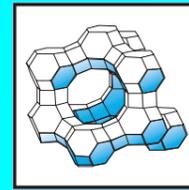




Solid-state NMR studies on the vapor-phase Beckmann rearrangement of ¹⁵N-cyclohexanone oxime



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Introduction

The nature and location of active sites of the solid catalyst and role of additive during the vapor-phase Beckmann rearrangement of cyclohexanone oxime is a matter of debate. Recent solid-state NMR [1,2] and theoretical investigations [2] reveal the formation of reaction intermediates, products, and by-products of the reaction. However, the adsorption (protonated or non-protonated) and reaction behavior of reactants and products on silanol and bridging OH groups in different catalysts are still uncertain and merits further investigations. In addition, the literature concerning the influence of additives on the species (reactants, products, and by-products) 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, the adsorption and reaction behavior of the species formed via the vapor-phase Beckmann rearrangement of ¹⁵N-cyclohexanone oxime on MFI-type zeolites (silicalite-1 and H-ZSM-5) and mesoporous SBA-15 materials have been investigated by solid-state ¹⁵N CP/MAS NMR spectroscopy. To study the influence of the additive methanol, ¹⁵N CP/MAS NMR spectra of ¹⁵N-oxime/catalyst mixtures in the absence and presence of ¹³C-methanol were recorded. Furthermore, the conversion of methanol during the reaction of ¹⁵N-oxime/catalyst mixtures was investigated by ¹³C CP/MAS NMR spectroscopy.

Experimental Section

¹⁵N-cyclohexanone oxime/catalyst mixtures were prepared by mixing 15 and 20 mg of ¹⁵N-oxime with 150 and 200 mg of dehydrated zeolite and SBA-15 material under dry nitrogen flow, respectively. ¹³C-methanol vapor was loaded into the mixtures using vacuum line. The mixtures were then transferred into a 7 mm MAS rotor. Solid-state ¹⁵N and ¹³C CP/MAS NMR spectra were recorded on a Bruker MSL 400 spectrometer at resonance frequencies of 40.53 and 100.58 MHz using a 7 mm MAS probe with the sample spinning rates of ca. 3.5 and 4.7 kHz, respectively. ¹⁵N and ¹³C CP/MAS NMR spectra were obtained with the contact period of 5 ms and the recycle delay of 2 s.

Results and Discussion

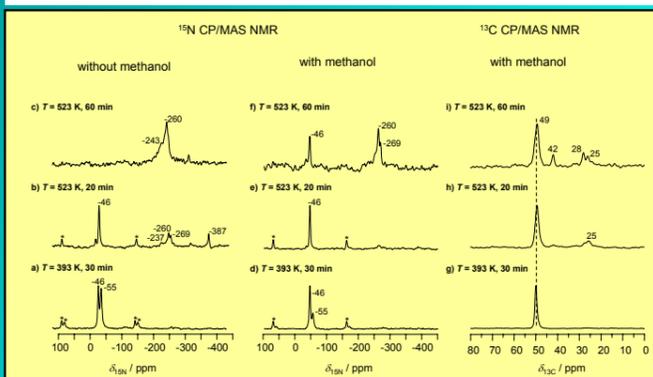


Figure 1. ¹⁵N CP/MAS NMR spectra recorded upon conversion of ¹⁵N-cyclohexanone oxime on silicalite-1 ($n_S/n_{Al} = 1700$) in the absence (left) and presence (middle) of ¹³C-methanol. ¹³C CP/MAS NMR spectra (right) show the conversion of ¹³C-methanol. The reaction temperatures and heating times are given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

The assignments of ¹⁵N MAS NMR signals observed in this work are summarized in Table 1. On siliceous catalysts (silicalite-1 and SBA-15), ¹⁵N-cyclohexanone oxime interacts with SiOH groups via hydrogen bonding as indicated by the signals in the range of -30 to -46 ppm (Figs. 1a, 1b, 1d, 1e, 2a-2c, and 2e). In contrast, exclusively on Brønsted acidic catalysts, such as H-ZSM-5, the reactant interacts strongly with Brønsted acid sites and form N-protonated cyclohexanone oxime as shown by the signal at -160 ppm (Figs. 4a, 4b, 4d, and 4e). On siliceous catalysts, in addition to the main product ϵ -caprolactam (-255 to -262 ppm), by-products hydroxylamine (-269 to -282 ppm) and amines (-380 to -387 ppm) were also observed.

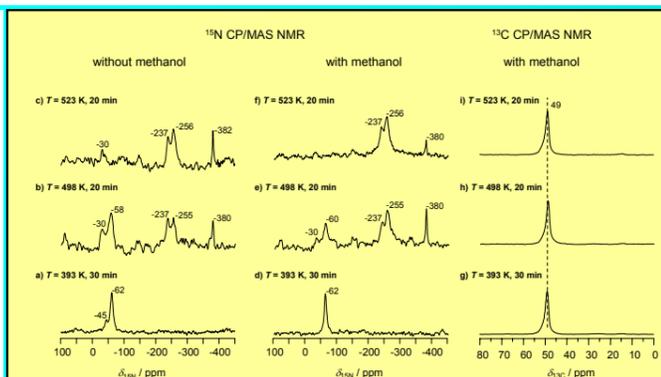


Figure 2. ¹⁵N CP/MAS NMR spectra recorded upon conversion of ¹⁵N-cyclohexanone oxime on siliceous SBA-15 ($n_S/n_{Al} = 1800$) in the absence (left) and presence (middle) of ¹³C-methanol. ¹³C CP/MAS NMR spectra (right) show the presence of ¹³C-methanol. The reaction temperatures and heating times are given in the Figure. Asterisks in the NMR spectra denote spinning sidebands.

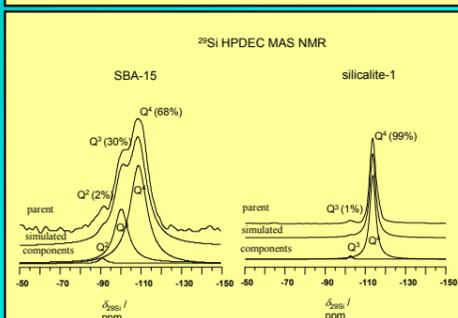
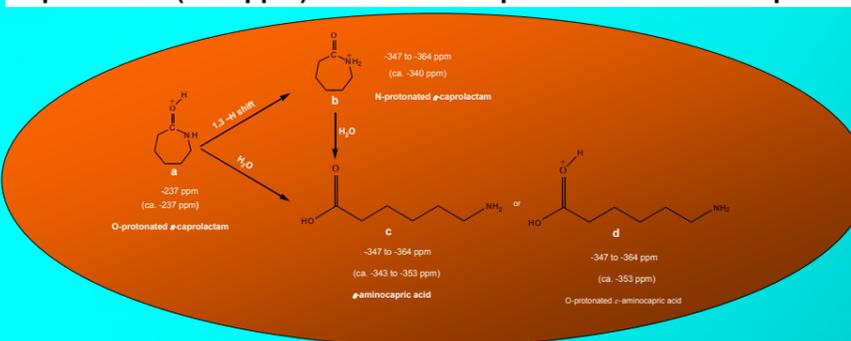


Figure 3. ²⁹Si HPDEC MAS NMR spectra of siliceous SBA-15 (left) and silicalite-1 (right) and their simulation.

In case of silicalite-1, the formation of amines was suppressed when ¹³C-methanol was used as an additive, which is evidenced by the disappearance of signal at -387 ppm (Fig. 1e, and 1f). Furthermore, the additive methanol (49 ppm) was also converted into hydrocarbons (25-28 ppm) and isopropylamine (42 ppm) as shown by ¹³C CP/MAS NMR spectra (Fig. 1, right). The isopropylamine was observed as a result of the reaction of isobutane and hydroxyl amine, which is a by-product of the Beckmann rearrangement. On SBA-15, however, no influence and conversion of methanol on the adsorbed species was found (Fig. 2). Interestingly, the formation of O-protonated ϵ -caprolactam was observed on both siliceous and Brønsted acidic catalysts as indicated by the signal at -237 ppm in the spectra of the ¹⁵N-oxime/catalyst mixtures (Figs. 1b, 1c, 2b, 2c, 2e, 2f, 4b, 4c, and 4f). However, on siliceous catalysts, the formation of O-protonated ϵ -caprolactam depends on the number of highly acidic Q³ (Si(OSi)₃OH) silanol groups (Fig. 3). Further conversion of O-protonated ϵ -caprolactam occur exclusively on Brønsted acidic H-ZSM-5 zeolite (Scheme 1). The conversion of O-protonated ϵ -caprolactam was enhanced by the presence of methanol. Since methanol dehydrates into dimethylether (60 ppm) and water on acidic H-ZSM-5, this water promotes the further conversion of O-protonated ϵ -caprolactam (-237 ppm) into non- or O-protonated ϵ -aminocaproic acid (-347 to -364 ppm) as shown in Scheme 1.

Table 1. Assignments of ¹⁵N CP/MAS NMR signals of the species observed during the vapor-phase Beckmann rearrangement of ¹⁵N-cyclohexanone oxime.

δ_{15N} / (ppm)	Assignments
-30 to -46	¹⁵ N-cyclohexanone oxime interacting with SiOH groups of zeolites and mesoporous materials via hydrogen bonding
-51 to -62	unconverted ¹⁵ N-cyclohexanone oxime on zeolites and mesoporous materials
-145 to -160	N-protonated cyclohexanone oxime, exclusively formed on Brønsted acid sites of zeolites and mesoporous materials
-237 to -243	O-protonated ϵ -caprolactam on Q ³ silanol groups (Si(OSi) ₃ OH) and Brønsted acid sites
-255 to -262	physically adsorbed ϵ -caprolactam on SiOH groups and Brønsted acid sites
-269 to -282	hydroxylamine
-340 to -364	N-protonated ϵ -caprolactam, or non- or O-protonated ϵ -aminocaproic acid, exclusively formed on Brønsted acid sites
-375 to -387	amines formed on SiOH groups of siliceous zeolites and mesoporous materials



Scheme 1. Suggested mechanism of the conversion of O-protonated ϵ -caprolactam on Brønsted acidic H-ZSM-5 zeolite. The ¹⁵N NMR shift values represented without parentheses were obtained in this work, while the values in the parentheses were obtained from the NNMR predictor software [3] or literature[2].

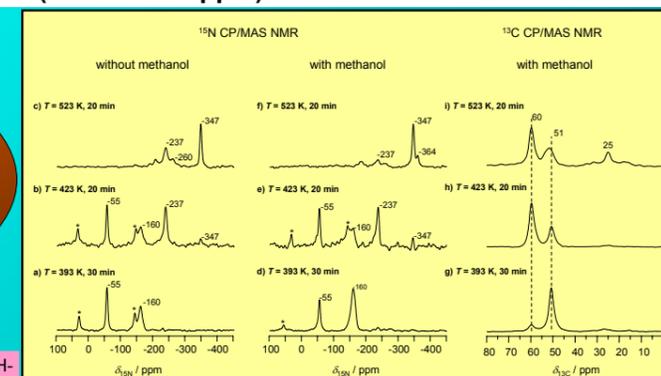


Figure 4. ¹⁵N CP/MAS NMR spectra recorded upon conversion of ¹⁵N-cyclohexanone oxime on H-ZSM-5 ($n_S/n_{Al} = 14$) in the absence (left) and presence (middle) of ¹³C-methanol. ¹³C CP/MAS NMR spectra (right) show the conversion of ¹³C-methanol. The reaction temperatures and heating times are given in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

Conclusions

The investigations revealed that O-protonated ϵ -caprolactam is formed on Brønsted acid sites of H-ZSM-5 and on Q³ silanol groups (Si(OSi)₃OH) of silicalite-1 and siliceous SBA-15. On siliceous catalysts, the adsorption of ϵ -caprolactam and the formation of O-protonated ϵ -caprolactam depend on the number of Q³ silanol groups. Further conversion and hydration of O-protonated ϵ -caprolactam were observed exclusively on Brønsted acidic H-ZSM-5 zeolite. ¹³C MAS NMR spectroscopy was utilized 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, formation of isopropylamine was observed on silicalite-1 as a result of the reaction of isobutane and hydroxyl amine, which is a by-product of the Beckmann rearrangement. Water formed via the dehydration of methanol on H-ZSM-5 promotes the conversion of O-protonated ϵ -caprolactam into non- or O-protonated ϵ -aminocaproic acid. On the siliceous SBA-15, no conversion of methanol was found.

Acknowledgements

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References

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- [3] NNMR Predictor & dB 9.0, Advanced Chemistry Development, Inc.: Toronto, Ontario, Canada.