

Beckmann Rearrangement of ^{15}N -Cyclohexanone Oxime on Zeolites Silicalite-1, H-ZSM-5, and H-[B]ZSM-5 Studied by Solid-State NMR Spectroscopy

V. R. Reddy Marthala, Yijiao Jiang, Jun Huang, Wei Wang,* Roger Gläser, and Michael Hunger*

Institute of Chemical Technology, University of Stuttgart, D-70550 Stuttgart, Germany

Received September 4, 2006; E-mail: michael.hunger@itc.uni-stuttgart.de; wang.wei@itc.uni-stuttgart.de

To replace the conventional method for synthesizing ϵ -caprolactam in concentrated sulfuric acid or oleum, the vapor-phase Beckmann rearrangement of cyclohexanone oxime on solid acid catalysts has received increasing interest as an environmentally benign process.^{1,2} It was found that high-silica ZSM-5 zeolite (silicalite-1)³ and boron-substituted zeolite ZSM-5 (H-[B]ZSM-5)⁴ are highly active and selective as catalysts for the transformation of cyclohexanone oxime to ϵ -caprolactam. In earlier studies, strong Brønsted acid sites in zeolites were suggested to be crucial in catalyzing this reaction by protonating the oxime.^{1,2} However, further investigations showed that weakly acidic silanol groups and T-vacancies are responsible for the high activity and selectivity toward the ϵ -caprolactam.^{1,2}

Recently, the possible reaction mechanism of the vapor-phase Beckmann rearrangement has been studied experimentally^{5,6} and theoretically.^{5,7,8} Utilizing ^{13}C and ^{15}N MAS NMR spectroscopy together with theoretical calculations, Fernandez et al.⁵ investigated the Beckmann rearrangement of acetophenone oxime on siliceous and aluminum-containing zeolites Beta. In the present work, the first solid-state NMR study of the Beckmann rearrangement of cyclohexanone oxime on the zeolites silicalite-1, H-ZSM-5, and H-[B]ZSM-5 and evidence for the formation of reaction intermediates and byproducts are reported.

Figure 1a shows the ^{15}N CP/MAS NMR spectrum of pure ^{15}N -cyclohexanone oxime, which was synthesized via the reaction of ^{15}N -hydroxylamine·HCl and cyclohexanone. The single signal at -55 ppm is due to the ^{15}N -label in cyclohexanone oxime. The ^{15}N CP/MAS NMR spectrum shown in Figure 1b was recorded after preparing the physical mixture of ^{15}N -cyclohexanone oxime and silicalite-1 and heating at 423 K. In addition to the signal at -55 ppm due to pure ^{15}N -cyclohexanone oxime, a new low-field signal appeared at -46 ppm. This signal, which does not occur without heating at 423 K, is due to ^{15}N -cyclohexanone oxime interacting with the SiOH groups of silicalite-1 via hydrogen bonding. A similar low-field shift of about 10 ppm was observed by Fernandez et al.⁵ for the hydrogen bonding of ^{15}N -acetophenone oxime with the SiOH groups of siliceous zeolite Beta.

Studying the interaction of ^{15}N -cyclohexanone oxime with the Brønsted acid sites of zeolite H-ZSM-5, the ^{15}N CP/MAS NMR spectrum of the physical mixture shows a new high-field signal at -160 ppm, which occurs already at room temperature (Figure 1c). This signal was assigned to ^{15}N -cyclohexanone oxime protonated by the acidic bridging OH groups (SiOHAl) in the vicinity of framework aluminum atoms in zeolite H-ZSM-5.^{5,6} In the ^{15}N CP/MAS NMR spectrum of the physical mixture of ^{15}N -cyclohexanone oxime and zeolite H-[B]ZSM-5 heated at 423 K, a high-field signal occurs at -153 ppm (Figure 1d). As expected for silanol groups in the vicinity of framework boron atoms (SiOH[B]) in zeolite H-[B]ZSM-5, which are characterized by a lower acid strength in comparison with the SiOHAl groups in zeolite H-ZSM-5, the signal

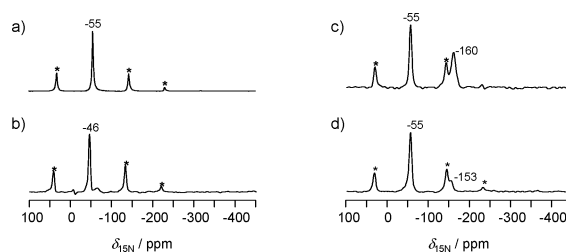


Figure 1. ^{15}N CP/MAS NMR spectra of pure ^{15}N -cyclohexanone oxime (a), ^{15}N -cyclohexanone oxime physically mixed with silicalite-1 and heated at 423 K (b), ^{15}N -cyclohexanone oxime physically mixed with H-ZSM-5 (c), and ^{15}N -cyclohexanone oxime physically mixed with H-[B]ZSM-5 and heated at 423 K (d). All spectra were recorded at room temperature. Asterisks denote spinning sidebands.

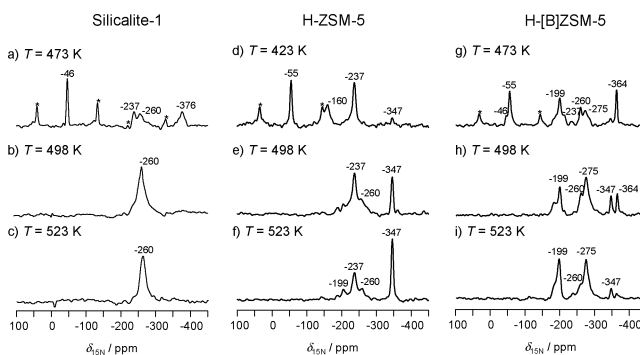


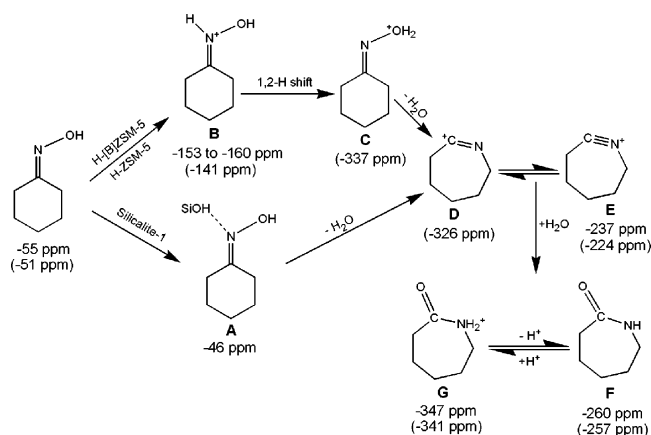
Figure 2. ^{15}N CP/MAS NMR spectra recorded at room temperature after conversion of ^{15}N -cyclohexanone oxime on silicalite-1 (left), H-ZSM-5 (middle), and H-[B]ZSM-5 (right). The reaction temperatures are indicated in the Figure. Asterisks denote spinning sidebands.

of protonated ^{15}N -cyclohexanone oxime is slightly shifted to lower field.

Further experiments focused on the conversion of ^{15}N -cyclohexanone oxime on the zeolites silicalite-1, H-ZSM-5, and H-[B]ZSM-5 by stepwise heating the physical mixtures of the reactant and the zeolite catalysts at temperatures between 423 and 523 K. According to Figure 2a, the Beckmann rearrangement on silicalite-1 starts at about 473 K, which is indicated by new signals at -237 , -260 , and -376 ppm. After raising the reaction temperature to 498 and 523 K (Figure 2b,c), the spectra consist of a single signal at -260 ppm. This signal is caused by ϵ -caprolactam, the final product of the Beckmann rearrangement.^{5,6} The signal at -376 ppm is a hint for the formation of an amine as a byproduct,⁶ while the origin of the signal at -237 ppm is discussed in the following.

In the literature,^{1,2,5,7,8} the mechanism of the vapor-phase Beckmann rearrangement of cyclohexanone oxime on zeolite catalysts depicted in Scheme 1 is suggested. The chemical shift values given in the scheme are the ^{15}N NMR shifts observed experimentally in the present study. The chemical shift values given

Scheme 1



in parentheses were obtained via ref 9. The first steps of the Beckmann rearrangement of cyclohexanone oxime on the zeolite catalysts under study are the adsorption of the reactant molecules via hydrogen bonding at SiOH groups in silicalite-1 (A) or the N-protonation of the reactant by hydroxyl groups in zeolites H-ZSM-5 and H-[B]ZSM-5 (B). Quantum chemical studies of Bucko et al.⁸ indicate that the 1,2-H shift leading to O-protonated cyclohexanone oxime C is followed by the formation of carbenium ions D as intermediates. A more stable state of this intermediate is the nitrilium ion E. The ^{15}N NMR shift of -224 ppm predicted for this intermediate indicates that species E may be responsible for the signal at -237 ppm.⁹ This assignment is supported by the decrease of the signal at -237 ppm, while the signals of nonprotonated and protonated ϵ -caprolactam (F and G, respectively) at -260 and -347 ppm, respectively, are raised. In agreement with Scheme 1, species E is consumed during formation of the final product ϵ -caprolactam.

The Beckmann rearrangement of ^{15}N -cyclohexanone oxime on zeolite H-ZSM-5 starts at about 423 K (Figure 2d). In addition to the signal of protonated and noninteracting ^{15}N -cyclohexanone oxime at -160 ppm and -55 ppm, respectively, a signal at -347 ppm due to protonated ϵ -caprolactam occurs. The spectrum in Figure 2d is dominated by a signal at -237 ppm, which already appeared in the spectrum of silicalite-1 heated at 473 K (Figure 2a).

A more complicated situation was found for the Beckmann rearrangement of ^{15}N -cyclohexanone oxime on zeolite H-[B]ZSM-5 (Figure 2g–i). The same signals as for the conversion of ^{15}N -cyclohexanone oxime on silicalite-1 and H-ZSM-5 were observed: The signals of the nonconverted reactant at -55 ppm, of the hydrogen-bonded reactant at -46 ppm, and of nitrilium ions at -237 ppm, and of nonprotonated and protonated ϵ -caprolactam at -260 and -347 ppm, respectively. In addition, side reactions lead to byproducts causing signals at -199, -275, and -364 ppm. These byproducts may be the reason for the loss of the ϵ -caprolactam selectivity of H-[B]ZSM-5 after a short time on stream in comparison with silicalite-1 as described by Forni et al.¹⁰

Dehydration of cyclohexanone oxime causes the formation of 5-cyano-1-pentene.^{10,11} The latter species is responsible for the ^{15}N CP/MAS NMR signal at -199 ppm, assuming a partial protonation of this compound, which leads to a predicted mean resonance position of -194 ppm.⁹ The water formed by this reaction causes the hydrolysis of cyclohexanone oxime molecules and the formation of cyclohexanone and hydroxylamine (signal at -275 ppm). The assignments of the signals at -199 and -275 ppm to the dehydration and hydrolysis products of cyclohexanone oxime is

supported by the simultaneous increase of both signals upon heating the reaction mixture at 498 and 523 K (Figure 2h,i). As suggested by Shouro et al.¹¹ for the Beckmann rearrangement of oximes on FSM-16-type materials, the preferred conversion of cyclohexanone oxime to 5-cyano-1-pentene on H-[B]ZSM-5 may originate from a reversible cleavage of the unstable -Si-OH-B- bridges in this catalyst.

Formation of water on the working zeolite catalyst H-[B]ZSM-5, for example, by dehydration of cyclohexanone oxime to 5-cyano-1-pentene, can also cause hydrolysis of the reaction product ϵ -caprolactam. In the presence of water, ϵ -caprolactam is converted into ϵ -aminocaproic acid, which is the first reaction step on the route from ϵ -caprolactam to polyamide.¹² Because ϵ -aminocaproic acid has a predicted ^{15}N NMR shift of -353 ppm,⁹ this species is probably the reason for the ^{15}N CP/MAS NMR signal at -364 ppm observed in the spectra of H-[B]ZSM-5.

In summary, this solid-state NMR investigation of the Beckmann rearrangement on MFI-type zeolite catalysts with different acid strengths (see Supporting Information) shows that the conversion of cyclohexanone oxime is catalyzed both by SiOH groups, as in silicalite-1, and by acidic SiOH[B] and SiOHAl groups, as in zeolites H-[B]ZSM-5 and H-ZSM-5. The protonation of the reaction product ϵ -caprolactam in the latter case leads to a strong adsorption on the catalysts surface. This may result in a (i) reduced activity of zeolites H-[B]ZSM-5 and H-ZSM-5 with respect to silicalite-1 and (ii) consecutive reactions, for example, formation of byproducts, such as hydrolysis and polymerization products. These byproducts can affect the selectivity for ϵ -caprolactam and lead to catalyst deactivation. In all zeolite catalysts under study, nitrilium ions occur as intermediates of the vapor-phase Beckmann rearrangement causing a ^{15}N CP/MAS NMR signal at -237 ppm.

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Supporting Information Available: Procedures of sample preparation and synthesis of ^{15}N -cyclohexanone oxime, parameters of ^{15}N CP/MAS NMR experiments, and the ^1H MAS NMR characterization of the hydroxyl coverage of the zeolite catalysts under study. This material is available for free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Sato, H. *Catal. Rev. - Sci. Eng.* **1997**, *39*, 395–424.
- (2) Dahlhoff, G.; Niederer, J. P. M.; Hoelderich, W. F. *Catal. Rev. - Sci. Eng.* **2001**, *43*, 381–441.
- (3) (a) Heitmann, G. P.; Dahlhoff, G.; Hoelderich, W. F. *J. Catal.* **1999**, *186*, 12–19. (b) Ichihashi, H.; Kitamura, M. *Catal. Today* **2002**, *73*, 23–28. (c) Takahashi, T.; Nasution, M. N. A.; Kai, T. *Appl. Catal., A* **2001**, *210*, 339–344. (d) Forni, L.; Fornasari, G.; Giordano, G.; Lucarelli, C.; Katovic, A.; Trifiro, F.; Perri, C.; Nagy, J. B. *Phys. Chem. Chem. Phys.* **2004**, *6*, 1842–1847.
- (4) (a) Hoelderich, W. F. *Catal. Today* **2000**, *62*, 115–130. (b) Heitmann, G. P.; Dahlhoff, G.; Hoelderich, W. F. *J. Catal.* **2000**, *194*, 122–129. (c) Hoelderich, W. F.; Roeseler, J.; Heitmann, G. P.; Liebens, A. T. *Catal. Today* **1997**, *37*, 353–366.
- (5) Fernandez, A. B.; Boronat, M.; Blasco, T.; Corma, A. *Angew. Chem.* **2005**, *117*, 2422–2425; *Angew. Chem., Int. Ed.* **2005**, *44* (16), 2370–2373.
- (6) Parker, W. O. N. *Magn. Reson. Chem.* **1999**, *37*, 433–436.
- (7) Sirijaraensri, J.; Truong, T. N.; Limtrakul, J. *J. Phys. Chem. B* **2005**, *109*, 12099 and references therein.
- (8) Bucko, T.; Hafner, J.; Benco, L. *J. Phys. Chem. A* **2004**, *108*, 11388–11397.
- (9) *NNMR Predictor & dB 9.0*, Advanced Chemistry Development, Inc.: Toronto, Ontario, Canada.
- (10) Forni, L.; Patriachi, E.; Fornasari, G.; Trifiro, F.; Katovic, A.; Giordano, G.; Nagy, J. B. *Stud. Surf. Sci. Catal.* **2005**, *155*, 281–290.
- (11) Shouro, D.; Ohya, Y.; Mishima, S.; Nakajima, T. *Appl. Catal., A* **2001**, *214*, 59–67.
- (12) March, J. *Advanced Organic Chemistry, Reactions, Mechanisms, and Structures*, 3rd edition; Wiley: New York, 1985; pp 1346.

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