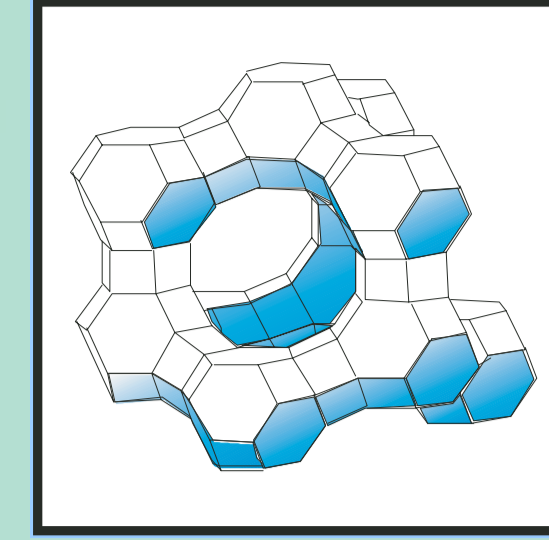


Beckmann rearrangement of ^{15}N -cyclohexanone oxime to ϵ -caprolactam on silicalite-1, H-ZSM-5, and H-[B]ZSM-5 studied by solid-state NMR spectroscopy

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Introduction

Vapor phase Beckmann rearrangement of cyclohexanone oxime to ϵ -caprolactam on solid acid catalysts has received increasing interest as an environmentally benign process. Many investigations reveal that silicalite-1 and H-[B]ZSM-5 are highly active and selective as catalysts in this reaction. However, until now, the mechanism of the conversion of cyclohexanone oxime to ϵ -caprolactam on the surface sites of solid catalysts is a matter of controversial discussions. Recently, the possible reaction mechanism of the vapor-phase Beckmann rearrangement of acetophenone oxime on zeolites beta has been studied by solid-state ^{13}C and ^{15}N MAS NMR spectroscopy and compared with theoretical calculations [1]. In our work, we present first solid-state NMR evidence for the formation of protonated and non-protonated reactant and product molecules, intermediates, and by-products during the vapour phase Beckmann rearrangement of ^{15}N -enriched cyclohexanone oxime on zeolites silicalite-1, H-ZSM-5, and H-[B]ZSM-5, which are characterized by surface hydroxyl groups of different nature and with different acid strengths. In addition, the conversion of cyclohexanone oxime- d^{11} over zeolite H-ZSM-5 has also been studied by solid-state ^1H MAS NMR spectroscopy.

Experimental Section

Solid-state ^{15}N CP/MAS and ^1H MAS NMR spectra were recorded on a Bruker MSL 400 spectrometer using 7 mm and 4 mm MAS probes with the sample spinning rates of ca. 3.5 and 8.5 kHz, and at resonance frequencies of 40.53 and 400.1 MHz, respectively. ^{15}N CP/MAS NMR spectra were obtained with a contact period of 5 ms and a recycle delay of 2 s. Between 1600 (H-ZSM-5) and 40000 (silicalite-1) decays were accumulated for each ^{15}N CP/MAS NMR spectrum. All ^{15}N MAS NMR spectra were referenced to nitromethane (0.0 ppm) by calibrating to ^{15}N -enriched pyridine (-62.0 ppm). ^1H MAS NMR spectra were recorded after single pulse excitation with a pulse length of 2.1 μs , repetition time of 10 s, and an accumulation number of 400.

Results and Discussion

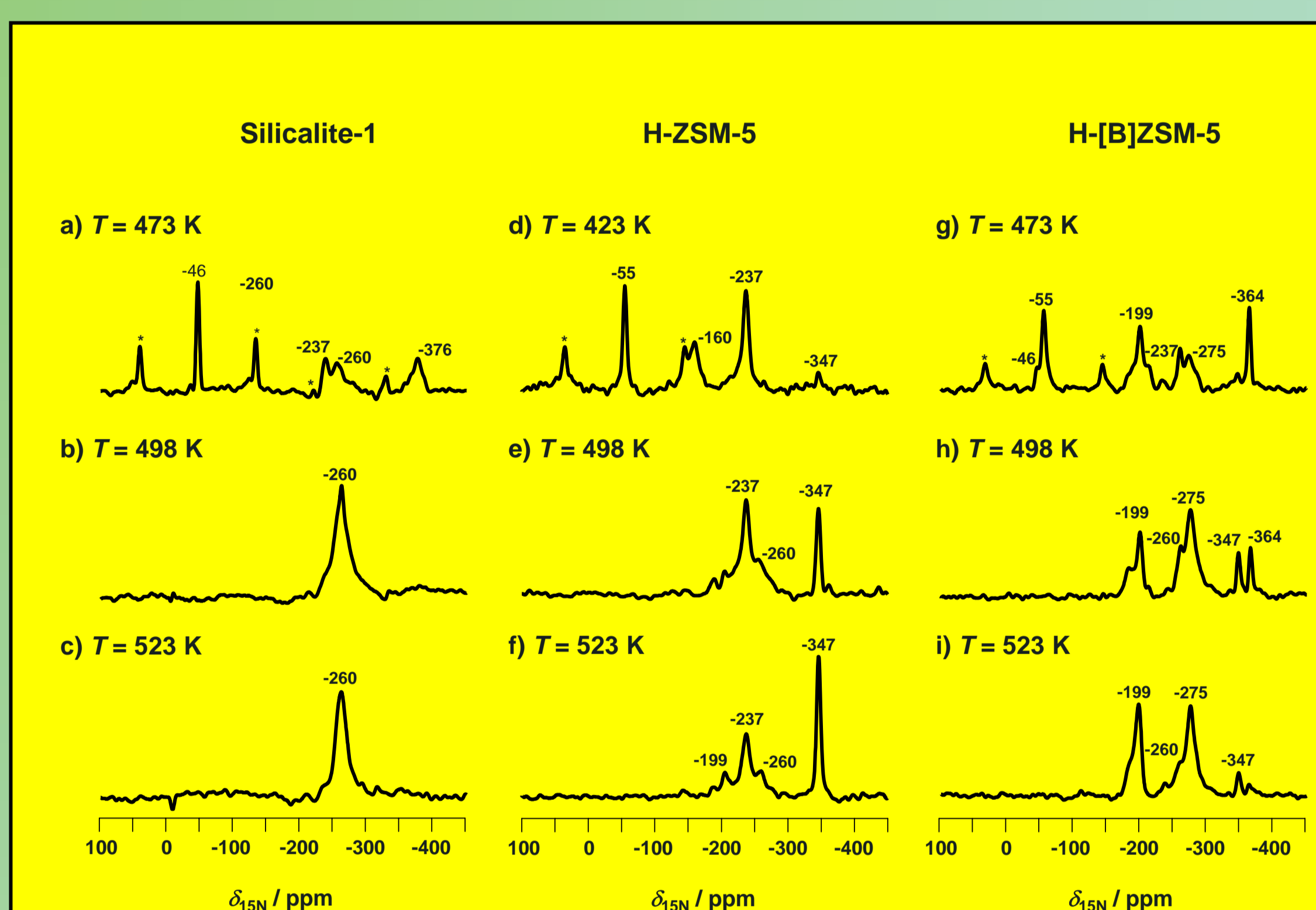


Figure 1. ^{15}N CP/MAS NMR spectra recorded at room temperature after conversion of ^{15}N -cyclohexanone oxime on silicalite-1 (left), H-ZSM-5 (middle), and H-[B]ZSM-5 (right). The reaction temperatures are indicated in the Figure. Asterisks denote spinning sidebands.

Fig. 1 shows ^{15}N CP/MAS NMR spectra recorded upon the conversion of ^{15}N -cyclohexanone oxime to ϵ -caprolactam by stepwise heating of the physical mixtures of the reactant and the MFI-type catalysts at different reaction temperatures [2], while, Fig. 2 shows the ^1H MAS NMR spectra of dehydrated zeolite H-ZSM-5, and H-ZSM-5 loaded with cyclohexanone oxime- d^{11} and heated at temperatures between 393 and 523 K. The signals in dehydrated zeolite H-ZSM-5 at 1.8 and 4.0 ppm are assigned to SiOH and SiOH[Al] groups, respectively (Fig. 2a).

The signal at -55 ppm in Figs. 1d and 1g is due to unconverted ^{15}N -cyclohexanone oxime [3], while the corresponding ^1H MAS NMR signal of cyclohexanone oxime- d^{11} adsorbed on H-ZSM-5 and heated at 393 and 423 K occurs at 11.2 ppm (Figs. 2b-2c) [3]. The broad signal in the range of 2.1-2.8 ppm is due to ring protons of reactant and product molecules (Figs. 2b-2f) [3].

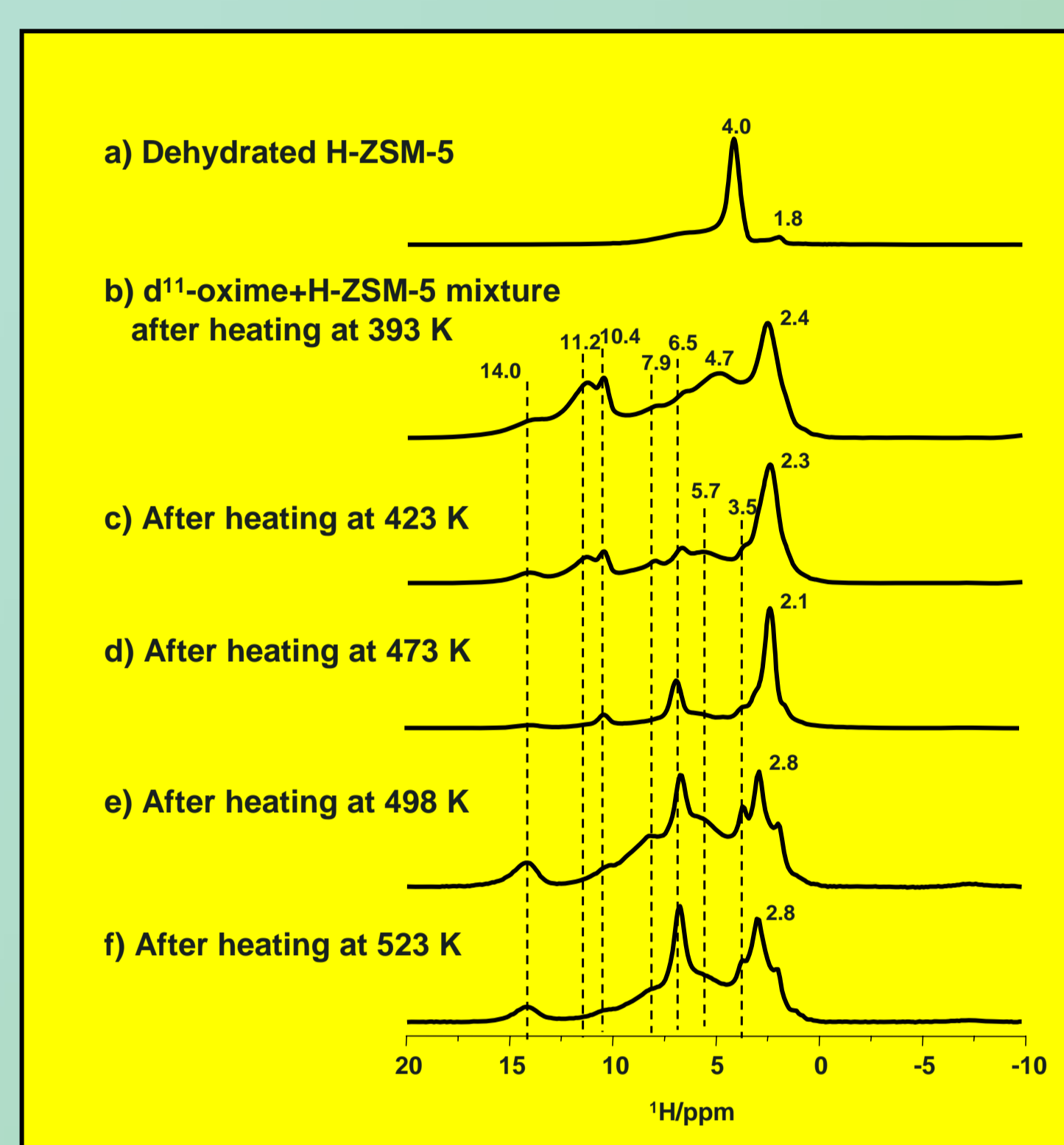


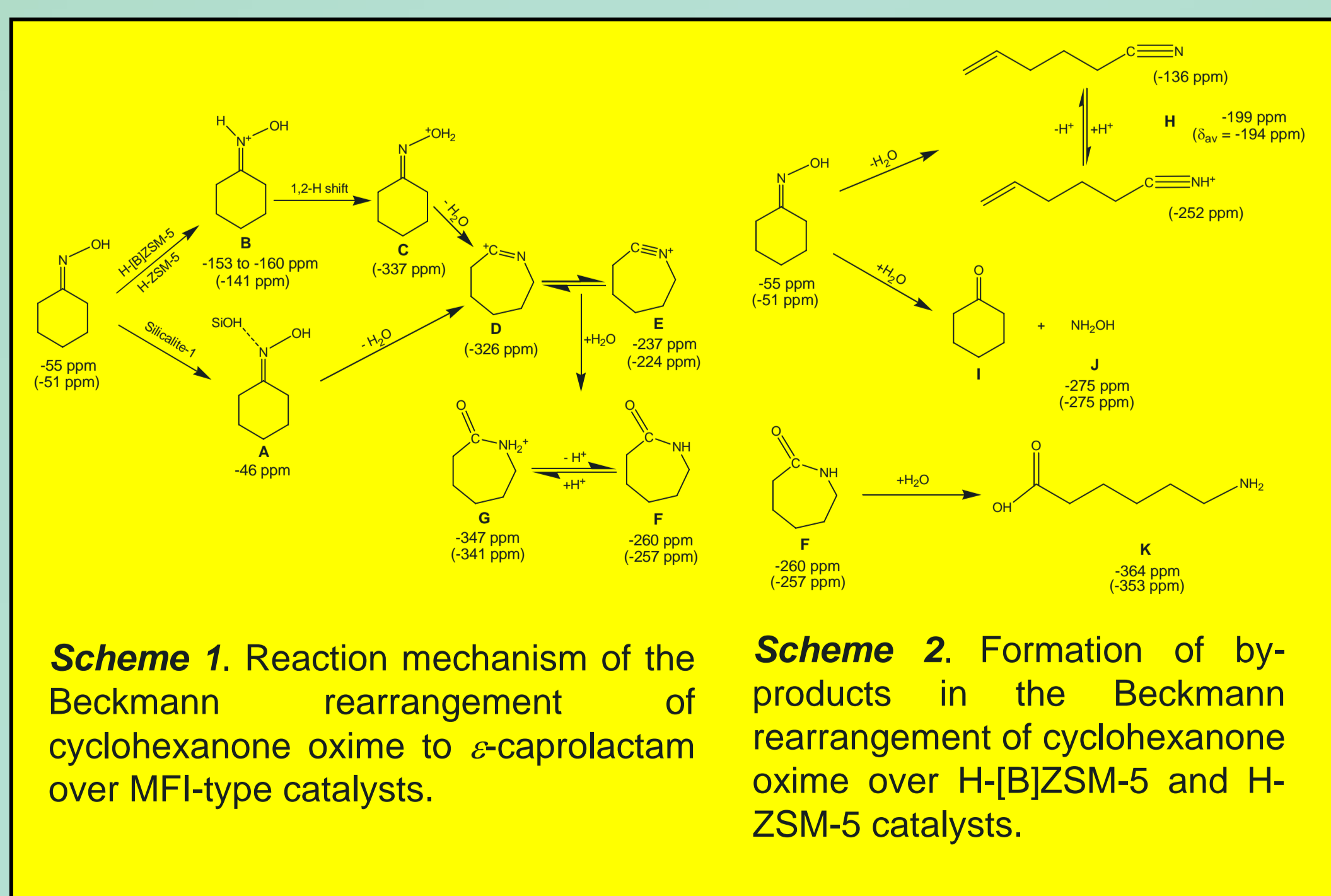
Figure 2. ^1H MAS NMR spectra of (a) dehydrated zeolite H-ZSM-5, and mixtures of (b-f) cyclohexanone oxime- d^{11} and H-ZSM-5 after heating at different reaction temperatures. The reaction temperatures are indicated in the Figure.

The ^{15}N CP/MAS NMR signals at -46 ppm in Figs. 1a and 1g and at -160 ppm in Fig. 1d are assigned to H-bonded and N-protonated oximes [1, 3], respectively (Scheme 1). These signal assignments are further supported by the ^1H MAS NMR spectrum shown in Fig. 2. The H-bonded oxime, which is adsorbed on SiOH groups, is indicated by the signal at 10.4 ppm, while the signal at 14.0 ppm indicates the formation of N-protonated oxime on SiOH[Al] groups of zeolite H-ZSM-5.

Upon heating of the mixtures of ^{15}N -cyclohexanone oxime and the zeolites at 423 to 523 K, nitrilium ions appeared at -237 ppm (Figs. 1a, 1d-1f, and 1g) [3], which are intermediates of the Beckmann rearrangement of cyclohexanone oxime (Scheme 1). The corresponding ^1H MAS NMR signal appeared at 3.5 ppm, when the mixture of cyclohexanone oxime- d^{11} and zeolite H-ZSM-5 was heated at reaction temperatures between 423 to 523 K (Figs. 2c-2f).

ϵ -caprolactam, the final product of Beckmann rearrangement of cyclohexanone oxime, causes the ^{15}N CP/MAS NMR signal at -260 ppm occurring in Figs. 1a-1c, 1e, 1f, and 1g-1i. In the case of zeolites H-ZSM-5 and H-[B]ZSM-5, due to the existence of bridging hydroxyl groups, the protonated form of ϵ -caprolactam occurs and causes the signal at -347 ppm (Figs. 1d-1f, 1h, and 1i). Similarly, formation of non-protonated and protonated ϵ -caprolactam was observed by ^1H MAS NMR spectroscopy (Figs. 2b-2f), when the mixture of cyclohexanone oxime- d^{11} and H-ZSM-5 was heated at 423 to 523 K. The ^1H MAS NMR signals 7.9 and 6.5 ppm are assigned to non-protonated and protonated ϵ -caprolactam, respectively [3].

Additional ^{15}N CP/MAS NMR signals at -376 ppm (Fig. 1a), -199 ppm (Figs. 1f, and 1g-1i), -275 ppm (Figs. 1g-1i), and -364 ppm (Figs. 1g and 1h) are due to by-products, such as amine, partially protonated 5-cyano-1-pentene, hydroxylamine, and ϵ -aminocaproic acid [3], respectively. These by-products are formed by dehydration and hydration reactions (Scheme 2). In the case of Beckmann rearrangement of cyclohexanone oxime- d^{11} over zeolite H-ZSM-5, a ^1H MAS NMR signal at 5.7 ppm represents partially protonated 5-cyano-1-pentene[3], a by-product of the Beckmann rearrangement.



Conclusions

In summary, this work is the first solid-state NMR study of the Beckmann rearrangement of ^{15}N -enriched cyclohexanone oxime on zeolite catalysts with surface OH groups of different acid strength (silicalite-1 < H-[B]ZSM-5 < H-ZSM-5). Depending on the acid strength of the catalytically active surface OH groups, the reactant cyclohexanone oxime and the reaction product ϵ -caprolactam exist in the non-protonated or protonated state. 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. In zeolite H-ZSM-5, the nitrilium ions were observed also upon heating at 498 and 523 K, which may be due to a stabilizing effect of the strong Brønsted acid sites in this catalyst. The formation of a number of by-products was observed as a result of the dehydration and hydrolysis of the reactant cyclohexanone oxime and of the reaction product ϵ -caprolactam. In addition, ^1H MAS NMR studies of the conversion of cyclohexanone oxime- d^{11} over zeolite H-ZSM-5 also reveal the formation of protonated reactants, protonated products, nitrilium ion, and by-products.

Acknowledgements

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