



# In situ solid-state NMR investigations of the vapor-phase Beckmann rearrangement of $^{15}\text{N}$ -cyclohexanone oxime on MFI-type zeolites and mesoporous SBA-15 materials in the absence and presence of the additive $^{13}\text{C}$ -methanol

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## ABSTRACT

The stepwise conversion of  $^{15}\text{N}$ -cyclohexanone oxime into  $\epsilon$ -caprolactam via the vapor-phase Beckmann rearrangement on silicalite-1 ( $n_{\text{Si}}/n_{\text{Al}} = 1700$ ), siliceous SBA-15 ( $n_{\text{Si}}/n_{\text{Al}} = 1800$ ), H-ZSM-5 ( $n_{\text{Si}}/n_{\text{Al}} = 14$ ), and [Al]SBA-15 ( $n_{\text{Si}}/n_{\text{Al}} = 8.7$ ) in the absence and presence of  $^{13}\text{C}$ -methanol was investigated by solid-state  $^{15}\text{N}$  and  $^{13}\text{C}$  CP/MAS NMR spectroscopy. The MFI-type zeolites and SBA-15 materials are characterized by different acid strengths and pore diameters. The surface OH concentrations in silicalite-1, SBA-15, H-ZSM-5, and [Al]SBA-15 materials were determined to 0.31, 2.81, 1.12, and 1.29  $\text{mmol g}^{-1}$ , respectively.  $^1\text{H}$ ,  $^{29}\text{Si}$ , and  $^{15}\text{N}$  MAS NMR measurements revealed that the Brønsted acidic OH groups of H-ZSM-5 and [Al]SBA-15 and the large concentration of  $\text{Q}^3$  silanol groups ( $\text{Si}(\text{OSi})_3\text{OH}$ ) in siliceous SBA-15 led to the formation of O-protonated  $\epsilon$ -caprolactam. On loading and heating of  $^{15}\text{N}$ -cyclohexanone oxime on H-ZSM-5 in the presence of methanol, water was formed via dehydration of methanol into dimethyl ether. These water molecules promoted the conversion of O-protonated  $\epsilon$ -caprolactam species into  $\epsilon$ -aminocaproic acid. In addition, on both silicalite-1 and H-ZSM-5 catalysts, partial conversion of methanol into hydrocarbons, such as isobutane, was observed. Furthermore, isopropylamine was formed on silicalite-1 by the reaction of isobutane and byproducts of the Beckmann rearrangement, such as hydroxylamine. In contrast, no influence and conversion of methanol were found during the Beckmann rearrangement of  $^{15}\text{N}$ -cyclohexanone oxime on the mesoporous SBA-15 and [Al]SBA-15 materials.

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## 1. Introduction

The principal raw material in the manufacture of nylon-6 fibers,  $\epsilon$ -caprolactam, is produced mainly via the liquid-phase Beckmann rearrangement reaction [1–3]. The conventional process has two important disadvantages: the production of large amounts of ammonium sulfate as a byproduct and the corrosive reaction medium due to the necessary use of sulphuric acid or oleum. The demand for environmentally benign processes is growing [4,5]. The new synthesis method for the production of  $\epsilon$ -caprolactam is the vapor-phase Beckmann rearrangement of cyclohexanone oxime on solid catalysts. This route has gained increasing interest as an environmentally, economically, and energetically favorable process [1–5]. In the first industrial application, the vapor-phase Beckmann rearrangement process is performed on siliceous MFI zeolite as a catalyst, with methanol vapor used as an additive in this reaction system [1,2].

Up to now, various solid catalysts, including zeolites [6–9] and mesoporous materials [10–13], have been investigated for the

vapor-phase Beckmann rearrangement of cyclohexanone oxime. The highest selectivity toward  $\epsilon$ -caprolactam was achieved by using MFI-type zeolites with high silica content [1–3,6]. However, there has been debate concerning the nature (silanol or bridging OH groups) and location (external or internal surface) of the active sites present in the catalysts [1,2,6,14–17]. Recent solid-state NMR [18–20] and in situ FT-IR [21] investigations showed that both silanol and bridging OH groups are accessible and active in the reaction. From adsorption [22], theoretical [1,2], and solid-state NMR [18] studies, it has been concluded that the reactant cyclohexanone oxime is able to penetrate into the pores of MFI-zeolites and can be converted in these pores. On the other hand, some investigators have posited that weakly acidic silanol groups or silanol nests near the pore mouth of MFI-type zeolite are more selective toward  $\epsilon$ -caprolactam. Generally, bridging hydroxyl groups, such as in H-ZSM-5, have been found to be less selective [1,2,6].

Previous investigations have shown that a significantly improved selectivity toward  $\epsilon$ -caprolactam can be achieved by using solvents or additives [1,2,23–27]. Among the various solvents used in the Beckmann rearrangement of cyclohexanone oxime, the application of polar solvents, such as methanol, has led to lower catalyst deactivation rates and higher selectivities toward the desired

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product compared with those achieved with nonpolar solvents, such as benzene [23–27]. Investigations into the role of additives have found that the improved selectivity could be due to the blockage of silanols at the outer surface of silicalite-1 particles [1–3]. This finding is supported by FT-IR studies showing the reaction of terminal silanols with methanol to methoxy species [3]. Another explanation for the improved selectivity is the effect of the polarity of methanol molecules and of their OH groups [23–27]. Because polar solvents increase the desorption rate of  $\epsilon$ -caprolactam by decreasing the contact time on the catalyst surface, the solvents also minimize catalyst deactivation [23–27].

Although recent solid-state NMR [18–20] and theoretical investigations [18] have revealed the formation of reaction intermediates, products, and byproducts of the reaction, the adsorption (protonated or nonprotonated) and reaction behavior of reactants and products on silanol and bridging OH groups in different catalysts remain unclear and merit further investigation. In addition, the literature on the influence of additives on the species (reactants, products, and byproducts) formed during the Beckmann rearrangement, the adsorption and desorption behavior of these species in the absence and presence of methanol, and the conversion of additives at different reaction temperatures is very scarce and controversial. In the present work, we studied the adsorption and reaction behavior of the species formed via the vapor-phase Beckmann rearrangement of  $^{15}\text{N}$ -cyclohexanone oxime on MFI-type zeolites and mesoporous SBA-15 materials by solid-state  $^{15}\text{N}$  CP/MAS NMR spectroscopy. To study the influence of the additive methanol,  $^{15}\text{N}$  CP/MAS NMR spectra of  $^{15}\text{N}$ -oxime/catalyst mixtures in the absence and presence of  $^{13}\text{C}$ -methanol were recorded. Furthermore, the conversion of methanol during the conversion of  $^{15}\text{N}$ -oxime/catalyst mixtures was investigated by  $^{13}\text{C}$  CP/MAS NMR spectroscopy.

## 2. Experimental

### 2.1. Materials

#### 2.1.1. Synthesis of silicalite-1

Silicalite-1 catalyst was synthesized as described previously [22]. Initially, 31.50 g of demineralized water and 10.83 g of ammonium hydroxide were combined in a beaker, and then 12.00 g of silicic acid hydrate powder ( $\geq 99\%$ , Fluka) was slowly added to the mixture under strong stirring. Finally, 22.77 g of tetrapropylammonium hydroxide (1.0 M, Aldrich) was added, and the resulting mixture was stirred for another 3 h. The synthesis solution was then transferred into a stainless steel autoclave with a Teflon insert and heated at 448 K under permanent shaking for 28 h. The product was recovered by filtration, washed thoroughly with deionized water, dried at 353 K for 24 h, and then calcined for 6 h at 823 K in a flow of synthetic air (20 vol% oxygen, 60 l/h).

#### 2.1.2. Synthesis of H-ZSM-5

H-ZSM-5 ( $n_{\text{Si}}/n_{\text{Al}} = 14$ ) zeolite was synthesized as described previously [28]. The typical procedure comprised two steps: seed gel preparation and synthesis gel preparation. The seed gel was prepared by dissolving and thoroughly mixing 1.38 g of sodium hydroxide (99%, Merck) and 11.70 g of tetrapropylammonium hydroxide (1.0 M, Aldrich) in 71.03 g of distilled water. Then 15.89 g of silicic acid hydrate ( $\geq 99\%$ , Fluka) was added to this mixture in portions under strong stirring. When all of the silicic acid had been added, the mixture was stirred for 1 h at ambient temperature and then at 373 K for another 16 h. For synthesis gel preparation, 0.88 g of sodium hydroxide and 1.03 g of sodium aluminate (Riedel-de-Häen) were dissolved and mixed thoroughly in 86.78 g of distilled water. To this mixture, 11.31 g of silicic acid was added in portions under stirring. When all of the silicic acid

had been added, the mixture was stirred vigorously for 1 h at ambient temperature. Then 5.00 g of seed gel from the first step was added to the mixture and stirred for another 1 h. The mixture was then transferred to an autoclave with a Teflon insert and heated at 453 K for 40 h. The product was recovered by filtration, washed thoroughly with deionized water, dried at 353 K for 24 h, and then calcined for 6 h at 823 K in a flow of synthetic air (20 vol% oxygen, 60 l/h). To obtain H-ZSM-5, the calcined material was ion-exchanged with a 0.40 M ammonium nitrate solution for 6 h and then with a 0.10 M ammonium nitrate solution for 12 h at 353 K. After ion exchange, the material was calcined at 773 K.

#### 2.1.3. Synthesis of siliceous SBA-15

The typical procedure for synthesizing the siliceous SBA-15 material [29] is as follows. First, 6.00 g of triblock copolymer ( $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ ) was dissolved in 29.40 g of hydrochloric acid (37%, concentrated). To this mixture, 192.00 g of demineralized water was added. Finally, 13.20 g of tetraethylortho silicate (98%, Aldrich) was added dropwise under stirring. The final mixture was stirred at room temperature for 10 min and then at 313 K for 24 h. Finally, the mixture was transferred into a stainless steel autoclave and heated at 373 K for 24 h. The product was recovered by filtration, washed thoroughly with deionized water, dried at 353 K for 24 h, and then calcined for 6 h at 823 K in a flow of synthetic air (20 vol% oxygen, 60 l/h).

#### 2.1.4. Synthesis of [Al]SBA-15

To synthesize the aluminum-containing SBA-15 material ([Al]SBA-15) [30,31], 4.40 g of triblock copolymer ( $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ ) was dissolved in 118.00 g of hydrochloric acid (0.1%, concentrated). To this mixture, 7.00 g of tetramethylortho silicate ( $>99\%$ , Fluka) was added dropwise under stirring, along with 1.00 g of aluminumtriisopropylate ( $>98\%$ , Merck) in 10.00 g of hydrochloric acid, and the resulting mixture was stirred at 313 K for 24 h. After the pH of the mixture was adjusted to 7.00 via the addition of ammonium hydroxide solution, the mixture was transferred into a stainless steel autoclave and heated at 373 K for 24 h. The product was recovered by filtration, washed thoroughly with deionized water, dried at 353 K for 24 h, and then calcined for 6 h at 823 K in a flow of synthetic air (20 vol% oxygen, 60 l/h).

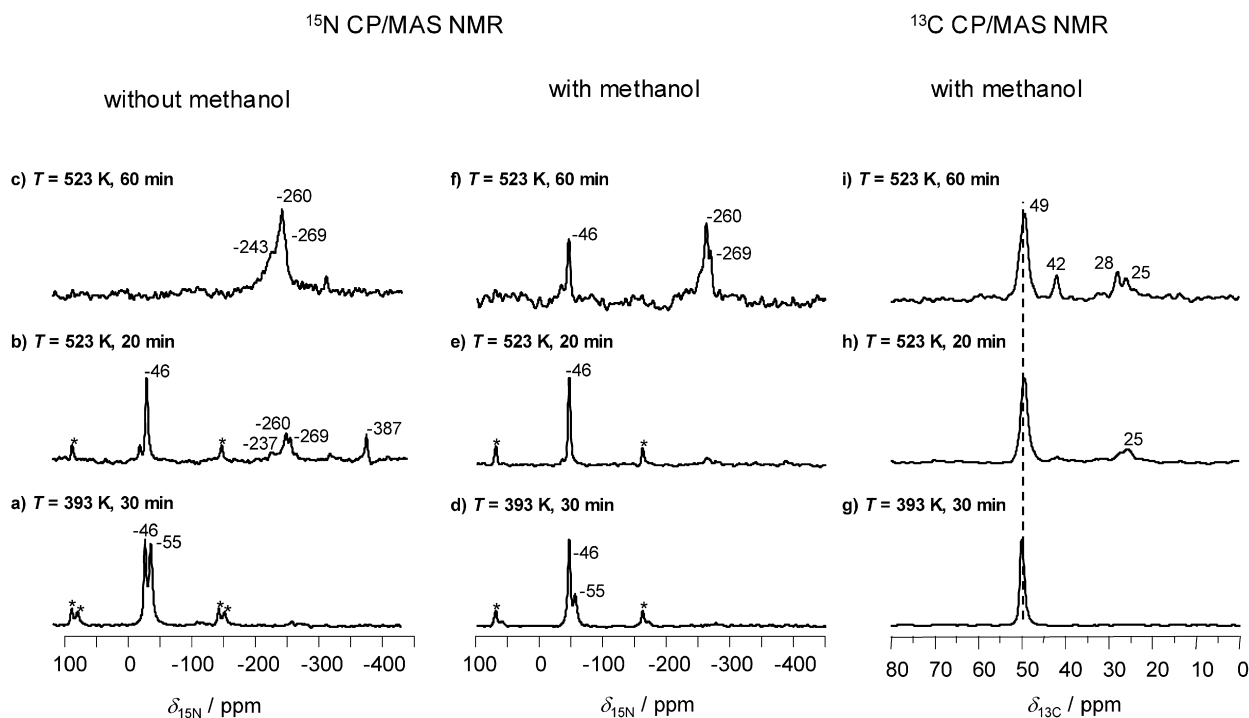
#### 2.1.5. Synthesis of $^{15}\text{N}$ -labeled cyclohexanone oxime

Organic synthesis of the reactant molecule (i.e.,  $^{15}\text{N}$ -cyclohexanone oxime) was accomplished as described previously [19].

### 2.2. Catalyst characterization

The catalysts used in the present investigations were characterized by X-ray diffraction (XRD) (Bruker D8), ICP/OES (Varian),  $\text{N}_2$  adsorption (Micrometrics ASAP 2010), and solid-state NMR spectroscopy (Bruker MSL 400). The XRD patterns of these catalysts were identical with the patterns reported in the literature [29–32]. The physicochemical properties of the catalysts, including  $n_{\text{Si}}/n_{\text{Al}}$  ratio, concentration of surface hydroxyl groups ( $n_{\text{OH}}$ ), BET surface areas, pore volume, and average pore diameters, are presented in Table 1. The OH concentration given in Table 1 (column 3) was obtained by quantitative evaluation of the  $^1\text{H}$  MAS NMR spectra of the dehydrated samples.

Before the solid-state  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{15}\text{N}$  NMR measurements, all of the catalysts were dehydrated under vacuum ( $p < 10^{-2}$  mbar) at 723 K for 12 h and sealed in glass tubes. Mixtures of  $^{15}\text{N}$ -cyclohexanone oxime and dehydrated silicalite-1 or H-ZSM-5 were prepared as follows. First, 20 mg of  $^{15}\text{N}$ -cyclohexanone oxime was evacuated at room temperature and mixed with ca. 300 mg of dehydrated zeolite (silicalite-1 or H-ZSM-5) in a glove box under dry nitrogen. In the case of mixtures of  $^{15}\text{N}$ -cyclohexanone oxime



**Fig. 1.**  $^{15}\text{N}$  CP/MAS NMR spectra recorded upon conversion of  $^{15}\text{N}$ -cyclohexanone oxime on silicalite-1 ( $n_{\text{Si}}/n_{\text{Al}} = 1700$ ) in the absence (left) and presence (middle) of  $^{13}\text{C}$ -methanol.  $^{13}\text{C}$  CP/MAS NMR spectra (right) show the conversion of  $^{13}\text{C}$ -methanol. The reaction temperatures and heating times are given in the figure. Asterisks in the NMR spectra denote spinning sidebands.

**Table 1**  
Physiochemical properties of the catalysts used in this study

Catalyst	$n_{\text{Si}}/n_{\text{Al}}$	$n_{\text{OH}}$ (mmol g $^{-1}$ )	BET surface area (m $^2$ g $^{-1}$ )	Pore volume (cm $^3$ g $^{-1}$ )	Average pore diameter (nm)
Silicalite-1	1700	0.31	365	0.20	0.55 <sup>a</sup>
H-ZSM-5	14	1.12	338	0.16	0.55 <sup>a</sup>
SBA-15	1800	2.81	986	1.00	5.65
[Al]SBA-15	8.7	1.29	672	1.54	8.97

<sup>a</sup> According to Ref. [32].

and dehydrated mesoporous catalysts (SBA-15 or [Al]SBA-15), the amounts of  $^{15}\text{N}$ -oxime and catalysts used were 15 and 150 mg, respectively. To study the influence of the additive,  $^{13}\text{C}$ -methanol ( $^{13}\text{C}$ -enrichment of 99%, chemical purity of 98%+, purchased from Cambridge Isotope Laboratories, Inc.) was adsorbed on the  $^{15}\text{N}$ -oxime/catalyst mixtures at a partial pressure of 70 mbar using a vacuum line. The methanol loadings of the  $^{15}\text{N}$ -oxime/silicalite-1,  $^{15}\text{N}$ -oxime/SBA-15,  $^{15}\text{N}$ -oxime/H-ZSM-5, and  $^{15}\text{N}$ -oxime/[Al]SBA-15 mixtures were 0.7, 1.4, 0.7, and 1.4 mmol g $^{-1}$ , respectively. Subsequently, the samples were transferred into 7-mm rotors for MAS NMR investigation. Before the  $^{13}\text{C}$  and  $^{15}\text{N}$  CP/MAS NMR spectra were recorded at room temperature, the aforementioned mixtures were heated to 393–523 K for the durations specified in the figures.

$^1\text{H}$  MAS NMR spectra of the dehydrated samples were obtained on a Bruker MSL 400 spectrometer at a resonance frequency of 400.13 MHz with sample spinning of 8.0 kHz. The spectra were recorded using a pulse length of 2.1  $\mu\text{s}$  and a recycle delay of 10 s.  $^{15}\text{N}$  and  $^{13}\text{C}$  CP/MAS NMR spectra of the reaction mixtures were recorded at resonance frequencies of 40.53 and 100.58 MHz, respectively, and with sample spinning rates of 3.5–4.7 kHz. CP/MAS NMR spectra were obtained with a contact period of 5 ms and a recycle delay of 2 s.  $^{15}\text{N}$  and  $^{13}\text{C}$  CP/MAS NMR spectra were referenced to nitromethane (0.0 ppm) and tetramethylsilane (0.0 ppm), respectively.  $^{29}\text{Si}$  MAS NMR measurements were performed at a resonance frequency of 79.5 MHz with a rotation frequency of

4 kHz. The dipolar decoupling (HPDEC) technique was applied with a pulse length of 5  $\mu\text{s}$  and a repetition time of 30 s.

### 3. Results and discussion

#### 3.1. Beckmann rearrangement of $^{15}\text{N}$ -oxime on silicalite-1 in the absence and presence of $^{13}\text{C}$ -methanol as an additive

Silicalite-1 ( $n_{\text{Si}}/n_{\text{Al}} = 1700$ ) is an MFI-type zeolite containing silanol groups, but no bridging OH groups act as strong Brønsted acid sites. This catalyst is known to be weakly acidic. The  $^{15}\text{N}$  CP/MAS NMR spectra shown in Fig. 1 (left and middle) were recorded after the conversion of  $^{15}\text{N}$ -cyclohexanone oxime into  $\epsilon$ -caprolactam with and without the presence of  $^{13}\text{C}$ -methanol as an additive. The assignments of the  $^{15}\text{N}$  CP/MAS NMR signals observed in this work are summarized in Table 2. The  $^{15}\text{N}$  CP/MAS NMR signal at  $-55$  ppm shown in Figs. 1a and 1d is due to unconverted  $^{15}\text{N}$ -cyclohexanone oxime [19,33]. The additional signal at  $-46$  ppm is a result of the interaction of  $^{15}\text{N}$ -oxime with silicalite-1 [19,20]. The appearance of new signals when the  $^{15}\text{N}$ -oxime/silicalite-1 mixture containing no methanol was heated to 523 K for 20 and 60 min (Figs. 1b and 1c, respectively) indicates the conversion of  $^{15}\text{N}$ -oxime. The corresponding signals at  $-260$ ,  $-269$ , and  $-387$  ppm are caused by the formation of  $\epsilon$ -caprolactam, hydroxylamine, and amines, respectively [19,33]. Due to the residual line width of solid-state NMR spectroscopy, the signal of hydroxylamine ( $-269$  ppm) could not be resolved in Fig. 1c, but it occurs as a broad shoulder. In addition, a small peak in the range of  $-237$  to  $-243$  ppm was seen (Figs. 1b and 1c). Tentatively, this signal has been attributed to nitrilium ions [19,33] or to O-protonated  $\epsilon$ -caprolactam [18]. The latter assignment has been supported by theoretical calculations [18]. In agreement with previous studies, the formation of O-protonated  $\epsilon$ -caprolactam is more favorable than the formation of N-protonated  $\epsilon$ -caprolactam [17,34]; therefore, assigning the signal at  $-237$  ppm to O-protonated  $\epsilon$ -caprolactam is appropriate. However, it has

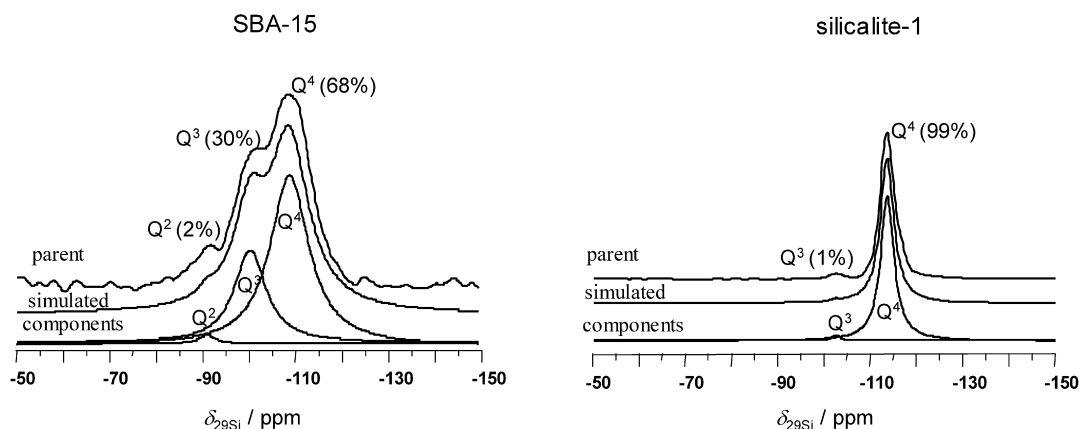
$^{29}\text{Si}$  HPDEC MAS NMR

Fig. 2.  $^{29}\text{Si}$  HPDEC MAS NMR spectra of siliceous SBA-15 (left) and silicalite-1 (right) and their simulation.

Table 2

Assignments of  $^{15}\text{N}$  CP/MAS NMR signals of the species observed during the vapor-phase Beckmann rearrangement of  $^{15}\text{N}$ -cyclohexanone oxime

$\delta_{^{15}\text{N}}$ (ppm)	Assignments	Ref.
–30 to –46	$^{15}\text{N}$ -cyclohexanone oxime interacting with SiOH groups of zeolites and mesoporous materials via hydrogen bonding	[19,20,33]
–51 to –62	Unconverted $^{15}\text{N}$ -cyclohexanone oxime on zeolites and mesoporous materials	[18,19,33]
–145 to –160	N-protonated cyclohexanone oxime, exclusively formed on Brønsted acid sites of zeolites and mesoporous materials	[18–20,33]
–237 to –243	O-protonated $\epsilon$ -caprolactam on $\text{Q}^3$ silanol groups ( $\text{Si}(\text{OSi})_3\text{OH}$ ) and Brønsted acid sites	[18]
–255 to –262	Physically adsorbed $\epsilon$ -caprolactam on SiOH groups and Brønsted acid sites	[18–20,33]
–269 to –280	Hydroxylamine	[19,33]
–347 to –364	N-protonated $\epsilon$ -caprolactam, or non- or N-protonated $\epsilon$ -aminocaproic acid, exclusively formed on Brønsted acid sites	[19,33,44]
–375 to –387	Amines formed on SiOH groups of siliceous zeolites and mesoporous materials	[18,19,33]

been reported that these species are formed exclusively on materials with strong Brønsted acid sites, such as H-ZSM-5 and mordenite [17,18]. In contrast, in our earlier work [19] as well as in the present study, we observed formation of the O-protonated  $\epsilon$ -caprolactam on weakly, moderately, and strongly acidic catalysts. Nevertheless, the intensity of the signal at –237 ppm was weaker for silicalite-1 (Figs. 1b and 1c) than for H-ZSM-5 (see Figs. 4b and 4c). We explain the reason for these differing signal intensities in Section 3.2.

We found slightly different spectra when the  $^{15}\text{N}$ -oxime/silicalite-1 mixture containing  $^{13}\text{C}$ -methanol was heated to 523 K for 20 and 60 min (Figs. 1e and 1f, respectively) compared with the experiments performed without  $^{13}\text{C}$ -methanol (Figs. 1b and 1c). In this case, heating at 523 K for 60 min was required to achieve conversion of  $^{15}\text{N}$ -cyclohexanone oxime (Fig. 1f), indicating a lower catalyst reactivity. This could be due to a total coverage of silanol groups by methanol and partial conversion of methanol into surface methoxy silanol groups. In addition, due to the presence of methanol as an additive, O-protonated  $\epsilon$ -caprolactam (–237 to –243 ppm) and the amines (–387 ppm) were not observed in the  $^{15}\text{N}$  CP/MAS NMR spectra shown in Figs. 1e and 1f. This indicates that the enhanced selectivity to  $\epsilon$ -caprolactam in the gas phase could be caused by a decrease in the energy barrier for the product desorption. No side reactions leading to the formation of amines occurred with methanol as an additive. This finding is

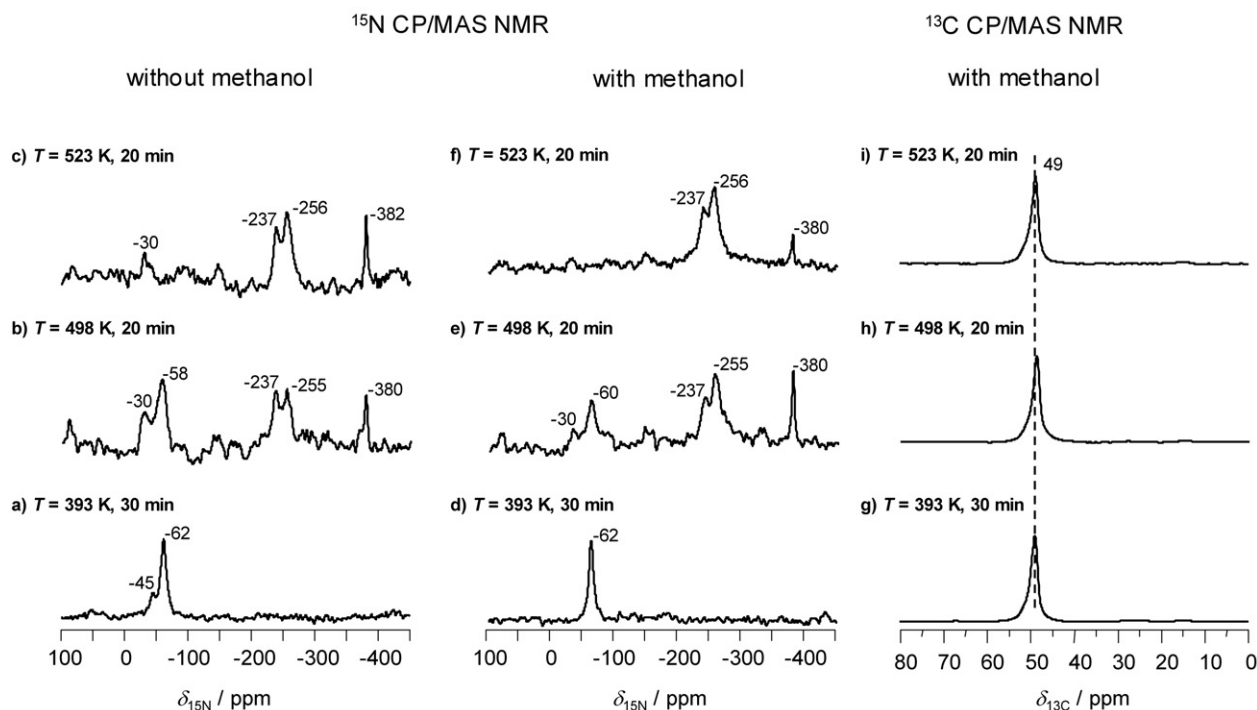
supported by catalytic studies of Ichihashi and Kitamura [3], who reported that the selectivity to  $\epsilon$ -caprolactam increased with increasing  $n_{\text{Si}}/n_{\text{Al}}$  ratio for silicalite-1 compared with H-ZSM-5 and was enhanced for silicalite-1 from ca. 75% to 95% by the addition of methanol to the reaction system [3].

The  $^{13}\text{C}$  CP/MAS NMR spectra of the  $^{15}\text{N}$ -oxime/silicalite-1 mixture containing  $^{13}\text{C}$ -methanol (Figs. 1g–1i, right) consisted of a signal at ca. 49 ppm, attributed to  $^{13}\text{C}$ -methanol. Due to the residual line width of MAS NMR spectroscopy, signals due to methoxy groups (48–50 ppm) are covered by the signal of methanol (49 ppm) [35,36]; however, the spectra recorded at 523 K (Figs. 1h and 1i) showed peaks at 25, 28, and 42 ppm, indicating the conversion of methanol into hydrocarbons (e.g., isobutane) and alkylamines (e.g., isopropylamine) [37–40]. Isopropylamine (42 ppm) may be formed via the reaction of isobutane with hydroxylamine, which is formed as a byproduct of the Beckmann rearrangement. The conversion of methanol on weakly acidic silicalite-1 may be due to (i) high methanol coverage ( $0.7 \text{ mmol g}^{-1}$ ) with respect to the number of silanol groups ( $n_{\text{OH}} = 0.31 \text{ mmol g}^{-1}$ ) and electronic confinement effects [41] for methanol clusters in the micropore system of silicalite-1, and (ii) the effect of residual framework aluminum atoms ( $n_{\text{Si}}/n_{\text{Al}} = 1700$ ).

### 3.2. Beckmann rearrangement of $^{15}\text{N}$ -oxime on siliceous SBA-15 in the absence and presence of $^{13}\text{C}$ -methanol as an additive

The mesoporous SBA-15 materials studied here are characterized by large pore diameters of ca. 6 nm. Therefore, no pore diffusion limitations are associated with respect to either the reactant,  $^{15}\text{N}$ -cyclohexanone oxime, or the reaction product,  $\epsilon$ -caprolactam. On the other hand, the concentration of silanol groups was significantly higher in SBA-15 ( $n_{\text{OH}} = 2.81 \text{ mmol g}^{-1}$ ) compared with silicalite-1 ( $n_{\text{OH}} = 0.31 \text{ mmol g}^{-1}$ ). Furthermore, different silicon environments, such as  $\text{Q}^4$  ( $\text{Si}(\text{OSi})_4$ ),  $\text{Q}^3$  ( $\text{Si}(\text{OSi})_3\text{OH}$ ), and  $\text{Q}^2$  ( $\text{Si}(\text{OSi})_2(\text{OH})_2$ ) species, were found in mesoporous SBA-15 (Fig. 2, left), whereas exclusively  $\text{Q}^4$  and  $\text{Q}^3$  species were present in silicalite-1 (Fig. 2, right). According to Rosenholm et al. [42], the silanol groups of  $\text{Q}^3$  species ( $\text{pK}_a$  values of 2–4.5 [42]) are more acidic than those of  $\text{Q}^2$  species ( $\text{pK}_a$  value of ca. 8.5 [42]). As shown in Fig. 2, the relative intensity of  $\text{Q}^3$  silanol groups ( $\text{Si}(\text{OSi})_3\text{OH}$ ) in SBA-15 (30%) was much higher than the relative intensity of these OH groups in silicalite-1 (1%). Consequently, it mechanistic investigations on SBA-15 ( $n_{\text{Si}}/n_{\text{Al}} = 1800$ ) were of interest.

Fig. 3 illustrates the progress of the Beckmann rearrangement reaction of the  $^{15}\text{N}$ -oxime/SBA-15 mixture in the absence and pres-



**Fig. 3.**  $^{15}\text{N}$  CP/MAS NMR spectra recorded upon conversion of  $^{15}\text{N}$ -cyclohexanone oxime on siliceous SBA-15 ( $n_{\text{Si}}/n_{\text{Al}} = 1800$ ) in the absence (left) and presence (middle) of  $^{13}\text{C}$ -methanol.  $^{13}\text{C}$  CP/MAS NMR spectra (right) show the presence of  $^{13}\text{C}$ -methanol. The reaction temperatures and heating times are given in the figure. Asterisks in the NMR spectra denote spinning sidebands.

ence of  $^{13}\text{C}$ -methanol as an additive. Table 2 presents the assignments of the  $^{15}\text{N}$  CP/MAS NMR signals. The  $^{15}\text{N}$  CP/MAS NMR signal at ca.  $-60$  ppm shown in Figs. 3a, 3b, 3d, and 3e is due to unconverted oxime. Because silicalite-1 and siliceous SBA-15 are weakly acidic catalysts, the signals at  $-30$  to  $-45$  ppm are assigned to the oxime interacting with silanol groups via hydrogen bonding [19,20]. New  $^{15}\text{N}$  CP/MAS NMR signals occurred on heating the mixtures to 498 and 523 K in the absence and presence of methanol, indicating the conversion of the  $^{15}\text{N}$ -cyclohexanone oxime (Figs. 3b, 3c, 3e, and 3f). The assignments of these signals are similar to those for silicalite-1 (Table 2).

Moreover, the signal of O-protonated  $\epsilon$ -caprolactam species at ca.  $-237$  ppm was more pronounced and resolved in the spectra of SBA-15 (Figs. 3b, 3c, 3e, and 3f) than in the spectra of silicalite-1 (Figs. 1b and 1c). This could be due to the larger number of  $\text{Q}^3$  silanol groups in SBA-15 compared with silicalite-1. This high concentration of  $\text{Q}^3$  silanol groups with  $\text{p}K_{\text{a}}$  values of 2–4.5 [42] in SBA-15 is responsible for the formation of O-protonated  $\epsilon$ -caprolactam. In contrast, silicalite-1 contained much fewer  $\text{Q}^3$  silanol groups and exhibited very weak formation of O-protonated  $\epsilon$ -caprolactam (Figs. 1b and 1c). The  $^{15}\text{N}$  CP/MAS NMR spectra recorded upon heating of the  $^{15}\text{N}$ -oxime/SBA-15 mixtures in the absence and presence of methanol (Fig. 3) demonstrate no difference. This indicates that here, unlike in the case of silicalite-1, methanol did not affect the adsorbed species and the formation of amines (ca.  $-387$  ppm), byproducts of the Beckmann rearrangement. According to the results of  $^{15}\text{N}$  CP/MAS NMR spectroscopy, conversion of  $^{15}\text{N}$ -cyclohexanone oxime on SBA-15 occurred already at 498 K (Figs. 2b and 2e), that is, at a lower reaction temperature than on silicalite-1 (523 K), indicating the greater activity of the former material due to the greater number of  $\text{Q}^3$  silanol groups.

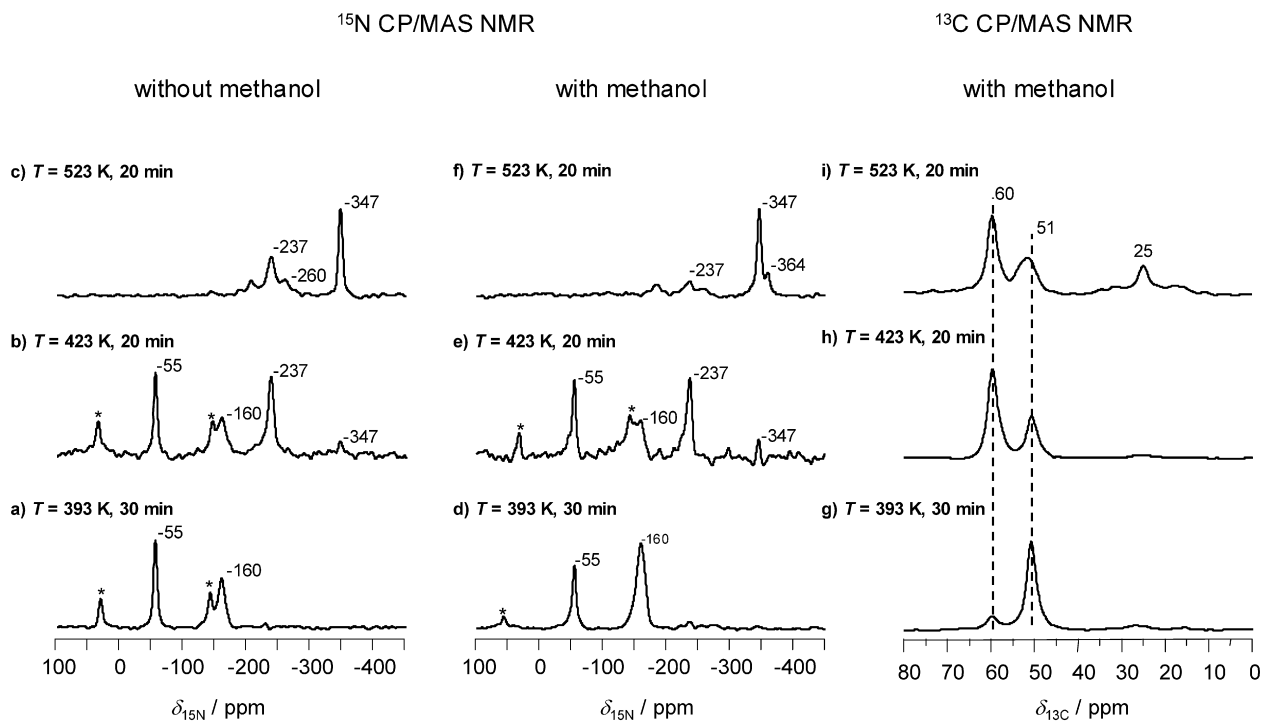
Previous catalytic studies of cyclohexanone oxime conversion on siliceous SBA-15 [13] and silicalite-1 [1–3] have indicated a much lower selectivity to  $\epsilon$ -caprolactam for the former catalyst. Considering the present  $^{15}\text{N}$  CP/MAS NMR investigation, the afore-

mentioned catalytic behavior may be explained by three phenomena: (i) on SBA-15, the product was adsorbed in the O-protonated state (signal at  $-237$  ppm), that is, adsorption of the reaction product was much stronger on SBA-15 than on silicalite-1; (ii) byproducts, such as amines (signals at  $-380$  ppm), formed on SBA-15; and (iii) the addition of methanol had no effect on the aforementioned species in the case of SBA-15.

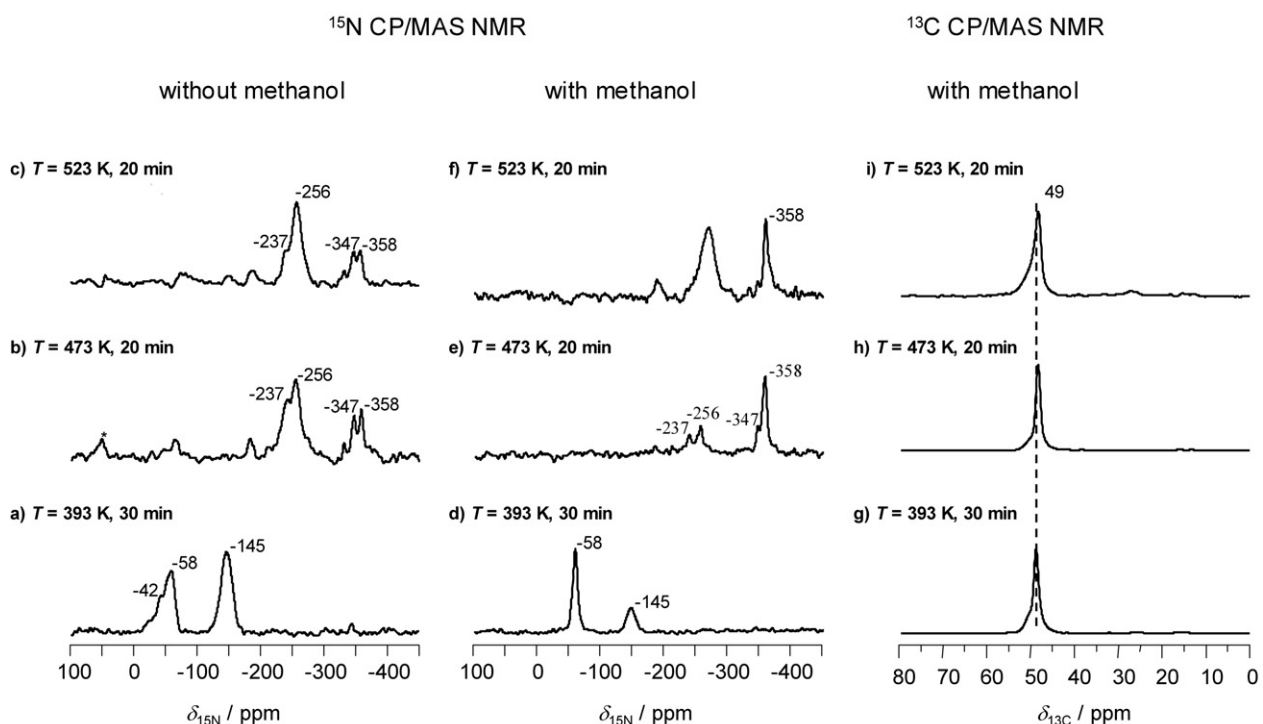
The  $^{13}\text{C}$  CP/MAS NMR spectra of the  $^{15}\text{N}$ -oxime/silicalite-1 mixture in the presence of methanol recorded on heating at different reaction temperatures (Figs. 2g–2i) consist of a single signal at 49 ppm due to  $^{13}\text{C}$ -methanol. This finding indicates that no conversion of methanol occurred on siliceous SBA-15, in contrast to silicalite-1. This may be due to the low methanol coverage ( $1.4 \text{ mmol g}^{-1}$ ) with respect to the large number of silanol groups ( $n_{\text{OH}} = 2.81 \text{ mmol g}^{-1}$ ) in SBA-15, as well as the lack of electronic confinement effects for the methanol molecules in the mesopores of this catalyst.

### 3.3. Beckmann rearrangement of $^{15}\text{N}$ -oxime on H-ZSM-5 and [Al]SBA-15 in the absence and presence of $^{13}\text{C}$ -methanol as an additive

Microporous H-ZSM-5 zeolite contains silanol groups as well as bridging OH groups acting as strong Brønsted acid sites. In contrast, the Brønsted acid sites of aluminum-containing mesoporous SBA-15 ([Al]SBA-15) are caused by terminal silanol groups in the vicinity of framework aluminum atoms [43]. In the vapor-phase Beckmann rearrangement of cyclohexanone oxime, [Al]SBA-15 is more selective to  $\epsilon$ -caprolactam than siliceous SBA-15 [13], whereas H-ZSM-5 is less selective than silicalite-1 [1–3,6]. Furthermore, the Brønsted acid sites of [Al]SBA-15 have lower acid strength compared with those of H-ZSM-5 [43]. Therefore, it is of interest to study the behavior of the different species formed on these materials via the Beckmann rearrangement of  $^{15}\text{N}$ -cyclohexanone oxime in the absence and presence of methanol. Figs. 4 and 5 show the  $^{15}\text{N}$  and  $^{13}\text{C}$  CP/MAS NMR spectra recorded on the Beckmann rearrangement of  $^{15}\text{N}$ -cyclohexanone oxime with



**Fig. 4.**  $^{15}\text{N}$  CP/MAS NMR spectra recorded upon conversion of  $^{15}\text{N}$ -cyclohexanone oxime on H-ZSM-5 ( $n_{\text{Si}}/n_{\text{Al}} = 14$ ) in the absence (left) and presence (middle) of  $^{13}\text{C}$ -methanol.  $^{13}\text{C}$  CP/MAS NMR spectra (right) show the conversion of  $^{13}\text{C}$ -methanol. The reaction temperatures and heating times are given in the figure. Asterisks in the NMR spectra denote spinning sidebands.

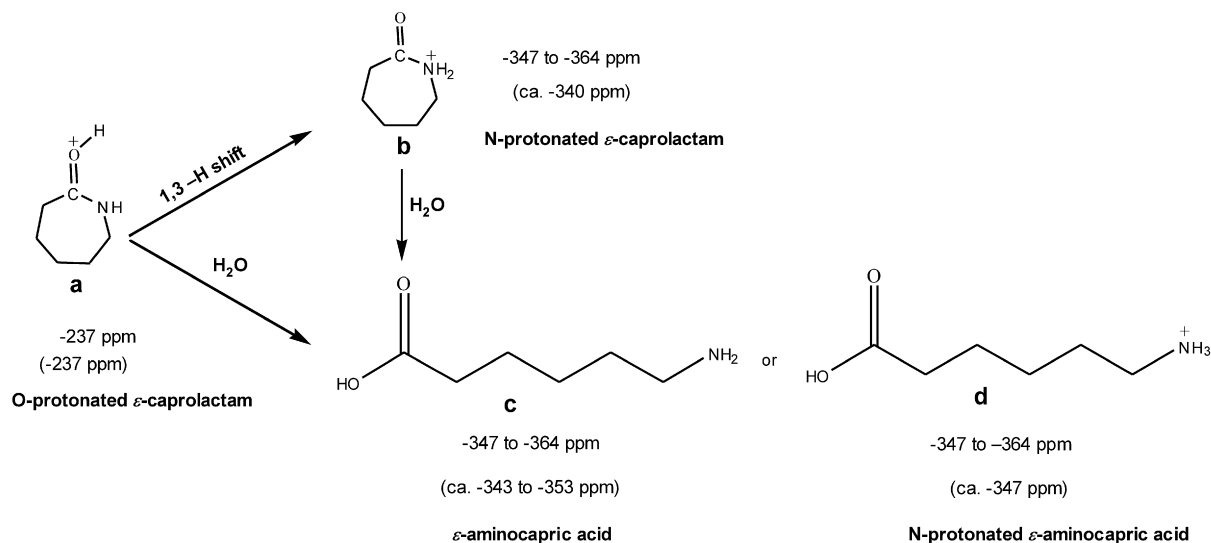


**Fig. 5.**  $^{15}\text{N}$  CP/MAS NMR spectra recorded upon conversion of  $^{15}\text{N}$ -cyclohexanone oxime on [Al]SBA-15 ( $n_{\text{Si}}/n_{\text{Al}} = 8.7$ ) in the absence (left) and presence (middle) of  $^{13}\text{C}$ -methanol.  $^{13}\text{C}$  CP/MAS NMR spectra (right) show the presence of  $^{13}\text{C}$ -methanol. The reaction temperatures and heating times are given in the figure. Asterisks in the NMR spectra denote spinning sidebands.

and without  $^{13}\text{C}$ -methanol on both H-ZSM-5 ( $n_{\text{Si}}/n_{\text{Al}} = 14$ ) and [Al]SBA-15 ( $n_{\text{Si}}/n_{\text{Al}} = 8.7$ ), respectively.

The  $^{15}\text{N}$  CP/MAS NMR spectra shown in Figs. 4a, 4b, 4d, and 4e consist of signals at  $-55$  and  $-160$  ppm due to unconverted and N-protonated  $^{15}\text{N}$ -cyclohexanone oxime, respectively [18–20,

33]. It is noteworthy that the N-protonation, occurring exclusively on Brønsted acid sites, always leads to a high-field shift (lower chemical shift values) of the resonance position [33]. In the spectra of the  $^{15}\text{N}$ -cyclohexanone oxime/[Al]SBA-15 mixture, the signals of unconverted oxime, oxime hydrogen bonded to SiOH groups, and



**Fig. 6.** Suggested mechanism of the conversion of O-protonated  $\epsilon$ -caprolactam on Brønsted acidic catalysts, such as H-ZSM-5 and [Al]SBA-15. The  $^{15}\text{N}$  CP/MAS NMR shift values represented without parentheses were obtained in this work, while the values in the parentheses were obtained from the NNMR predictor software [33] or literature [18,44].

N-protonated oxime adsorbed on Brønsted acidic OH groups appeared at  $-58$ ,  $-42$ , and  $-145$  ppm, respectively (Figs. 5a and 5d). After the mixture of  $^{15}\text{N}$ -cyclohexanone oxime and H-ZSM-5 was heated to  $423$ – $523$  K, the spectra exhibited different new signals, indicating the conversion of  $^{15}\text{N}$ -cyclohexanone oxime (Figs. 4b, 4c, 4e, and 4f). The weak signal at  $-260$  ppm (Fig. 4c) is due to  $\epsilon$ -caprolactam, the main reaction product of the Beckmann rearrangement [18–20,33]. In the spectra of [Al]SBA-15 (Figs. 5b, 5c, 5e, and 5f), the signal corresponding to  $\epsilon$ -caprolactam appeared at ca.  $-256$  ppm.

Furthermore, on the Brønsted acidic OH groups in H-ZSM-5 and [Al]SBA-15, the conversion of O-protonated  $\epsilon$ -caprolactam (Fig. 6a) into N-protonated  $\epsilon$ -caprolactam (Fig. 6b) and nonprotonated or N-protonated  $\epsilon$ -aminocaproic acid (Figs. 6c and 6d) was indicated by the signals at  $-347$  and  $-358$  to  $-364$  ppm, respectively (Figs. 4b, 4c, 4e, 4f and 5b, 5c, 5e, 5f). The signal assignments are given in Table 2. Because the  $^{15}\text{N}$  CP/MAS NMR signals of N-protonated  $\epsilon$ -caprolactam and nonprotonated or N-protonated  $\epsilon$ -aminocaproic acid occur in the same chemical shift range, distinguishing these products is difficult. It should be mentioned that these species are exclusively formed on Brønsted acid sites, but not on the silanol groups of silicalite-1 (Fig. 1, left and middle) and SBA-15 (Fig. 3, left and middle). In addition, the Brønsted acidic OH groups in H-ZSM-5 and [Al]SBA-15 also promote the  $1,3$ -H shift and hydration of O-protonated  $\epsilon$ -caprolactam (Fig. 6).

The hydration reaction of O-protonated  $\epsilon$ -caprolactam is further supported by the  $^{15}\text{N}$  CP/MAS NMR spectra shown in Figs. 4c and 4f. In the absence of methanol, the  $^{15}\text{N}$  CP/MAS NMR spectra of the  $^{15}\text{N}$ -oxime/H-ZSM-5 mixture heated at  $523$  K even showed a signal at  $-237$  ppm caused by O-protonated  $\epsilon$ -caprolactam adsorbed on bridging hydroxyl groups (Fig. 4c). When methanol was present in the  $^{15}\text{N}$ -cyclohexanone oxime/H-ZSM-5 mixture, almost complete conversion of O-protonated  $\epsilon$ -caprolactam was observed at  $523$  K (Fig. 4f), as indicated by the significantly decreased signal of O-protonated  $\epsilon$ -caprolactam at  $-237$  ppm. This finding demonstrates that water formed during the dehydration of methanol into dimethyl ether (DME) promoted the conversion of O-protonated  $\epsilon$ -caprolactam (Fig. 6). In contrast, due to the weakly acidic surface OH groups in silicalite-1 and SBA-15, further conversion of O-protonated  $\epsilon$ -caprolactam was suppressed. As a result, the signals in the range of  $-347$  to  $-364$  ppm (see Table 2 for the assignments) were not found in the  $^{15}\text{N}$  CP/MAS NMR spectra of the

$^{15}\text{N}$ -oxime/silicalite-1 (Fig. 1, left and middle) and  $^{15}\text{N}$ -oxime/SBA-15 (Fig. 3, left and middle) mixtures in the absence and presence of methanol.

Qualitative comparison of catalytic data available in the literature [3,6,13] with the results of the present  $^{15}\text{N}$  CP/MAS NMR study of the vapor-phase Beckmann rearrangement on Brønsted acidic catalysts, such as H-ZSM-5 and [Al]SBA-15, indicate two factors behind the decreased  $\epsilon$ -caprolactam selectivity compared with silicalite-1: (i) the formation of O-protonated and N-protonated  $\epsilon$ -caprolactam on the catalyst surface (i.e., of strongly adsorbed reaction products) and (ii) the formation of polymerization products, such as nonprotonated or N-protonated  $\epsilon$ -aminocaproic acid (Fig. 6).

The  $^{13}\text{C}$  CP/MAS NMR spectrum of the  $^{15}\text{N}$ -cyclohexanone oxime/H-ZSM-5 mixture in the presence of  $^{13}\text{C}$ -methanol recorded on heating at  $523$  K (Fig. 4i) demonstrated the conversion of methanol ( $51$  ppm) into dimethyl ether ( $60$  ppm) and hydrocarbons ( $25$  ppm). In agreement with the weak Brønsted acidity of [Al]SBA-15, no conversion of methanol was observed on this material (Figs. 5g to 5i).

#### 4. Conclusion

In this work, we studied the vapor-phase Beckmann rearrangement of  $^{15}\text{N}$ -cyclohexanone oxime on MFI-type zeolites and mesoporous SBA-15 materials in the absence and presence of methanol as an additive by  $^{15}\text{N}$  and  $^{13}\text{C}$  CP/MAS NMR spectroscopy. Our aim was to clarify the adsorption and reaction behavior of reaction intermediates, products, byproducts, and carbonaceous deposits. For this purpose, mixtures of  $^{15}\text{N}$ -cyclohexanone oxime with MFI-type zeolites and mesoporous SBA-15 materials were studied on heating to  $393$ – $523$  K. Our findings reveal that O-protonated  $\epsilon$ -caprolactam was formed on Brønsted acid sites of H-ZSM-5 and [Al]SBA-15 and on  $Q^3$  silanol groups ( $\text{Si}(\text{OSi})_3\text{OH}$ ) of silicalite-1 and siliceous SBA-15. On siliceous catalysts, the adsorption of  $\epsilon$ -caprolactam and the formation of O-protonated  $\epsilon$ -caprolactam depended on the number of  $Q^3$  silanol groups. Further conversion and hydration of O-protonated  $\epsilon$ -caprolactam were observed exclusively on Brønsted acidic catalysts, such as H-ZSM-5 and [Al]SBA-15. Due to the strong adsorption of the reaction product on siliceous SBA-15, [Al]SBA-15, and H-ZSM-5, as well as the formation of amines on siliceous SBA-15 and of polymerization products on [Al]SBA-15 and H-ZSM-5, the selectivity to  $\epsilon$ -caprolactam was lower than that on

silicalite-1. Furthermore, formation of the aforementioned byproducts leads to catalyst deactivation.

We used  $^{13}\text{C}$  MAS NMR spectroscopy to study the conversion of the additive methanol. On silicalite-1 and H-ZSM-5, hydrocarbons were formed and deposited at increasing reaction temperatures. Furthermore, the formation of isopropylamine was observed on silicalite-1 as a result of the reaction of isobutane and hydroxylamine, which is a byproduct of the Beckmann rearrangement. The water formed via the dehydration of methanol on H-ZSM-5 promoted the conversion of O-protonated  $\epsilon$ -caprolactam into nonprotonated or N-protonated  $\epsilon$ -aminocaproic acid. No methanol conversion was observed on the SBA-15.

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