Study of the Beckmann rearrangement of acetophenone oxime over porous solids by means of solid state NMR spectroscopy

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The Beckmann rearrangement of acetophenone oxime using zeolite H-beta and silicalite-N as catalysts has been investigated by means of ¹⁵N and ¹³C solid state NMR spectroscopy in combination with theoretical calculations. The results obtained show that the oxime is N-protonated at room temperature on the acid sites of zeolite H-beta. At reaction temperatures of 423 K or above, the two isomeric amides, acetanilide and *N*-methyl benzamide (NMB) are formed, and interact with the Brønsted acid sites of zeolite H-beta through hydrogen bonds. The presence of residual water hydrolyzes the two amides, while larger amounts inhibit the formation of NMB and cause the total hydrolysis of the acetanilide. Over siliceous zeolite silicalite-N, containing silanol nests as active sites, the oxime is adsorbed through hydrogen bonds and only acetanilide is formed at reaction temperatures of 423 K or above. In the presence of water, the reaction starts at 473 K, still being very selective up to 573 K, and the amide is partially hydrolyzed only above this temperature.

Introduction

The Beckmann rearrangement of ketoximes into amides is a common reaction used in organic chemistry, and has been widely studied for many years.¹ One of the most important industrial applications of this reaction is the transformation of cyclohexanone and cyclododecanone oximes into *ɛ*-caprolactam and ω -laurolactam, respectively, which are raw materials in the fabrication of fibers (nylon). The industrial production of lactams by the Beckmann rearrangement of cyclic oximes is classically catalyzed by liquid acids and much work has been carried out with the objective of substituting this homogeneous process for an environmentally friendly, heterogenous one.^{2–4} The research efforts of the last fifteen years have led to the commercialization of a cleaner process by using silica-rich MFI-type zeolite, consisting of a three-dimensional network of 10-membered ring channels (average pore diameter 5.5 Å), as catalysts. Sumitomo Chemical Co. has constructed a production plant which has been working in Japan since 2003.^{5–7}

Another potential industrial application of the Beckmann rearrangement reaction is the synthesis of paracetamol (*N*-acetyl-*p*-aminophenol). Conventionally, this product is commercially synthesized by acetylating *p*-aminophenol with acetic anhydride, but this process presents some difficulties because of the occurrence of unwanted reactions. An alternative, new process involves the Beckmann rearrangement of 4-hydroxyacetophenone oxime with liquid acids,⁸ however, the use of these catalysts requires extensive purification of the final reaction product for human use.⁹ Therefore, environmentally friendly solid acids such as zeolites have been successfully used

as catalysts in the liquid-phase Beckmann rearrangement of 4-hydroxyacetophenone oxime to paracetamol.^{10–11}

Acetanilide is an amide related to paracetamol which has also been synthesized by the Beckmann rearrangement of the corresponding (acetophenone-) oxime using solid acids as catalysts.^{12–14} Acetanilide possesses industrial interest as an intermediate in the synthesis of pharmaceuticals and as an additive in hydrogen peroxide, varnishes, polymers and rubbers. However, there are only a few publications on the heterogeneous rearrangement of acetophenone oxime and most of them in the liquid phase.^{12–14}

The aim of this work is to investigate the reaction mechanism of the Beckmann rearrangement of acetophenone oxime using zeolites containing active sites of differing nature as catalysts. This knowledge is essential to the design of catalysts with adequate properties for the potential development of green technologies to produce linear amides of pharmacological interest, containing benzyl groups with different ring substituents. For this purpose, we have studied the rearrangement of acetophenone oxime over two different zeolites: Al-containing zeolite beta with Brønsted acid sites, and silicalite with silanol nests as active sites, combining in situ solid state NMR and theoretical calculations. Zeolite beta possesses a threedimensional network of 12-membered ring channels with an average pore diameter of ca. 6.7 Å. Defective silicalite zeolite was chosen because of its good catalytic performance in the rearrangement of cyclic oximes.7,15,16

Experimental

Materials

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Zeolite H-beta (Si/Al = 12.5, crystal sizes of 0.1–0.2 μm), produced by Zeolyst, is commercially available (CP811) and

presents only minor amounts of extra-framework (octahedral) aluminium as detected by solid state ²⁷Al NMR. Silicalite was synthesized following the method described in previous publications,^{16,17} and subsequently submitted to basic treatment to generate silanol nests (silicalite-N) as follows: 5 g of zeolite calcined at 823 K for 12 h were impregnated with 20 g of an aqueous solution of ammonia (25 wt%) and ammonium nitrate (7.5 wt%) and heated in a stainless steel autoclave at 373 K overnight.¹⁶ The final silicalite-N (crystal sizes around 0.5 µm) catalyst was recovered after washing with deionized water, filtering and drying at 383 K for 4 h. (α -¹³C, ¹⁵N)-Acetophenone oxime was prepared mixing 14.4 mmol of ¹⁵N-hydroxylamine hydrochloride (98% ¹⁵N, Cambridge Isotope Laboratories) with 4.3 mmol of α -¹³C-acetophenone, 24.4 mmol of sodium acetate and 222.2 mmol of water, and heating at 368 K for 1 h. Before use, the ¹⁵N-acetophenone oxime was re-crystallized in ether and identified by NMR.

Solid state NMR spectroscopy

Solid state NMR spectra were recorded at room temperature on a Bruker AV 400 WB spectrometer. Samples were dehydrated at 673 K overnight reaching a final pressure of 10^{-5} mbar. To record ¹H NMR spectra, a portion of the sample was transferred into a rotor within a glove box under an atmosphere of N₂. The spectra were recorded with a BL4 probe spinning the sample at 10 kHz, by using 90° pulses of 5 µs and recycle delays of 15 s. To study the reaction, 300 mg of catalyst outgassed at 673 K was mixed with 15 mg of $(\alpha$ -¹³C, ¹⁵N)-acetophenone oxime and homogenized under an inert atmosphere in a glove box. A portion of the mixture was introduced into a glass insert, which was sealed after outgassing at room temperature. The ¹H to ¹⁵N ($^{1}H/^{15}N$) cross-polarization (CP) MAS spectra were recorded with a 1 H 90° pulse of 5 µs, a contact time of 5 ms and a recycle delay of 5 s. The ¹H to ¹³C (¹H/¹³C) CP-MAS spectra were recorded with a 90° pulse for ¹H of 5 μ s, a contact time of 5 ms and a recycle delay of 5 s.

Computational details

Silanol defects and Brønsted acid sites were simulated by means of the Si(OSiH₃)₃OH and Al(OSiH₃)₃(OH)SiH₃ cluster models, respectively, as described in previous work.¹⁸ The geometries of the two zeolitic clusters and the complexes resulting from the adsorption of acetophenone oxime, and of the possible reaction products (acetanilide, N-methyl benzamide, aniline,...) were optimized using the density functional B3PW91 method and the standard 6-31G(d,p) basis set.¹⁹⁻²¹ In these calculations, the coordinates of all atoms except the terminal H of the SiH₃ 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.^{22,23} ¹⁵N and ¹³C chemical shifts were calculated as $\delta = \sigma_{ref} - \sigma$, and corrected with the equations obtained from a preliminary study of the performance of B3PW91 functional.¹⁸ All calculations in this work were performed using the GAUSSIAN98 computer program.24

Results and discussion

Theoretical calculations

The calculations on the adsorption of acetophenone oxime over silanol and Brønsted acid sites in zeolite beta has been previously reported by our group.¹⁸ Our results indicated that the N-protonated oxime is readily formed upon adsorption at Brønsted acid sites, whereas the oxime is adsorbed over silanol groups forming H-bonds.¹⁸ These conclusions agree with theoretical and experimental results reported by other groups.^{25–27} Here, we focus our study on the interaction of the reaction products of the Beckmann rearrangement of acetophenone oxime with these same types of zeolite sites *i.e.*, silanols and bridging hydroxyl groups.

The reaction product of the Beckmann rearrangement of acetophenone oxime is acetanilide, which results from the migration of the phenyl group in the anti position with respect to the hydroxyl group. Although this reaction is highly stereospecific, we have also considered the N-methyl benzamide (NMB) isomer, as it has been reported to appear as a by-product of the rearrangement of acetophenone oxime.¹² Accordingly, we have optimized the adsorption complexes of the two amides, acetanilide and NMB, on silanol (Acetanilide/Silanol and NMB/Silanol) and bridging Si-OH-Al (Acetanilide/Brønsted and NMB/Brønsted) zeolite groups, and obtained the models depicted in Scheme 1. The ¹⁵N and ¹³C (the ¹³C-carbonyl group) NMR chemical shifts and adsorption energies, calculated using density functional methods, are summarized in Table 1. The distances between the amides and zeolite hydroxyl groups, depicted in the models of Scheme 1, are consistent with the formation of hydrogen bonds, which are shorter with Brønsted acid sites, resulting in more stable complexes (models Acetanilide/Brønsted and NMB/Brønsted in Scheme 1). Regarding chemical shifts, the results summarized in Table 1 show that $\delta^{15}N_{calc}$ of acetanilide and NMB experience larger shifts to low field when they interact with bridging hydroxyl groups, where they are more strongly adsorbed. We must note that the ¹⁵N chemical shifts calculated for NMB/Brønsted and the two acetanilide complexes, i.e., Acetanilide/Brønsted and Acetanilide/Silanol, are in the range -235 to -256 ppm, while displacement to high field is calculated for NMB/Silanol ($\delta^{15}N_{calc} = -284.6$ ppm, see Table 1). The structural models calculated for acetanilide and NMB suggest that neither of the two amides becomes protonated on Brønsted acid sites (Scheme 1), in contrast with the formation of O-protonated lactams (cyclic amides) reported previously.^{28,29} This difference suggests that acetanilide and NMB are less basic than cyclic caprolactam and ω -laurolactam.

The presence of residual water, difficult to completely remove from the reaction medium, can produce some hydrolysis of the oxime and/or the amide, depending on the catalyst properties. Accordingly, we have also theoretically calculated the complexes resulting from the interaction of the hydrolysis products of acetanilide (aniline and acetic acid) and of NMB (benzoic acid and methylamine) with a zeolite Brønsted acid site as depicted in Scheme 2. The simulation of the interaction with silanol groups has been omitted, since no noticeable changes on chemical shifts are expected according to the results for the amides reported in Table 1.

calc/ppm	o C _{cale} /ppm	o re _{exp} /ppm	$o C_{exp}/ppm$
-247.8	165.5	_	176.0
-248.0	174.2	-246.0	173.0
-235.9	175.6	-230.0	177.0
-248.2	168.2	-250.0	176.0
-293.2	165.8		166.0
-284.6	175.1	а	а
-255.7	177.3	-245.0	168.0^{b}
-	$\begin{array}{r} -247.8 \\ -248.0 \\ -235.9 \\ -248.2 \\ -293.2 \\ -284.6 \\ -255.7 \end{array}$	$\begin{array}{cccc} -247.8 & 165.5 \\ -248.0 & 174.2 \\ -235.9 & 175.6 \\ -248.2 & 168.2 \\ -293.2 & 165.8 \\ -284.6 & 175.1 \\ -255.7 & 177.3 \end{array}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

Table 1 Adsorption energies calculated for the models depicted in Scheme 1. Calculated and experimental ¹⁵N and ¹³C isotropic chemical shifts for acetanilide and NMB both isolated and in models (a)-(d) in Scheme 1, and for acetanilide interacting with water

The ¹⁵N and ¹³C (of the carboxylate group) NMR chemical shifts calculated for the complexes of Scheme 2 by using ab initio methods, together with the experimental values reported in the bibliography are summarized in Table 2. We must note that, according to Scheme 2, both amines, i.e., aniline and methylamine, become protonated on the Brønsted acid sites of the zeolite; though their δ^{15} N values are only slightly shifted when compared with the neat amine (see Table 2).

Solid state NMR spectroscopy

Zeolite characterization by ¹H NMR. The active sites present in the zeolites H-beta and silicalite-N dehvdrated at 673 K. used here as catalysts, have been characterized in a previous publication by infrared spectroscopy,³¹ and here by means of ¹H NMR (see Fig. 1). The spectrum of acidic zeolite H-beta (Fig. 1(c)) shows an intense peak at 1.8 ppm of isolated silanols and a band at 4.0 ppm assigned to bridging hydroxyl

Si-OH-Al groups. These ¹H signals are associated with the infrared bands in the range 3725-3745 cm⁻¹ and 3605 cm⁻¹, respectively.³⁰⁻³² Hydroxyl groups bonded to non-framework aluminium species appear in the range 2.6-3.6 ppm (see Fig. 1(b)), and are probably related to the infrared band at 3780 cm⁻¹.30-32

The ¹H NMR spectrum of the parent silicalite, which has been included in Fig. 1 for comparison purposes, consists mainly of a peak of isolated SiOH groups at 1.8 ppm (Fig. 1(a)). The spectrum of silicalite-N, shown in Fig. 1(b), evidences the creation of structural defects in the MFI zeolite framework by submitting the sample to a basic treatment. Besides isolated silanols (signal at 1.8 ppm), the spectrum of silicalite-N (Fig. 1(b)) shows a shoulder at 2.2 ppm usually assigned to geminal or vicinal SiOH groups (infrared band at around 3690 cm^{-1}).^{16,31,32} and an additional



Scheme 1 Optimized structures of acetanilide (a, c) and N-methyl benzamide (b, d) adsorbed on bridging Si-OH-Al (a, b) and silanol zeolite groups (c, d). Bond distances are expressed in angstroms.





Scheme 2 Optimized structures of (a) aniline, (b) acetic acid, (c) methylamine, and (d) benzoic acid interacting with bridging Si-OH-Al zeolite groups. Bond distances are expressed in angstroms.

Si

 Table 2
 Calculated and experimental ¹⁵N and ¹³C isotropic chemical shifts of the hydrolysis products of acetanilide and NMB adsorbed on Brønsted acid sites depicted in Scheme 2

	δ $^{15}{ m N_{calc}}/$ ppm	δ $^{13}C_{calc}/$ ppm	$\frac{\delta}{\rm ppm}^{15}{\rm N_{exp}}/$	$\delta^{13}C_{exp}$
Acetic acid/Brønsted Benzoic acid/Brønsted	_	183.3 175.8	_	182 a
Aniline/Brønsted Methylamine/Brønsted	$-329.7 \\ -360.7$	_	$-330 \\ -360$	

^{*a*} Appears in the amide region and, thus, is difficult to detect.



Fig. 1 ¹H MAS NMR spectra of zeolites dehydrated at 673 K overnight: (a) silicalite, (b) silicalite-N and (c) H-beta.

band at 3.6 ppm that can be associated with the broad infrared hydroxyl band centred at 3500 cm^{-1} , assigned to silanol nests (see Fig. 1(b)).^{16,31}

¹⁵N and ¹³C NMR of the Beckmann rearrangement of $(\alpha^{-13}C, {}^{15}N)$ acetophenone oxime. Fig. 2 shows the ${}^{13}C$ and ${}^{15}N$ NMR spectra recorded for the Beckmann rearrangement of $(\alpha^{-13}C, {}^{15}N)$ -acetophenone oxime over zeolite H-beta, containing Brønsted acid sites. The ${}^{13}C$ NMR signals come from the ${}^{13}C$ -labelled α -carbons of the oxime, the ${}^{13}CO$ carbonyl groups of amides and the ${}^{13}COOH$ carboxylate groups of the acids produced by hydrolysis of the amide .

The oxime is adsorbed at room temperature by capturing the zeolite acidic proton; it becomes ¹⁵N-protonated, giving broad ¹³C and ¹⁵N peaks at 166.5 ppm and -148.5 ppm, respectively (Fig. 2(a) and (a')). A sharper and weaker ¹³C component at 155 ppm in the spectrum of Fig. 2(a) can indicate the presence of some amounts of non-interacting oxime. Heating the reaction system at 423 K produces the practical disappearance of the ¹³C and ¹⁵N signals of the oxime and the appearance of new resonances as can be observed in the spectra of Fig. 2(b) and (b'). The ¹⁵N NMR spectrum of Fig. 2(b') shows two peaks in the chemical shift range typical of amides, one at -230 ppm and another,

weaker, at -245 ppm, which are attributed to 15 N-acetanilide and ¹⁵N-NMB, respectively. This assignment is made by comparison with the ¹⁵N chemical shifts calculated theoretically for the two amides interacting with a bridging hydroxyl group, listed in Table 1. It should be noted that the signal at -245 ppm could also be attributed to ¹⁵N-acetanilide interacting with silanol groups or with trace amounts of water present in the system (see Table 1). However, the presence of NMB in the products was confirmed by mass spectroscopy, reinforcing the assignment of the -245 ppm signal to ¹⁵N-NMB adsorbed on a Brønsted acid site. Besides these two peaks, the ¹⁵N spectrum (Fig. 2(b')) displays weak signals at -330 ppm and -360 ppm attributed to ¹⁵N-protonated aniline and ¹⁵N-protonated methylamine on Brønsted acid sites (see Scheme 2), according to the chemical shifts listed in Table 2. These amines must come from the hydrolysis of acetanilide (aniline) and NMB (methylamine) with residual amounts of water present in the reaction system. The ¹³C NMR spectrum recorded after heating at this same temperature (423 K, Fig. 2(b)) shows a band at 176 ppm due to ¹³CO-acetanilide and a weaker signal at 168 ppm from ¹³CO-NMB (see Table 1) with a shoulder at 182 ppm due to ¹³COOH-acetic acid, again indicating hydrolysis of acetanilide. The signal of benzoic acid ($\delta^{13}C = 175.8$ ppm) coming from the hydrolysis of NMB must be overlapped in the main broad resonance of the spectrum. Besides these signals, a very weak ¹³CO-acetophenone signal appears at 193 ppm pointing to some hydrolysis of the oxime.

The increase of the reaction temperature of the acetophenone oxime on zeolite H-beta to 473 K does not appreciably change the ¹³C and ¹⁵N spectra, producing only a better resolution of the peak of ¹⁵N-NMB at -245 ppm, and an enhancement of the relative intensity of the anilinium cation, as shown in Fig. 2(c) and (c'). Changes in the product distribution are evident after the reaction temperature of 623 K; the ¹⁵N NMR spectrum (Fig. 2(d')) shows only some increase in the relative intensity of NMB, but new signals are evident in the better resolved ¹³C spectrum (Fig. 2(d)). The spectrum of Fig. 2(d) clearly shows the ¹³C peaks of acetanilide (and probably benzoic acid) at 176 ppm, and of NMB at 168 ppm, as well as that of acetic acid at 182 ppm and the very weak peak of acetophenone at 193 ppm. Besides these signals, which were already present at lower reaction temperatures, a new one appears at 155 ppm (Fig. 2(d)). This latter peak is attributed to a secondary product formed from NMB and/or acetanilide at higher reaction temperatures (above 573 K) on zeolites containing Brønsted acid sites; however, we have failed in its identification by different methods.

The main ¹⁵N and ¹³C NMR spectroscopic results of this reaction over siliceous zeolite beta were reported in our previous publication.¹⁸ The ¹⁵N NMR spectra are quite similar to those depicted in Fig. 3 for the transformation of $(\alpha^{-13}C, {}^{15}N)$ -acetophenone oxime over silicalite-N. The spectrum recorded after the adsorption of the oxime at room temperature, displayed in Fig. 3(a), shows a very sharp peak at -21 ppm due to unadsorbed oxime; however, inspection of the spectrum shows a very weak, broad resonance centred at -48 ppm from the ¹⁵N-oxime adsorbed on silanol groups.



Fig. 2 ${}^{1}H/{}^{13}C$ (a–d) and ${}^{1}H/{}^{15}N$ (a'–d') CP-MAS NMR spectra of (α - ${}^{13}C$, ${}^{15}N$)-acetophenone oxime: (a) + (a') adsorbed on zeolite H-beta at room temperature, and subsequently treated during 1 h at (b) + (b') 423 K, (c) + (c') 473 K, and (d) + (d') 623 K.

Comparison of this spectrum with that recorded when the same oxime is mixed with zeolite beta containing defective silanol groups suggests a weaker interaction of the oxime with silicalite-N,¹⁸ which can be due to a lower concentration of connectivity defects. However, although the oxime enters the pores of Al-containing zeolite ZSM-5 (spectrum not shown) to become protonated, we cannot completely discard the limitations of diffusion of the oxime into the pores of silicalite.

As shown in Fig. 3(b), when the $(\alpha^{-13}C, {}^{15}N)$ -oximesilicalite-N system is heated at 423 K, a new signal grows at -250 ppm. Although the position of this peak is close to that of ${}^{15}N$ -NMB on zeolite H-beta, the $\delta^{15}N_{calc}$ of the two amides interacting with silanol groups allows its assignment to ${}^{15}N$ -acetanilide ($\delta^{15}N_{calc} = -248$ ppm for the model Acetanilide/Silanol, Scheme 1, Table 1). When the reaction temperature is increased to 473 K, the spectrum of Fig. 3(c) is obtained, which shows a unique signal of acetanilide at $\delta^{15}N = -250$ ppm, indicating that the reaction is complete at this temperature.

A remarkable result here is the formation of the amide isomer NMB over Brønsted acid sites, which is not expected according to the high stereospecificity of the migration of the alkyl group in the *anti* position to the hydroxyl group, though we must note that 5% of NMB has previously been reported in the Beckmann rearrangement of acetophenone oxime on zeolite HY.¹² The formation of the NMB isomer probably requires the prior isomerization of the oxime to place the methyl group in the *anti* position with respect to the hydroxyl group. This process involves rotation around the C–N bond and must be hindered for the neutral oxime having a C==N



Fig. 3 ${}^{1}H/{}^{15}N$ CP-MAS NMR spectra of (α - ${}^{13}C$, ${}^{15}N$)-acetophenone oxime: (a) adsorbed on zeolite silicalite-N at room temperature and subsequently treated during 1 h at (b) 423 K, (c) 473 K and (d) 523 K.

double bond (see Scheme 3). However, this rotation can occur to some extent in the N-protonated acetophenone oxime possessing a single C–N bond. Accordingly, no NMB is formed over siliceous zeolites, whereas some is formed over acidic H-beta.



Scheme 3 Rotation of the C–N bond for (a) the neutral acetophenone oxime, and (b) the N-protonated oxime.

Effect of water in the Beckmann rearrangement of ¹⁵Nacetophenone oxime. As shown above, when the Beckmann rearrangement is carried out using zeolite H-beta as catalyst, residual water in the reaction system partially hydrolyzes acetanilide and *N*-methyl benzamide. In order to better determine the effect of water, we have carried out the reaction by mixing the oxime with the non-dehydrated zeolites. In these conditions, the H₂O/oxime molar ratios are 21 and 7 for zeolites H-beta and silicalite-N, respectively.

Fig. 4 depicts the results obtained by ¹⁵N and ¹³C NMR spectroscopy for the reaction of (α -¹³C, ¹⁵N)-acetophenone oxime over zeolite H-beta. Despite the presence of water, the acetophenone oxime adsorbed on the acidic zeolite becomes N-protonated at room temperature, as evidenced in the ¹⁵N NMR spectrum of Fig. 4(a'). As shown in the spectrum of Fig. 4(b'), when the reaction temperature is raised to 473 K, the ¹⁵N peak of the ¹⁵N-protonated oxime disappears, while

two new signals appear, one at -250 ppm, in the amide region, and another one at -332 ppm from ¹⁵N aniline protonated on Brønsted acid sites (see Scheme 2 and Table 2). The corresponding ¹³C NMR spectrum (Fig. 4(b)) shows a peak for acetanilide at 176 ppm and another at 183 ppm due to acetic acid. The presence of anilinium and acetic acid clearly indicates the hydrolysis of acetanilide. The amide resonance is slightly high-field shifted and appears at a similar position to that of ¹⁵N-NMB on Brønsted acid sites (-250 ppm, see Scheme 1 and Table 1). However, neither the ¹⁵N nor the ${}^{13}C$ spectra (Fig. 4(b) and (b')) give any evidence for the formation of NMB or any of its hydrolysis products. This suggests that the ^{15}N peak at -250 ppm in the spectrum of Fig. 4(b') must be assigned to acetanilide, and that its chemical shift is changed by the presence of water. This assignment is supported by the ¹⁵N chemical shift calculated for the complex formed by the interaction of acetanilide with one molecule of water (see Table 1). The absence of NMB in the reaction products, further confirmed by mass spectrometry, suggests that water inhibits the isomerization of the oxime (or the migration of the syn-methyl group) during rearrangement. Further increase of the reaction temperature favours the hydrolysis of acetanilide, which is almost complete at 473 K, as can be seen in the spectra shown in Fig. 4(c) and 4(c').

Fig. 5 shows the ¹⁵N NMR spectra obtained after heating a mixture of zeolite silicalite-N without previous dehydration and ¹⁵N-acetophenone oxime. The results reported in Fig. 5 indicate that the presence of water has no dramatic influence on the Beckmann rearrangement reaction. The main effects of water are: (i) to increase the temperature at which the rearrangement starts to 473 K (from 423 K), and (ii) to hydrolyse some acetanilide at reaction temperatures of 573 K or higher.



Fig. 4 ${}^{1}H/{}^{13}C$ (a–d) and ${}^{1}H/{}^{15}N$ (a'–d') CP-MAS NMR spectra of (α - ${}^{13}C$, ${}^{15}N$)-acetophenone oxime: (a) + (a') adsorbed on non-dehydrated zeolite H-beta at room temperature and subsequently treated during 1 h at (b) + (b') 423 K, and (c) + (c') 473 K.



Fig. 5 ${}^{1}\text{H}/{}^{15}\text{N}$ CP-MAS NMR spectra of (α - ${}^{13}\text{C}$, ${}^{15}\text{N}$)-acetophenone oxime: (a) adsorbed on zeolite silicalite-N at room temperature, and subsequently treated during 1 h at (b) 373 K, (c) 473 K, (d) 573 K and (e) 623 K.

Conclusions

The results obtained in the Beckmann rearrangement reaction of acetophenone oxime over acidic zeolite H-beta and silicalite-N, dehydrated and in the presence of water, have led us to propose the reaction pathways shown in Schemes 4(a) and (b).

N-protonated acetophenone oxime is readily formed on the Brønsted acid sites at room temperature even in the presence of water. After heating at 423 K or above, both acetanilide and *N*-methyl benzamide (NMB) are formed, and a new unidentified secondary product formed from the amides appears at reaction temperatures above 573 K. Residual water produces partial hydrolysis of acetanilide to give aniline and acetic acid, and of NMB to give benzoic acid and methylamine. Both amines (methylamine and aniline) are protonated on the zeolite Brønsted acid sites. The presence of water in the reaction medium inhibits the formation of NMB; only acetanilide is formed, which is practically completely hydrolyzed above 473 K.

Pure siliceous silicalite-N is more selective to acetanilide than the acidic zeolite both in presence and absence of water in the reaction medium. Only part of acetophenone oxime forms hydrogen bonds with silanol groups at room temperature and reacts above 423 K to selectively give acetanilide. When water is present in the reaction medium (even if there is an excess with respect to the oxime) there is only partial hydrolysis of acetanilide above 523 K.

The results presented here suggest that, as for cyclic oximes, acid zeolites are more active and less selective catalysts than siliceous zeolites containing structural defects, *i.e.* silanol



Scheme 4 Reaction pathway for the Beckmann rearrangement of acetophenone oxime into acetanilide on zeolite hydroxyl groups: (a) bridging Si–OH–Al and (b) silanol.

groups, in the Beckmann rearrangement of linear oximes involving benzyl groups. However, they may require higher reaction temperatures, and, therefore, it may be necessary to carry out the reaction in the gas phase.

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