtered, dried at 110°C for 16 h, and ultimately calcined at 550°C for 12 h in air. Elemental analysis (ICP) gave a Si/Al ratio around 2500. The obtained silicalite (Sil) was additionally modified by a basic treatment similar to that described in (18). Five grams of silicalite was filled with 20 g of a mixture of aqueous solutions of ammonia (25 wt%) and ammonium nitrate (7.5 wt%, series I; 20 wt%, series II) into a glass beaker. This was put into a stainless steel autoclave and stirred at 90°C and autogeneous pressure for 1 h. The catalyst was then washed with deionized water, filtered, and dried at 110°C for 4 h. To investigate the influence of the basic treatment on the catalytic performance in the Beckmann rearrangement, two series (I and II) of this treatment, differing in the concentration of the ammonia solution, were applied to the silicalite (Table 3).

TABLE 2

Elemental Analysis (ICP) of Silica and Acid Solutions

Element (mg g^{-1})	Na	Al	Si	Ti	Fe	K	Ca
			Catalyst				
SiO_2	1.0	1.7	409	0.29	0.34	—	0.3
SiO_2(40-1 M)	—	1.1	402	0.26	0.29	—	0.3
SiO_2(40-0.1 M)	—	1.3	420	0.30	0.29	—	0.4
SiO_2(40-0.01 M)	—	1.5	417	0.30	0.36	—	0.1
SiO_2(100-1 M)	—	1.0	417	0.25	0.28	—	0.1
SiO_2(100-0.1 M)	—	1.2	413	0.29	0.28	—	0.3
SiO_2(100-0.01 M)	—	1.7	413	0.29	0.33	—	0.1
			Solution after treatment of catalyst				
40°C-1 M HCl	0.9	0.3	1.1	—	<0.1	<0.1	<0.1
40°C-0.1 M HCl	1.3	0.4	2.5	—	<0.1	<0.1	<0.1
40°C-0.01 M HCl	1.2	0.2	2.6	—	<0.1	<0.1	<0.1
100°C-1 M HCl	1.7	0.6	2.6	—	<0.1	<0.1	<0.1
100°C-0.1 M HCl	1.8	0.7	4.3	—	<0.1	<0.1	<0.1
100°C-0.01 M HCl	2.0	0.2	5.6	—	<0.1	<0.1	<0.1
			Solution without catalyst				
100°C-1 M HCl	—	—	1.1	—	—	—	—

TABLE 3

Alterations in the Basic Treatments I and II of Silicalite

Silicalite	NH_3 (aq)		NH_4NO_3 (aq)	
	Weight	Molar	Weight	Molar
	Basic treatment I			
Sil(I-11.0 M)	15 g (25 wt%)	11.0 M	5 g (7.5 wt%)	0.2 M
Sil(I-7.4 M)	10 g (25 wt%)	7.4 M	10 g (7.5 wt%)	0.5 M
Sil(I-3.7 M)	5 g (25 wt%)	3.7 M	15 g (7.5 wt%)	0.7 M
	Basic treatment II			
Sil(II-5.9 M)	8 g (25 wt%)	5.9 M	12 g (20 wt%)	1.5 M
Sil(II-4.4 M)	6 g (25 wt%)	4.4 M	14 g (20 wt%)	1.8 M
Sil(II-2.9 M)	4 g (25 wt%)	2.9 M	16 g (20 wt%)	2.0 M
Sil(II-1.5 M)	2 g (25 wt%)	1.5 M	18 g (20 wt%)	2.3 M

In addition, the crystalline silicalite was modified further after a hydrothermal treatment (steaming). The starting material for this procedure was silicalite Sil*(I-3.7M), which was previously modified by a basic treatment with aqueous ammonia, as described above. The silicalite (3 g) was put into a quartz glass tube, which was placed in an oven. Steaming took place at high temperatures (400–600°C) by passing a nitrogen stream through the powder bed, which was saturated with water (partial pressure 4.7 kN m^{-2}). The temperature of the hydrothermal treatment was varied, resulting in three modifications of the silicalite: Sil(H_2O-400), Sil(H_2O-500), and Sil(H_2O-600).

All the materials used as catalysts for the vapor-phase Beckmann rearrangement were pressed (without binder) into tablets, which were then crushed and sieved to obtain a fraction of 0.5- to 1-mm particle size.

Catalytic Tests

The vapor-phase Beckmann rearrangement was investigated in a fixed-bed reactor of 10-mm i.d. The catalyst charge was 1.5 g to give a catalyst bed approximately 40 mm in height. A solution of cyclohexanone oxime with ethanol as the solvent (weight ratio 1 : 9) was vaporized and fed through the reactor with nitrogen as the carrier gas. Typical reaction conditions were 300°C, 100 mbar, and a WHSV of 0.33 $g_{\mathrm{reactant}}\ g_{\mathrm{cat}}^{-1}\ h^{-1}$. Gaseous products were chilled in liquefied nitrogen and analyzed by gas chromatography

(HP6890/FS-SE-54) using methyl undecanoate as the internal standard. The experimental procedure and the positive effect of reducing the reaction pressure on caprolactam selectivity have been described elsewhere (4).

Characterization

The structures of the crystalline silicalites were determined with XRD using a Siemens D5000 (Cu$K\alpha_{1,2}$). Nitrogen sorption isotherms were measured at 77 K using a Coulter Omnisorp 100. FT-IR spectra were recorded on a Nicolet Protégé 460 spectrometer. For this, samples were pressed into self-supported wafers (5–10 mg cm^{-2}) that were placed into a self-made cell with KBr windows and a heater. The cell was connected to a vacuum pump, and the wafers were heated at 400°C and 1.33 Nm^{-2} until they were dehydrated. After 4 h, the cell was cooled down to 150°C and a spectrum of wave numbers from 4000 to 3200 cm^{-1} was recorded. Elemental analysis was done with ICP-AES on a SPECTROFLAME D (SPECTRO).

RESULTS AND DISCUSSION

Investigation of Amorphous Silica as a Catalyst

In previous work (5), we found that amorphous silica is inactive as a catalyst in the Beckmann rearrangement of cyclohexanone oxime to caprolactam. Selectivity to lactam was also poor. While this material was examined with infrared in the hydroxyl region, two peaks were detected and assigned to terminal silanols (∼3740 cm^{-1}) and vicinal-bonded silanols (∼3680 cm^{-1}). The latter are typical of the disturbed surface of an amorphous material. These hydroxyl groups are bonded in case they occur at distances shorter than 0.3 nm (19). High temperatures anneal these groups, a process which is reversible below 450°C (20). On the contrary, the crystalline silicalite with its ordered structure showed a small peak for terminal silanols only. This catalyst gave significantly lower selectivities to caprolactam; thus, we concluded that vicinal silanols are more suitable for the Beckmann rearrangement than terminal silanols, mainly due to the better adjustment of acid strength caused by the hydrogen bond.

On the basis of our findings about amorphous silica and silicalite (5), we extended our investigations of amorphous silica to confirm our assumption that surface vicinal silanols are active sites for the rearrangement reaction. Therefore, we treated the inactive starting material with hydrochloric acid to remove silicium atoms from the external surface and, thus, to enhance the creation of new silanol groups at these defective sites. The starting material and its modifications were catalytically tested in the Beckmann rearrangement.

The activity of the amorphous silica was enhanced considerably (Figs. 1 and 2). Whereas the untreated material gave a conversion only slightly higher than 10%, the starting conversion of the acid-treated catalysts reached values up to 50%. Nevertheless, the enhanced catalytic performance is impaired by a considerable loss of activity with time on stream (TOS).

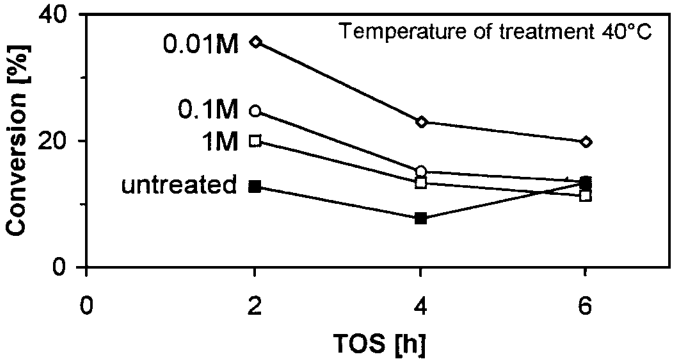

FIG. 1. Influence of HCl treatment (40°C) of silica on conversion. Reaction: $T = 300°C$; $p = 0.1$ bar; WHSV = 0.33 h^{-1}; solvent, ethanol; carrier, nitrogen; catalysts, SiO_2, SiO_2(40-1 M), SiO_2(40-0.1 M), and SiO_2(40-0.01 M).

Two effects are remarkable: on one hand, the conversion increased with the temperature of the acid treatment, as anticipated; on the other hand, the maximum conversion was not achieved with the highest but with the lowest concentration of hydrochloric acid used in this series of treatments. This effect can be explained by the maximum solubility of silica in an aqueous solution of pH at ca. 2 (5, 21). The maximum number of silicon atoms was removed from the material with an HCl concentration of 0.01 M, leading to the largest number of newly generated silanols. This is elucidated by the increase in the silicon content in the hydrochloric acid solution after treatment (Table 2).

The acid treatment also led to higher selectivities to caprolactam. The selectivity after 2 h TOS increased from 65% to 79%, replacing the initial material with the SiO_2(100-1 M) as a catalyst. Selectivities after 6 h TOS even reached values up to 87% (catalyst: SiO_2(100-0.1 M)).

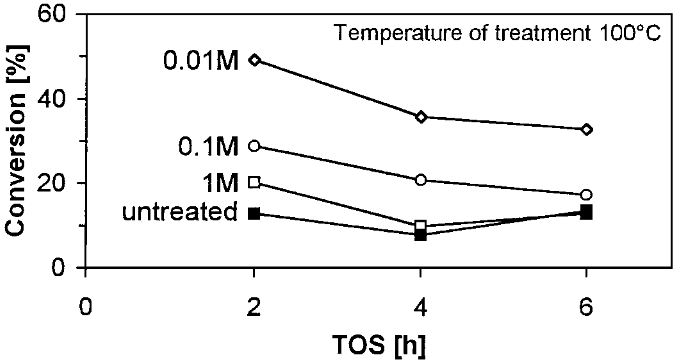

FIG. 2. Influence of HCl treatment (100°C) of silica on conversion. Reaction: $T = 300°C$; $p = 0.1$ bar; WHSV = 0.33 h^{-1}; solvent, ethanol; carrier, nitrogen; catalysts, SiO_2, SiO_2(100-1 M), SiO_2(100-0.1 M), and SiO_2(100-0.01 M).

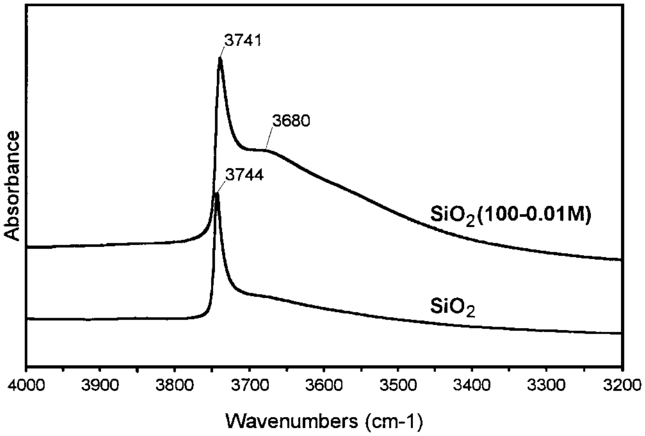

FIG. 3. FT-IR spectra of SiO_2 and SiO_2(100-0.01 M).

It was assumed that metal ions on the surface of the silica are responsible for the catalytic activity. However, according to the elemental analysis, the contents of Al, Fe, and Ti are more or less the same before and after the acid treatment (Table 2). The differences are within the accuracy of the ICP measurement. With the exception of silicon, none of the metals appeared to be extracted from the glass flask, used in the treatment (Table 2). Therefore, the ameliorated catalytic performance of the acid-treated silica compared to that of the untreated material cannot be caused by metal impurities in the silica D 11-10.

Whereas the higher catalytic activity after acid treatment was explained by a higher number of silanols on the silica's outer surface, the enhanced selectivity to caprolactam indicates the generation of a new active site. To determine these sites, we made FT-IR measurements of the initial SiO_2 material and of the modified SiO_2(100-0.01 M), which showed the best catalytic performance in the Beckmann rearrangement. The spectra of these materials are depicted in Fig. 3.

Both spectra show a very sharp peak around 3740 cm^{-1}, which is assigned to terminal silanols on the silica's surface. In the case of the untreated initial material, another band, around 3680 cm^{-1}, representing the vicinal hydrogen-bonded silanols, is visible as a small shoulder. The acid treatment of the silica caused a substantial increase in this peak, resulting in very broad absorption in the spectrum. Because this effect is accompanied by an improvement in the catalyst performance, it is concluded that these vicinal silanols are more favorable sites for the Beckmann rearrangement than their terminal counterparts. These results match those of our previous investigations, which compared the amorphous silica with crystalline silicalite (5). The present study, however, compares two catalysts that originate from the same starting material. Thus, the comparison of very different catalyst systems, such as silica and silicalite, can be avoided and the effects of the other properties of these materials excluded.

TABLE 4

Catalytic Results of Silicalite (Basic Treatment I)

	Molarity of ammonia			
	11.0 M	7.4 M	3.7 M	Untreated
Conversion (2 h TOS)	86%	85%	93%	27%
Selectivity (2 h TOS)	97%	98%	98%	39%

Note. Reaction: $T = 300°C$; $p = 0.1$ bar; WHSV = 0.33 h^{-1}; solvent, ethanol; carrier, nitrogen; catalysts, Sil(I-11.0 M), Sil(I-7.4 M), Sil(I-3.7 M), and Sil.

Investigation of Crystalline Silicalite as a Catalyst

Basic treatment with aqueous ammonia. The silicalite zeolite that was used as a catalyst showed slightly higher activity but much poorer selectivity than amorphous silica (5). Kitamura, Ichihashi, and Tojima (18) proposed a basic treatment with aqueous ammonia and ammonium nitrate to activate this catalyst in the Beckmann rearrangement; this treatment proved suitable for increasing both conversion and selectivity to values above 90%.

We applied this method to the silicalite by varying the concentrations of ammonia and ammonium nitrate to obtain two series of modifications (I and II) (Table 3).

The catalytic results of the first three silicalites after 2 h time on stream are listed in Table 4. The application of the basic treatment resulted in considerably higher activities of the silicalite, reaching conversions above 85%. Selectivity also increased to values of 98%. The untreated starting material showed a conversion and selectivity of only 27% and 39%, respectively. The best conversion was obtained after a milder basic treatment (Sil(I-3.7 M)) than after treatment with highly concentrated ammonia (Sil(I-11.0 M)).

The catalytic results of the second modification series II are given in Table 5.

In this series of the basic treatment, the conversion decreases with decreasing concentration of ammonia. At a molar ratio of 1.5 M, the conversion was even lower than that obtained with the untreated silicalite. Nevertheless, all modifications showed a very high selectivity, reaching values up to 99%.

TABLE 5

Catalytic Results of Silicalite (Basic Treatment II)

	Molarity of ammonia				
	5.9 M	4.4 M	2.9 M	1.5 M	Untreated
Conversion (2 h TOS)	82%	70%	37%	10%	27%
Selectivity (2 h TOS)	98%	99%	97%	94%	39%

Note. Reaction: $T = 300°C$; $p = 0.1$ bar; WHSV = 0.33 h^{-1}; solvent, ethanol; carrier, nitrogen; catalysts, Sil(II-5.9 M), Sil(II-4.4 M), Sil (II-2.9 M), Sil(II-1.5 M), and Sil.

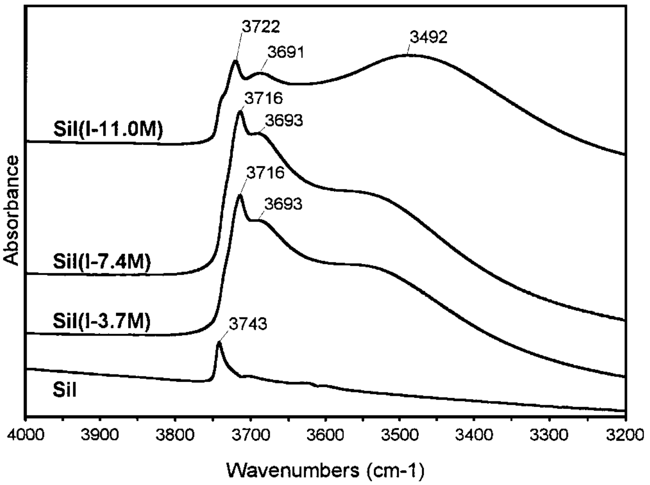

FIG. 4. FT-IR spectra of Sil, Sil(I-11.0 M), Sil(I-7.4 M), Sil(I-3.7 M).

Elemental analysis of the silicalite-1 revealed that the catalyst contained almost no impurities. Thus, ICP-AES analysis of the basic solutions was not made.

These results indicate that the basic treatment enhanced the selectivity of silicalite-1. Regarding the activity of the catalyst, an optimal ammonia concentration had to be applied to avoid a severe disturbance of the silicalite's external surface. Thus, due to a severe basic treatment, the arrangement of the active sites needed for the Beckmann rearrangement changed or were destroyed.

We found previously that significant improvement in the catalytic performance of the silicalite is accompanied by the appearance of a strong adsorption band around 3500 cm^{-1} in the FT-IR spectrum (5). This peak was also observed by Woolery *et al.* (22) and Marra *et al.* (23) who assigned the band to four neighboring silanol groups, which are hydrogen bonded and form a silanol nest. We already found that such silanols are the most favorable active sites for the Beckmann rearrangement (5). The spectra of the first three silicalite modifications are shown in Fig. 4.

The spectra of the modified silicalite all showed a strong adsorption band around 3500 cm^{-1}, which increased with increasing ammonia concentrations during the basic treatment. In contrast, the starting material Sil showed only a very small peak for terminal silanol groups at 3743 cm^{-1}. After the basic treatment, this band was barely visible as a shoulder, whereas more peaks were found at lower wave numbers. An exact assignment of the peak around 3720 cm^{-1} could not be made, but it is probably due to asymmetric hydroxyl-bonded silanols on the silicalite surface. The peak at 3690 cm^{-1} is assigned to vicinal silanols and the peak at 3500 cm^{-1} to silanol nests, both being hydrogen bonded. Whereas vicinal silanols were also found in the case of the amorphous silica, the silanol nests are typical of the crystalline structure of the silicalite. Their appearance is accompanied by a very high selectivity to caprolactam in the Beckmann rearrangement, which strongly suggests that these hydroxyl groups are the most favorable active sites for the production of caprolactam, even superior to vicinal silanols. Their arrangement on the external surface of the silicalite is most suitable, mainly due to the MFI structure.

We also found these silanol nests at 3500 cm^{-1} in the FT-IR spectrum of a dealuminated mordenite. The conversion rates obtained over the untreated mordenite were 30% with selectivities around 90%. After dealumination with aqueous hydrochloric acid, however, the activity decreased to conversions lower than 10%, whereas no effect on the selectivity was found. The catalytic yield continued to decrease, showing that the arrangement of silanol nests on the MOR structure is not favorable for the Beckmann rearrangement. Depending on the zeolite structure, different distances and angles between the single silanol groups are possible and determine the size of the silanol nest and the strength of the van der Waals bondings. Both factors may be decisive for catalytic performance, which was better in the case of the MFI structure.

The absorption at approximately 3500 cm^{-1} is most distinctive on the Sil(I-11.0 M), which was treated with highly concentrated ammonia. This catalyst did not show the highest catalytic activity, which may be the result of two effects: first, silanol nests were generated at the catalyst surface where the Beckmann rearrangement of cyclohexanone oxime takes place; second, destruction of the outer surface due to the basic strength of the employed solutions may have occurred, causing deterioration of the surface to a greater extent than necessary. In terms of good catalytic properties, the most suitable surface modification occurred on the Sil(I-3.7 M).

The FT-IR spectra of the four silicalites treated with low concentrations of ammonia are given in Fig. 5.

The spectra of the modifications Sil(II-1.5 M) and Sil (II-2.9 M) showed a very broad band between 3740 and

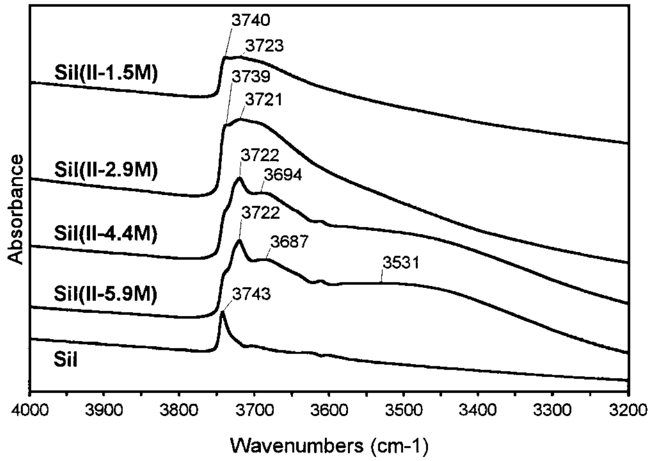

FIG. 5. FT-IR spectra of Sil, Sil(II-5.9 M), Sil(II-4.4 M), Sil(II-2.9 M), Sil(II-1.5 M).

3600 cm^{-1}, indicating the existence of terminal and vicinal hydrogen-bonded silanols (23). Their basic treatment was not apparently severe enough to create silanol nests, which can be derived from the missing absorption bands around 3500 cm^{-1}. This band appears for the first time in the spectrum of the Sil(II-4.4 M) and is broader for Sil(II-5.9 M). Nevertheless, the greatly increased selectivities of all modifications compared to the starting material indicates that hydrogen-bonded silanols are superior to their terminal counterparts. Their four-fold arrangement as silanol nests might be even more favorable than their occurrence as vicinal groups on the external surface of the MFI structure. This is shown by the lower activities of the modifications, Sil (II-1.5 M) and Sil(II-2.9 M) (only vicinal silanols), in contrast to the high conversion rates obtained with the Sil (II-4.4 M) and Sil(II-5.9 M) (both vicinal silanols and silanol nests).

Marra *et al.* (23) pointed out that the existence of certain silanol groups on the external surface of the silicalite is important for good catalysis, but they also mentioned that its structure is highly significant. Depending on the synthesis of this zeolite, its structure is monoclinic or orthorhombic. The symmetry of MFI can be determined by nitrogen adsorption, the structure by X-ray diffractometry.

The isotherms of the last three modifications and the initial material were obtained by nitrogen sorption and are shown in Fig. 6.

The untreated starting material Sil showed a pronounced step in its isotherm in the region of $0.2 < p/p^0 < 0.3$, which was attributed to the monoclinic structure of this zeolite (24).

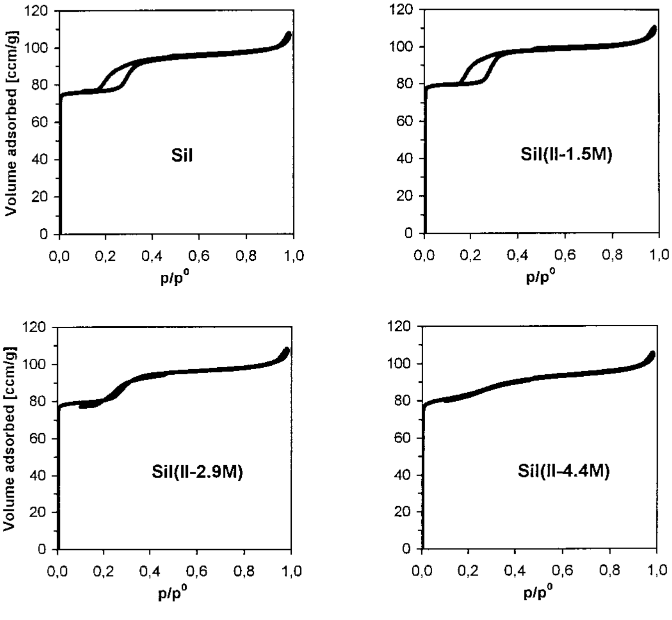

FIG. 6. Nitrogen adsorption isotherm of untreated silicalite Sil and treated Sil(II-4.4 M), Sil(II-2.9 M), and Sil(II-1.5 M).

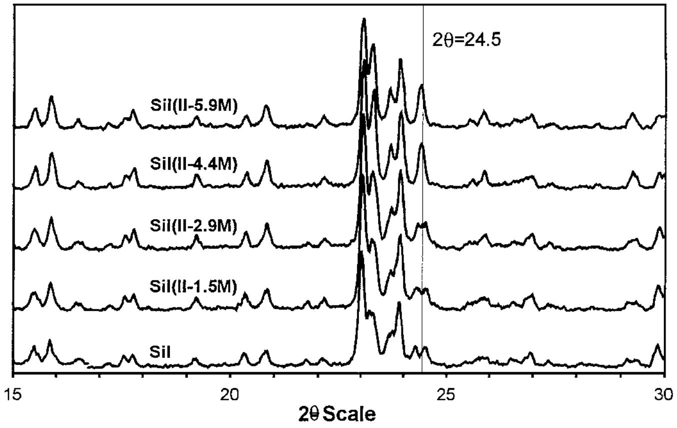

FIG. 7. XRD patterns of Sil, Sil(II-5.9 M), Sil(II-4.4 M), Sil(II-2.9 M), and Sil(II-1.5 M).

The change from the monoclinic to the orthorhombic structure was visualized by the disappearance of the distinctive step in the nitrogen sorption isotherm. This effect is explained by the larger number of defective sites or silanol nests (due to missing SiO_4 tetrahedra), which cause cavities to develop inside the zeolite framework (25, 26). As can be seen in Fig. 6, the treatment of Sil(II-4.4 M) led to a sufficient number of defective sites, thus causing the structure to become orthorhombic (the spectrum of Sil(II-5.9 M) is equal). This result matched the FT-IR spectrum (Fig. 5) of this modification, in which the broad adsorption around 3500 cm^{-1}, attributed to silanol nests, was present.

In contrast to Sil(II-4.4 M), the characteristic step in the isotherm of Sil(II-2.9 M) gradually arises and is sharply pronounced in the isotherm of the Sil(II-1.5 M). Likewise, the treatment of these silicalites was not severe enough; silanol nests did not develop on the external surface and the structure did not change from monoclinic to orthorhombic, as can be seen from the FT-IR spectra (Fig. 5).

Another way of determining the structure of the silicalite is by means of XRD (Fig. 7). A structural change from monoclinic to orthorhombic causes the unification of two peaks in the XRD pattern at a 2θ value around 24.5° (27).

The starting material and the Sil(II-2.9 M) and Sil(II-1.5 M) showed two peaks at $2\theta = 24.5°$ (monoclinic). In contrast, the two isolated peaks were united in the patterns of the Sil(II-5.9 M) and Sil(II-4.4 M) (orthorhombic). Like the nitrogen isotherms, these XRD measurements also match the FT-IR spectra of the silicalite and its modifications presented above.

It was concluded that, for high selectivities to caprolactam over silicalite as the catalyst, its structure does not necessarily have to become orthorhombic. The only condition is the presence of vicinal hydrogen-bonded silanols, which are only slightly acidic. Increasing the silicalite activity together with its selectivity, however, might require the generation of well-distributed silanol nests. This can be achieved by a basic treatment with aqueous ammonia, as demonstrated above.

Hydrothermal treatment. The assumption that silanol nests might be the most favorable active sites for the Beckmann rearrangement is supported by further investigations on the silicalite. In these studies, a silicalite containing a high number of these silanol groups, obtained after basic treatment, was subsequently treated with water vapor at high temperatures (steaming). In this procedure, silanol nests are annealed by reinserting silicium atoms into defective sites of the framework (25, 28), as is known from the literature. Furthermore, this process may also include a migration of internal defects to the external surface of the framework (28). Both effects cause amelioration and stabilization of the crystalline structure. It was our aim to produce silanol nests on the silicalite surface, and then remove them, to determine whether this would affect the catalytic performance of the material. Therefore, a silicalite treated with aqueous ammonia was exposed to steaming at 400, 500, and 600°C and employed as a catalyst in the Beckmann rearrangement.

The decrease in activity after hydrothermal treatment is depicted in Fig. 8. Increasing the steaming temperature substantially reduced the conversion rate. The hydrothermal treatment did not seem to affect the selectivity to caprolactam. All four catalysts showed selectivities above 98%. These results indicate the annealing of active sites on the surface of the silicalite. The nature of the remaining sites on the catalyst, however, was not affected since the selectivity did not change. FT-IR measurements of the starting material Sil*(I-3.7 M) and its modification Sil(H_2O-600) gave additional information about these effects (Fig. 9).

The decrease in the sharp band at 3720 cm^{-1} is considered to be a side effect of the steaming procedure and probably does not influence the catalytic performance. More important is the observation that the broad adsorption around 3500 cm^{-1} was significantly diminished by the hydrothermal treatment, mainly due to the destruction of silanol nests. Thus, the loss of catalytic activity might be due to the smaller number of silanol nests on the surface of the steamed, as was anticipated.

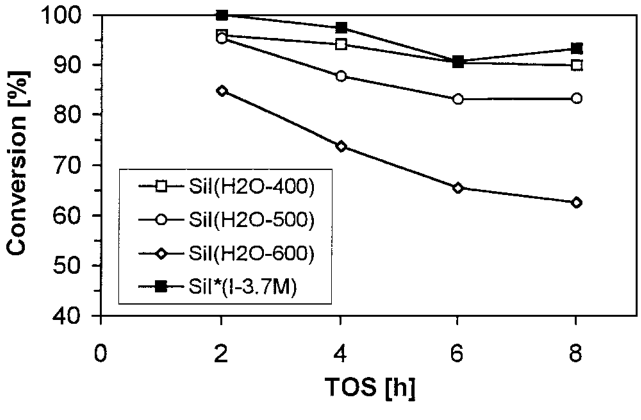

FIG. 8. Effect of steaming silicalite on conversion. Reaction: $T = 300°C$; $p = 0.1$ bar; WHSV = 0.33 h^{-1}; solvent, ethanol; carrier, nitrogen; catalysts, Sil(H_2O-400), Sil(H_2O-500), Sil(H_2O-600), and Sil*(I-3.7 M).

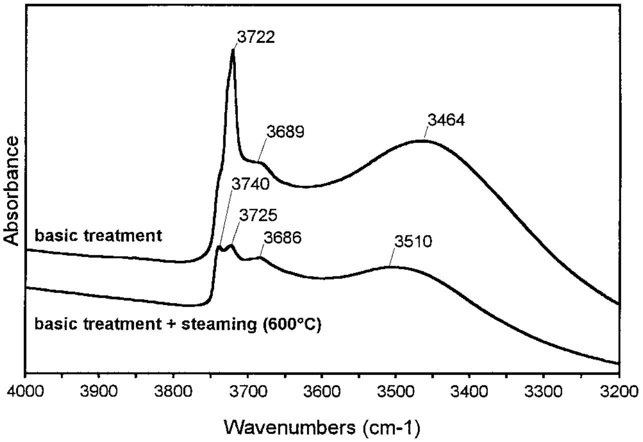

FIG. 9. FT-IR spectra of silicalites Sil*(I-3.7 M) and Sil(H_2O-600).

Analogous to the above investigations, these modifications of the silicalite were examined by nitrogen adsorption and X-ray diffractometry measurements. The isotherm of the starting material Sil*(I-3.7 M), which was treated with aqueous ammonia, did not show the characteristic step in the $0.2 < p/p^0 < 0.3$ region. This proved that the zeolite had an orthorhombic structure. In the three other isotherms, however, the step is present, most pronounced in the isotherm of the silicalite steamed at 600°C. Therefore, the hydrothermal treatment transforms the orthorhombic silicalite into the monoclinic form. This effect was due to the destruction of defective sites caused by the reinsertion of silicium atoms into the framework as mentioned above. This structural change is also visible in the XRD patterns of these silicalites. With an increase in the steaming temperature, the single peak at $2\theta = 24.5°$ was gradually divided into two single peaks, indicating the structural change from orthorhombic to monoclinic. The extent of this effect was most pronounced in the pattern of the Sil(H_2O-600), which was treated with the highest steaming temperature.

Although the annealing of some defective sites, i.e., silanol nests, was shown, it is obvious from the high selectivities obtained with the steamed silicalites that the remaining active sites were still hydrogen-bonded vicinal silanols and silanol nests. These latter results might again indicate the high efficiency of the silanol nests for the activity and selectivity in the heterogeneously catalyzed Beckmann rearrangement over silicalite catalysts.

Amorphous silica was inactive for the Beckmann rearrangement of cyclohexanone oxime, showing only poor selectivity to ε-caprolactam. Treatment with aqueous hydrochloric acid resulted in a substantial improvement in catalytic performance, accompanied by the appearance of vicinal hydrogen-bonded silanol groups. These silanols were superior to their terminal counterparts as active sites for the rearrangement reaction, mainly due to their slightly higher acidity.

On the ordered surface of a crystalline silicalite with numerous defective sites, these hydrogen-bonded silanols were, in part, arranged as silanol nests. A basic treatment with aqueous ammonia increased the number of these nests, whereas the starting material only featured terminal silanols. A side effect of these framework faults was the structural change from monoclinic to orthorhombic, which was observed by nitrogen sorption and XRD measurements. The presence of the silanol nests on the silicalite catalyst surface seems to strongly enhance conversion and selectivity to caprolactam. This strongly suggests that these nests are the most favorable sites for the Beckmann rearrangement. This assumption was supported when a silicalite, previously treated with aqueous ammonia, was subjected to hydrothermal treatment. This procedure led to the creation of defective sites, i.e., silanol nests, that were annealed, resulting in a significant loss of catalytic activity in the reaction.

ACKNOWLEDGMENTS

The authors greatly appreciate continued support by Degussa AG Hanau, Germany. Furthermore, we thank Mr. J. P. M. Niederer for synthesizing the silicalite and Mr. K. Vaessen for carrying out the nitrogen adsorption and XRD measurements.

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