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Priority Communication

NMR spectroscopy and theoretical calculations demonstrate the nature and location of active sites for the Beckmann rearrangement reaction in microporous materials

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Abstract

^{15}N solid-state NMR and theoretical calculations were combined to investigate the Beckmann rearrangement of ^{15}N-cyclohexanone oxime and ^{15}N-cyclododecanone oxime over two MFI-type zeolites as catalysts, H-ZSM-5 and silicalite, containing Brönsted acid sites and silanol groups, respectively. The results demonstrated that the Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam occurs in the interior of the pores of MFI zeolites and that O-protonated ε-caprolactam is formed over the Brönsted acid centers. The acid groups placed at the outer shell of the crystals, probably at the pore mouths, are also active; meanwhile, external silanol groups are significantly less active and less selective than the internal ones.

Keywords: Beckmann rearrangement; Oxime; Laurolactam; Caprolactam; ^{15}N NMR; Theoretical calculations; MFI; Silicalite,; ZSM-5; Zeolite

1. Introduction

In recent years, the social demand of clean and environmentally friendly technologies has prompted increased efforts to develop selective heterogeneous catalysts involving zeolites and molecular sieves [1]. One of the processes currently under investigation is the Beckmann rearrangement reaction of oximes into lactams [2,3], the most important industrial application of which is the transformation of cyclohexanone and cyclododecanone oximes into ε-caprolactam and laurolactam, respectively (Scheme 1), which are intermediates in the fabrication of fibers and resins [4]. The continuous research activity on the Beckmann rearrangement has resulted in a new heterogeneous process for the production of ε-caprolactam using high-silica MFI-type zeolites as catalysts [3].

Despite the efforts devoted to investigating the rearrangement of cyclohexanone oxime over zeolites, especially MFI-type zeolites, the exact nature of the active sites remains under debate [2,3,5–10]. There is a general agreement that bridging hydroxyl groups are more active but less selective than weakly acid silanol groups, because they favor undesired secondary reactions and catalyst deactivation [2,3,5–7]; however, there are discrepancies about the location of the active sites [2,3,5–10]. Some authors claim that the reaction must proceed at the outer shell or on the external surface of the crystals because of limited diffusion of ε-caprolactam through the micropores of MFI [2,3,5–7]. Meanwhile, other research groups conclude that both the oxime and the lactam are able to diffuse inside the pores of the MFI-type zeolites at the reaction temperatures, and that the reaction must occur, at least partially, in the interior of the pores [8–10].

In the present investigation, we combined theoretical calculations and in situ solid-state ^{15}N NMR spectroscopy to demonstrate the nature and location of the active sites for the Beckmann rearrangement of cyclohexanone oxime over MFI. We achieved this by comparing the reactivity of ^{15}N-cyclohexanone oxime and of the bulkier ^{15}N-cyclododecanone oxime. The nature of the active sites has been considered using two MFI zeolites as catalysts: pure silica Silicalite-N containing

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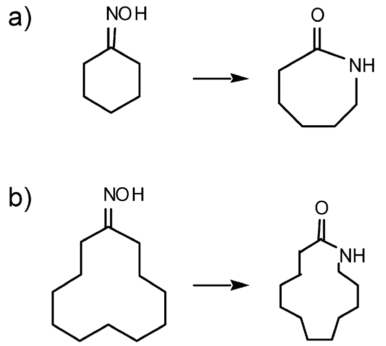
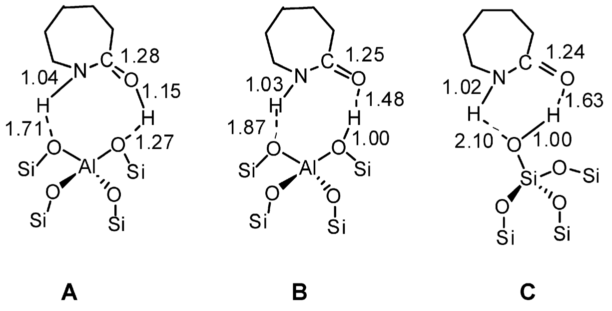


Scheme 1. Beckmann rearrangement reaction of (a) cyclohexanone oxime to ε-caprolactam, and (b) cyclododecanone oxime to laurolactam.



Scheme 2. Optimized structures of ε-caprolactam adsorbed on a zeolite Brönsted acid site (A and B) and on a silanol group (C). Distances are expressed in angstroms.

silanol defects, and zeolite H-ZSM-5 (Si/Al = 15) with Brönsted acid sites [8].

2. Experimental

2.1. Computational details

Silanol defects and Brönsted acid sites were simulated using the $Si(OSiH_3)_3OH$ and $Al(OSiH_3)_3(OH)SiH_3$ cluster models, respectively, as described previously [11]. The geometries of the two clusters, ε-caprolactam, and the complexes formed by adsorption of ε-caprolactam on the cluster models (structures A–C, Scheme 2), were optimized using the density functional B3PW91 method [12] and the standard 6-31G(d,p) basis set [13]. In these calculations, the coordinates of all atoms except the H terminations of the SiH_3 groups were fully optimized. Isotropic absolute chemical shielding constants were calculated with the B3PW91/6-31G(d,p) method on geometries optimized at the same level, using the gauge including atomic orbitals (GIAO) approach [14,15]. ^{15}N and ^{13}C chemical shifts were calculated as $\sigma = \sigma_{\text{ref}} - \sigma$ and corrected with the equations obtained from a preliminary study of the performance of B3PW91 functional [11]. All calculations in this work were performed using the Gaussian98 computer program [16].

2.2. Materials

Zeolite H-ZSM-5 (Si/Al = 15), produced by PQ Industries, is commercially available (CBV3020); zeolite Silicalite-N was synthesized and subsequently submitted to a basic treatment to generate silanol nests, as described previously [5,8]. ^{15}N-cyclohexanone oxime and ^{15}N-cyclododecanone oximes were synthesized using hydroxyl(^{15}N)amine hydrochloride (98% ^{15}N, Cambridge Isotope Laboratories) as described previously [8].

Table 1
Adsorption energies (E_{ads}) calculated for models A–C (Scheme 2) and isotropic NMR chemical shifts obtained from theoretical calculations ($\delta\ ^{15}N_{\text{calc}}$) and experimentally ($\delta\ ^{15}N_{\text{exp}}$). The chemical shifts are expressed in ppm relative to nitromethane

	E_{ads} (kcal mol^{-1})	$\delta\ ^{15}N_{\text{calc}}$ (ppm)	$\delta\ ^{15}N_{\text{exp}}$ (ppm)
ε-Caprolactam	–	−277.8	−275
Model A	−27.8	−244.5	−237
Model B	−26.1	−259.1	−260
Model C	−9.6	−268.3	−263

2.3. Solid-state NMR

A 300-mg sample of zeolite degassed at 673 K was mixed with ^{15}N-cyclohexanone oxime (15 mg) or ^{15}N-cyclododecanone oxime (26 mg) and homogenized under an inert atmosphere in a glove box. A portion of this mixture was introduced into a glass insert, which was sealed after a second degasification at room temperature. Prior to spectra acquisition, the samples were heated at increasing temperatures up to 523 K for 1 h. The NMR spectra were recorded at room temperature on a Bruker AV 400 WB spectrometer using a BL7 probe, with the samples spinning (MAS) at a rate of approximately 5 kHz. The ^{1}H to ^{15}N cross-polarization ($^{1}H/^{15}N$ CP MAS) spectra were recorded with a 90° pulse for ^{1}H of 5 µs, a contact time of 5 ms, and a recycle delay of 5 s.

3. Results and discussion

Scheme 2 describes the models calculated for the interaction of ε-caprolactam with bridging hydroxyl (A and B) and silanol defect groups (C) in zeolites, using density functional methods. The lactam adsorbs on the zeolite hydroxyl through the carbonyl oxygen, and the NH group forms a hydrogen bond with the adjacent framework oxygen atom (Scheme 2). When interacting with Brönsted acid centers, the lactam is protonated in complex A (Scheme 2) by capturing the proton of the acid site, which remains bonded to the zeolite in complex B (Scheme 2). The calculated adsorption energy shows a slightly higher stability for complex A (Table 1), suggesting that the lactam protonation is favored on Brönsted acid sites, which agrees with previous theoretical calculations [17]. To check these models, we calculated the ^{15}N NMR chemical shift of ε-caprolactam in complexes A, B, and C and compared the results with those obtained experimentally by in situ ^{15}N NMR. The chemical shifts of the lactam adsorbed through hydrogen bonds on either Brönsted acid (complex B) or silanol groups (complex C) of zeolites are similar (ca. −260 ppm), whereas that of the O-protonated ε-caprolactam (complex A) is shifted to low fields in about 20 ppm.

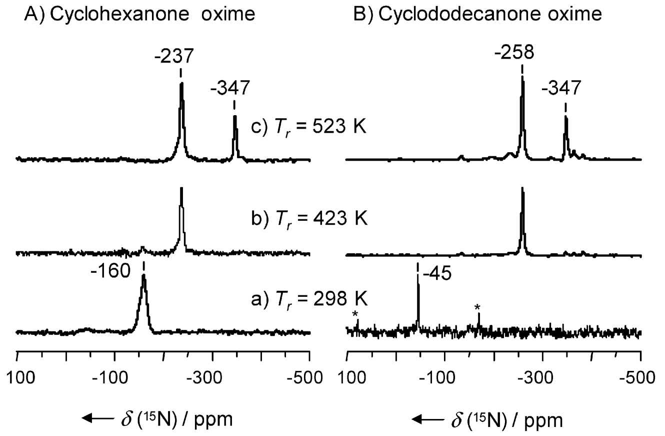


Fig. 1. $^1H/^{15}N$ CP MAS NMR spectra recorded at room temperature of (A) cyclohexanone oxime and (B) cyclododecanone oxime, over zeolite H-ZSM-5, (a) at room temperature, and subsequently treated at (b) 423 K and (c) 523 K. Asterisks indicate spinning side bands.

Fig. 1 shows the results obtained by ^{15}N NMR spectroscopy on zeolite H-ZSM-5 for the reaction of ^{15}N-cyclohexanone oxime (A) and ^{15}N-cyclododecanone oxime (B). The differences between the two oximes become apparent after the adsorption at room temperature. ^{15}N-cyclododecanone oxime shows a very sharp peak at −45 ppm as the solid oxime, indicating no interaction with the zeolite (Fig. 1Ba) [11,17,18]. In contrast, the ^{15}N-cyclohexanone oxime gives a peak at −160 ppm characteristic of the ^{15}N-protonated oxime [11,17,18], which necessarily must be formed on the Brönsted acid centers inside the zeolite pores (Fig. 1Aa). This result proves that cyclohexanone oxime is able to penetrate the interior of zeolite ZSM-5 even at room temperature, and that the external Brönsted acid sites are in a very low concentration and/or not able to protonate the (^{15}N-cyclododecanone) oxime. When the temperature increases to 423 K, the signals of the two oximes vanish and new resonances appear at −237 (Fig. 1Ab) and −258 ppm (Fig. 1Bb), which are attributed to ^{15}N-ε-caprolactam and ^{15}N-laurolactam, respectively. Comparison with the theoretical ^{15}N chemical shifts listed in Table 1 suggests that laurolactam is interacting with the zeolite surface through hydrogen bonds, whereas ε-caprolactam is protonated and then must remain adsorbed on the Brönsted acid sites in the interior of the MFI pores. Note that despite the very weak interaction with H-ZSM-5, the ^{15}N-cyclododecanone oxime rearranges at the same temperature as the protonated ^{15}N-cyclohexanone oxime, suggesting that the reaction must occur over active Brönsted acid sites, probably located at the pore mouths of the zeolite crystals. Any further increase in the reaction temperature favors the occurrence of secondary reactions, as indicated by the appearance of new signals in the region of amines (see the intense signal at −347 ppm in Figs. 1Ac and 1Bc).

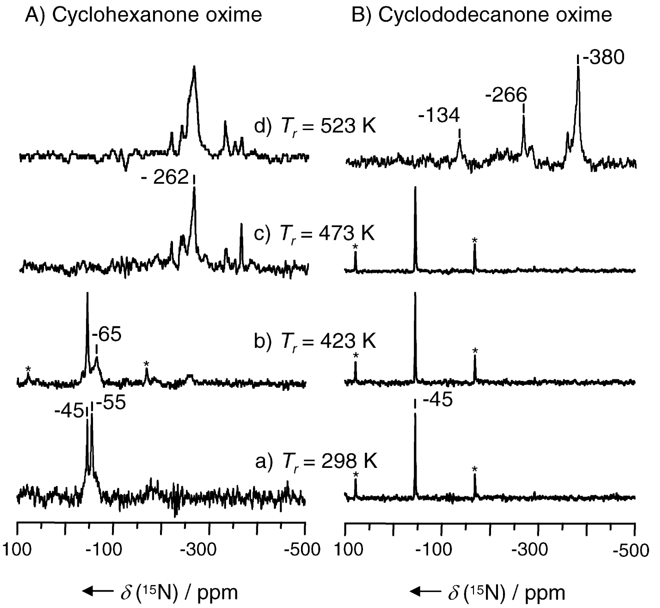


Fig. 2. $^1H/^{15}N$ CP MAS NMR spectra recorded at room temperature of (A) cyclohexanone oxime and (B) cyclododecanone oxime, over zeolite Silicalite-N, (a) at room temperature, and subsequently treated at (b) 423 K, (c) 473 K, and (d) 523 K. Asterisks indicate spinning side bands.

Fig. 2 depicts the results obtained by ^{15}N NMR spectroscopy on Silicalite-N for the reaction of ^{15}N-cyclohexanone (A) and ^{15}N-cyclododecanone (B) oximes. Again, the spectrum of ^{15}N-cyclododecanone oxime mixed with Silicalite-N at room temperature consists of a very sharp line at −45 ppm of oxime not interacting with the zeolite framework (Fig. 2Ba). Meanwhile, when ^{15}N-cyclohexanone oxime is adsorbed at room temperature on the same zeolite, the spectrum shows two sharp lines at −45 and at −55 ppm, the latter of which disappears after heating at 373 K, and a broad signal with the maximum at −65 ppm (Fig. 2Aa). This band indicates that part of ^{15}N-cyclohexanone oxime is strongly interacting through hydrogen bonds with the zeolite defects sites inside the pores (Figs. 2Aa and 2Ab). After heating at 473 K, the peak of ^{15}N-cyclohexanone oxime practically disappears, and the spectrum is dominated by a signal at −262 ppm of ^{15}N-ε-caprolactam adsorbed on the defective silanol groups of Silicalite-N (Fig. 2Ac). The spectrum remains almost unchanged after reaction temperatures up to 523 K (Fig. 2Ad), in agreement with the high selectivity toward ε-caprolactam reported for silicalite catalysts [2,3,5,7]. Again, different results are obtained on the reactivity of the bulky ^{15}N-cyclododecanone oxime over Silicalite-N; the transformation of the oxime requires a higher temperature (523 K) and leads to a different product distribution (Fig. 2Bd). Indeed, the spectrum recorded after the reaction at 523 K gives an intense peak at −380 ppm in the region of amines, a weak one at −134 ppm in the range of nitriles, and only a weak and narrow resonance of ^{15}N-laurolactam, probably on the outer shell of the zeolite.

4. Conclusions

To summarize, the results reported here give evidence that the Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam occurs in the interior of the pores of MFI zeolites and that the O-protonated lactam is formed on the bridging hydroxyl groups. The Brönsted acid sites placed at the outer shells of the crystals, probably at the mouth of the pores, are also active for the Beckmann rearrangement. The silanol groups located on the external zeolite surface are less active and less selective toward the lactam than the hydrogen bonded (silanol nests) in the interior of the zeolite pores.

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