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# Imine Chemistry in Zeolites: Observation of *gem*-Amino−Hydroxy Intermediates by in Situ $^{13}$C and $^{15}$N NMR[†]

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**Abstract:** Variable-temperature $^{13}$C NMR and $^{15}$N NMR with magic angle spinning were used to characterize the formation of imines by the reactions of benzaldehyde or acetone with ammonia on zeolites. When ammonia was adsorbed at cryogenic temperatures on zeolite HY (FAU) which was preloaded with benzaldehyde, it formed an appreciable amount of the tetrahedral *gem*-amino−hydroxy intermediate at temperatures as low as 163 K. As the sample was heated to slightly above room temperature, the intermediate dehydrated to form imine. The intermediate is persistent at 298 K and yields distinct isotropic chemical shifts at 78 ppm for $^{13}$C and −320 ppm for $^{15}$N. Benzaldehyde was cleanly converted to imine by reaction with ammonia on the medium-pore zeolite HZSM-5 (MFI), but no *gem*-amino−hydroxy intermediate was seen. We attribute this effect to the steric and reactivity differences that favor dehydration to form the less bulky imine product on HZSM-5. The experience of solution chemistry suggests that *gem*-amino−hydroxy intermediates from ketones are less stable than those from aldehydes, and this was also confirmed for reactions on zeolites. However, a small $^{13}$C signal at 81 ppm was observed during the low-temperature reaction of acetone and ammonia on HY, and this shift is identical to that seen for 2-aminopropan-2-ol in liquid ammonia. Low loadings of acetone and ammonia on HZSM-5 formed the imine cleanly, and this was stable with little secondary chemistry to 523 K. Secondary reactions were more pronounced for acetone and ammonia on HY, and these were used to explore and compare several reactant adsorption protocols. Sample heating generated a sequence of nitrogen-substituted products analogous to those seen in aldol reactions of acetone on the same zeolite. These species were partially converted to aromatic hydrocarbons at 523 K, but no pyridines were formed with these reaction conditions. The imines showed evidence of protonation and hydrogen bonding to the conjugate base site of the zeolite. We also characterized the temperature-dependent dynamics of imine products that exhibited broad $^{13}$C signals at room temperature, but sharp lines at low and high temperatures. The results of this study were used in combination with published theoretical studies of the interaction of ammonia with zeolites to suggest models of the association of reactants, intermediates, and products with the framework site.

## Introduction

The structure and reactivity of carbonyl compounds adsorbed on zeolites and other heterogeneous catalysts are of interest because several existing processes use the reactions of carbonyls on zeolites in the synthesis of bulk or fine chemicals, and because of the possibility of redesigned synthetic routes using solid acids. For example, the major commercial routes to pyridine and alkylpyridines include the reactions of acetone, aldehydes, and ammonia on zeolites or amorphous aluminosilicates, and a number of related processes have been proposed.[1−5] In recent papers we described the aldol reactions of aldehydes[6] and ketones[7] in zeolites. We also reported that cyclopentanol was readily converted to cyclopentylamine on a zeolite loaded with ammonia.[8] Bosácek and co-workers reported spectroscopic evidence that acetone reacts with ammonia on zeolite HZSM-5 (MFI) to form the corresponding imine.[9,10] The present investigation examined in detail the reactions of benzaldehyde/ammonia and acetone/ammonia on two zeolites with different pore sizes, the large-pore zeolite HY (FAU) and the medium-pore HZSM-5. Benzaldehyde was selected for this investigation for two reasons: tetrahedral *gem*-amino−hydroxy intermediates are known to form from aldehydes in liquid ammonia at low temperatures,[11] and, lacking an α hydrogen, benzaldehyde and its imine are incapable of aldol chemistry. Acetone was selected because of our experience with the aldol reactions of this compound.[7]

Using in situ variable-temperature $^{13}$C and $^{15}$N NMR, we observed the reaction sequence in Scheme 1. In particular, we were able to form the intermediate *gem*-amino−hydroxy **3** from

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[†] Dedicated to Professor Gary Maciel on the occasion of his 60th birthday.

[®] Abstract published in *Advance ACS Abstracts,* March 1, 1995.

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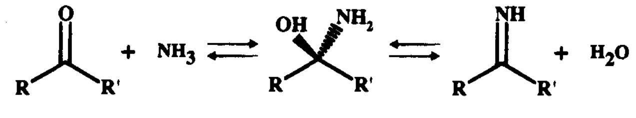
**Scheme 1**



**1**: R=Ph, R'=H
**2**: R=R'=$CH_3$
**3**: R=Ph, R'=H
**4**: R=R'=$CH_3$
**5**: R=Ph, R'=H
**6**: R=R'=$CH_3$

benzaldehyde at high concentrations in zeolite HY, and it persisted even at 298 K. At higher temperatures it was converted quantitatively to the imine **5**. We apparently also observed the intermediate **4** from the reaction of acetone, although the $^{13}$C spectra showed that it formed only in low concentrations and was not stable above 193 K. We were unable to observe the intermediates in the smaller-pore ZSM-5 catalyst, but imines did form, and **6** was stable on ZSM-5 at 523 K. Imines from ammonia are usually unstable in solution,[12] although N-substituted imines are important synthetic intermediates. Ammonia and acetone underwent more complex reactions on zeolite HY to yield nitrogen-substituted products analogous to those seen from the aldol reactions of acetone on that zeolite.[7] No aromatic heterocycles were seen at 523 K, but some of the observed products could be precursors to pyridine derivatives.

The stability of the intermediate **3** on zeolite HY and of the imines **5** and **6** on HZSM-5 greatly exceeds the experience of solution chemistry, and this highlights the possibility that zeolites and other porous inorganic materials may have properties significantly different from liquid reaction media.

## Experimental Section

**Catalyst Preparation and Reagents.** Zeolites HZSM-5 (framework Si/Al = 21) and $NH_4Y$ (framework Si/Al = 2.4, $N_2$ surface area greater than 800 $m^2/g$) were obtained from UOP Corp. The crystallinity and morphology of the HZSM-5 sample were verified by X-ray diffraction and electron microscopy. The acid site concentration in the HZSM-5 and HY samples was independently checked by several methods, including elemental analysis for aluminum, $^{27}$Al and $^{29}$Si MAS NMR, and quantitative $^{1}$H NMR and $^{13}$C NMR titrations. Catalysts were activated at 673 K by a procedure described elsewhere[13] and were used within 1 day of activation. [α-$^{13}$C]Benzaldehyde (99% $^{13}$C), [2-$^{13}$C]-acetone (99% $^{13}$C), [1,3-$^{13}C_2$]acetone (99% $^{13}$C), [$^{15}$N]ammonia (99% $^{15}$N), and [$^{15}$N]glycine (99% $^{15}$N) were obtained from Cambridge Isotopes.

**Sample Preparation for in Situ MAS NMR.** Except where stated otherwise, samples were prepared using the shallow-bed CAVERN device[14] to ensure a homogeneous distribution of adsorbates on the zeolites. Typically, 0.35 g of zeolite was loaded into a shallow-bed CAVERN and activated in vacuo to final pressures of less than $5 \times 10^{-5}$ Torr.

Adsorption protocols varied with the reactivity and vapor pressures of adsorbates. For the benzaldehyde/ammonia system, benzaldehyde was adsorbed onto zeolites at 298 K, and ammonia was then adsorbed either at 298 K or at 163 K using a liquid nitrogen/ethanol cold bath to cool the catalyst previously loaded with benzaldehyde. At least 0.5 h was allowed for the catalyst temperature to equilibrate prior to the adsorption of ammonia. Three different adsorption protocols were used for the acetone/ammonia system. In the sequential adsorption protocol, ammonia was adsorbed at 298 K, and acetone was then adsorbed at 298 or 163 K using the cryogenic adsorption techniques described above. In the simultaneous adsorption protocol, acetone and ammonia were mixed in the gas phase, and then the gas phase mixture was adsorbed onto the catalyst. The ammonium−Y adsorption protocol used an "ultra-shallow-bed CAVERN" to first activate the catalyst. The catalyst bed was then saturated with ammonia at 298 K, heated to 373 K for 2 h under vacuum, and kept under vacuum at 298 K for 24 h. The final pressure was less than $10^{-4}$ Torr. $^{15}$N MAS spectra of $NH_4Y$ samples prepared in this manner had a single, very sharp line. We believe that this method produces a very uniform distribution of ammonia and titration of all accessible Bronsted sites. For the result shown, 0.4 equiv of acetone was adsorbed onto the $NH_4Y$ at 298 K.

Regardless of adsorption protocol, the sample was loaded into the rotor within the CAVERN after adsorptions, and the rotor was capped. These steps were performed at the temperature of adsorption or lower to avoid warming the sample. Note that all CAVERN protocols resulted in sealed samples that were never exposed within a glovebox. The rotor was then transferred to the NMR probe, which had already been cooled to the desired temperature. $^{13}$C and $^{15}$N NMR spectra were then acquired as the probe temperature was raised to progressively higher temperatures.

**NMR Spectroscopy.** In situ $^{13}$C and $^{15}$N solid state NMR experiments were performed with magic angle spinning on a Chemagnetics CMX-360 MHz spectrometer operating at 90.5 MHz for $^{13}$C and 36.5 MHz for $^{15}$N. Hexamethylbenzene (17.4 ppm) and [$^{15}$N]glycine (−347.6 ppm) were used as external chemical shift standards for $^{13}$C and $^{15}$N, respectively. $^{13}$C chemical shifts are reported relative to TMS, and $^{15}$N chemical shifts relative to nitromethane. Chemagnetics-style pencil probes spun 7.5 mm zirconia rotors at 1−6.5 kHz with active spin speed control (±3 Hz).

The exact experimental protocol was intentionally varied from run to run, but in most cases the temperature was raised incrementally, and a variety of $^{13}$C and $^{15}$N spectra were obtained at each temperature. The $^{13}$C experiments included the following: cross-polarization[15] (CP, contact time = 2 ms, pulse delay = 1 s, 400−800 transients); cross-polarization with interrupted decoupling[16] (contact time = 2 ms, pulse delay = 1 s, 400−800 transients, dipolar dephasing time of 50 $\mu$s); and single-pulse excitation with proton decoupling (Bloch decay, pulse delay = 4−8 s, 200 transients). In the case of $^{15}$N experiments, cross-polarization spectra were obtained with a 1 s pulse delay, and typically 4000 scans were averaged. The contact times were 2 ms for the acetone/ammonia system and 1 ms for benzaldehyde/ammonia system. Occasionally, $^{15}$N Bloch decay spectra (100 s pulse delay, 400 scans) were also obtained. $^{15}$N spectra were generally more challenging to acquire as a result of long $T_1$ for many species and short $T_{1\varrho}$ for imine nitrogens.

## Results

**Benzaldehyde Alone.** Benzaldehyde is an ideal reactant for observing imine formation in zeolites without secondary reactions or the attendant problems of spectral assignment. Figure 1 shows a control experiment in which [α-$^{13}$C]benzaldehyde was adsorbed on zeolite HY without coadsorption of $NH_3$. At 298 K this adsorbate showed several characteristics of complexation by the Bronsted site: it was shifted 8 ppm downfield from its $^{13}$C shift of 192 ppm in $CDCl_3$ solution;[17] the line was slightly broad; and prominent spinning sidebands indicated that the adsorbate was incapable of isotropic reorientation on a ms time scale. The adsorbate was significantly more mobile at 393 K, as evidenced by the decrease in sideband intensity. A significant amount of the aldehyde underwent a disproportionation reaction[18] at 433 K to form stoichiometric amounts of [α-$^{13}$C]benzoic acid (175 ppm) and [9,10-$^{13}C_2$]9,10-dihydroanthracene (40 ppm). The latter was formed by the dimerization of [α-$^{13}$C]benzyl alcohol as confirmed by the direct study of the alcohol (spectra not shown).

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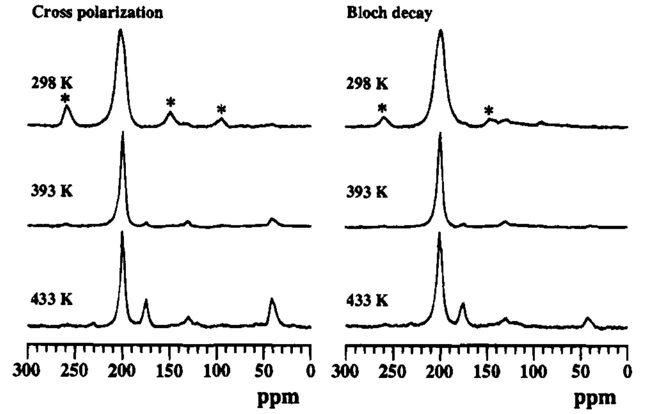

**Figure 1.** In situ $^{13}C$ MAS NMR study of [α-$^{13}C$]benzaldehyde alone on zeolite HY following adsorption at 298 K with a loading of ca. 0.5 equiv; both Bloch decay and cross-polarization spectra are shown, and asterisks denote spinning sidebands. Note that Bloch decay and cross-polarization yielded essentially equivalent spectra for this system. This is a control experiment for the latter studies with co-adsorbed ammonia. Benzaldehyde (200 ppm) was unreactive at room temperature. It underwent a disproportion reaction at 433 K to form benzoic acid (175 ppm) and 9,10-dihydroanthracene (40 ppm) derived from the dimerization of benzyl alcohol.

**Benzaldehyde and Ammonia.** Benzaldehyde was readily converted to the corresponding imine **5** upon adsorption onto HZSM-5 pretreated with an excess of [$^{15}N$]ammonia. $^{1}J_{C-N}$ scalar couplings are typically a few tens of Hz or less,[19] and no splittings were resolved in these studies. The $^{13}C$ study showed that most of the aldehyde was converted to imine (173 ppm) at 298 K, and the observation of a new peak at −214 ppm in the $^{15}N$ spectrum is strong confirmation of this assignment. Although the $^{13}C$ cross-polarization spectra reported in Figure 2 suggest no obvious intensity distortions (cf. Figure 1), the $NH_3$/$NH_4^+$ signal at −363 ppm is underrepresented in the $^{15}N$ spectrum due to the low CP efficiency of this species with the contact time used. $^{15}N$ Bloch decay spectra were generally prohibited by the very long $^{15}N$ $T_1$ of the imine nitrogens. Figure 2 also shows that the sample was unreactive at 523 K. Apparently, the Cannizzaro reaction of benzaldehyde was precluded by titration of the Bronsted sites.

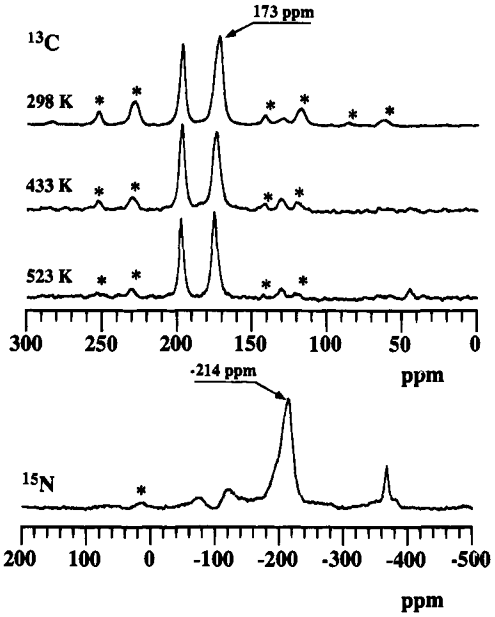

**Figure 2.** In situ $^{13}C$ and $^{15}N$ MAS NMR studies of the reactions of [α-$^{13}C$]benzaldehyde and [$^{15}N$]ammonia on zeolite HZSM-5 following adsorptions at 298 K. Arrows highlight signals from imine **5**. The loadings of ammonia and benzaldehyde were 1.2 and 1.0 equiv, respectively; only cross-polarization spectra are shown, and asterisks denote spinning sidebands. The $^{13}C$ spectra show that benzaldehyde (197 ppm) reacted with ammonia to form protonated imine **5** (173 ppm). The $^{13}C$ chemical shift of the imine was slightly temperature-dependent. The $^{15}N$ spectrum shows the protonated imine at −214 ppm and ammonia/ammonium (−363 ppm). Two weak downfield signals (−70 and −120 ppm) probably reflect imine **5** in less-acidic environments.

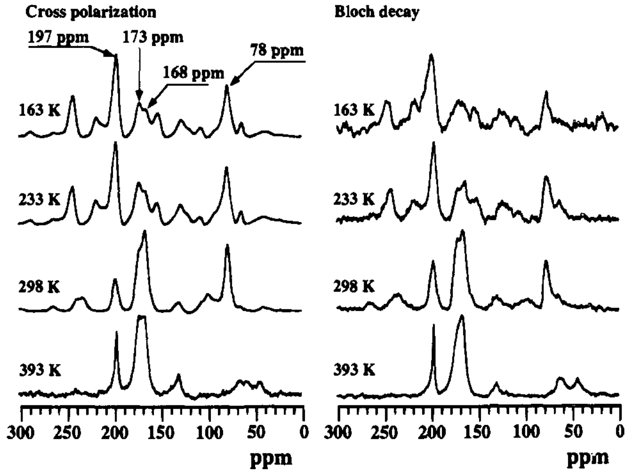

**Figure 3.** In situ $^{13}C$ MAS NMR study of the reactions of [α-$^{13}C$]benzaldehyde and [$^{15}N$]ammonia on zeolite HY following cryogenic adsorptions at 163 K. The loadings of benzaldehyde and ammonia were 0.6 and 0.9 equiv, respectively. Cross-polarization and Bloch decay spectra are shown. The spectra at 163 K show the formation of the *gem*-amino−hydroxyl intermediate **3** (78 ppm), which dehydrated to form protonated imine **5** (173 ppm) and nonprotonated imine **5** (168 ppm). Unreacted benzaldehyde was seen at 197 ppm. Upon raising the sample temperature to 298 K, approximately 80% of the benzaldehyde reacted. Further raising of the temperature to 393 K converted **3** completely to **5**.

The reaction of benzaldehyde and ammonia was much more insightful on zeolite HY, which has a larger pore structure and slightly lower acidity. Figure 3 reports $^{13}C$ spectra from one of several studies in which ammonia was adsorbed on HY at cryogenic temperature following treatment with benzaldehyde at room temperature. Isotropic $^{13}C$ signals are labeled for the CP spectrum at 163 K; the remaining features in that spectrum are spinning sidebands. At this temperature, the major constituent was unreacted aldehyde (197 ppm), and a small amount of imine remained in two environments with different degrees of protonation (173 and 168 ppm). The isotropic peak at 78 ppm is remarkable. It clearly represents a species present at a significant concentration, as indicated by the Bloch decay spectrum, and its relative integrated intensity as a function of temperature is consistent with it being an intermediate in the conversion of aldehyde to imine. Elementary concepts of $^{13}C$ chemical shift interpretation suggest that this shift corresponds to an $sp^3$-hybridized carbon with one directly attached oxygen and one directly attached nitrogen; two oxygens would give a shift 20 ppm further downfield, and two nitrogens or one oxygen and no nitrogen would be significantly upfield. Figure 4 presents additional spectroscopic evidence for the structure of this intermediate. Parts a and b of Figure 4 compare $^{13}C$ CP/MAS spectra at two spinning speeds to clarify the assignment of the isotropic peaks and sidebands. The very small chemical shift anisotropy implied by the small sidebands for the 78 ppm peak supports the assignment of that carbon to $sp^3$ hybridization. The interrupted decoupling spectrum in Figure 4c proves that

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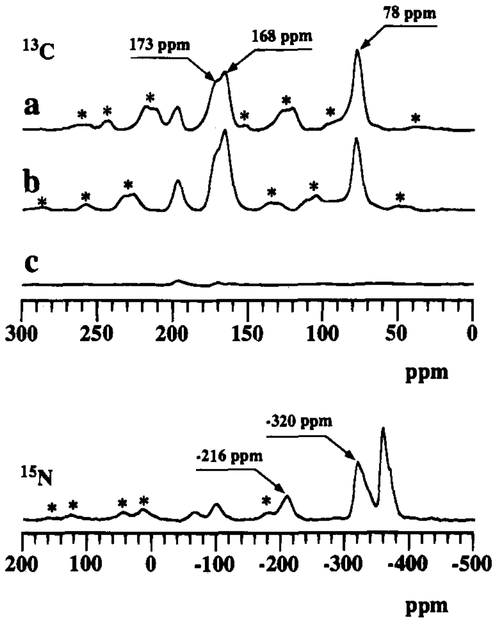
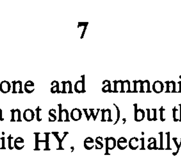


**Figure 4.** Selected $^{13}C$ and $^{15}N$ spectra characterizing species **3** and **5**. Asterisks denote spinning sidebands. This was the same sample as reported in Figure 3. Spectra a, b, and c were acquired at 298 K, and the $^{15}N$ spectrum was acquired at 233 K. a and b: CP spectra with spinning speeds of 4100 and 5500 Hz, respectively. The comparison of spectra a and b allows unambiguous identification of the isotropic peaks. (c) Interrupted decoupling spectrum. The $^{15}N$ spectrum shows the signal for **3** (−320 ppm) and protonated imine **5** (−216 ppm).

the 78 ppm peak (as well as the imine and aldehyde signals) correspond to CH or $CH_2$ carbons in molecules incapable of large amplitude motions on a 50 μs time scale. Finally, the −320 ppm peak in the $^{15}N$ spectrum, which goes away with complete conversion to imine (not shown), is consistent with a primary amine. Thus, the aggregate spectroscopic evidence combined with the limited possibilities for reactions in this system are strongly supportive of the formation of the *gem*-amino−hydroxy species **3** as a tetrahedral intermediate in the reactions of benzaldehyde and ammonia to form imine in zeolite HY. In the Discussion section, we will show that the observed $^{13}C$ chemical shifts are in close agreement with previous measurements of *gem*-amino−hydroxy species in $NH_3$ solutions.

**Acetone and Ammonia.** Figure 5 shows $^{13}C$ (both isotopomers) and $^{15}N$ spectra from representative in situ studies of acetone and ammonia on zeolite HZSM-5. The formation of imine **6** was favored by heating, and secondary reactions to form a small amount of the dimers **7** and **8** did not occur until 523 K. Without titration of the acid sites by ammonia, zeolite HZSM-5 is more active for aldol condensations of acetone. Attempts to observe the *gem*-amino−hydroxy intermediate on ZSM-5 at low temperatures were unsuccessful.



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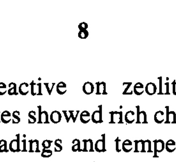

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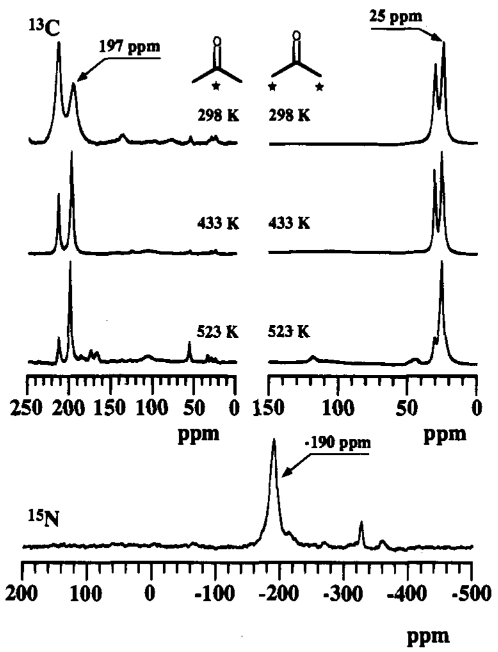


**Figure 5.** In situ $^{13}C$ and $^{15}N$ MAS NMR studies of the reactions of acetone and ammonia on zeolite HZSM-5 following the sequential adsorption protocol (see Experimental Section) at 298 K. Arrows highlight signals from imine **6**. The loadings of ammonia and acetone were 1.2 and 1.0 equiv, respectively. $^{13}C$ Bloch decay spectra and $^{15}N$ CP spectrum are shown, and the $^{13}C$ label positions are indicated by stars. The $^{13}C$ spectra at 298 K show the imine **6** (197 ppm in 2-$^{13}C$ isotopomer and 25 ppm in 1,3-$^{13}C$ isotopomer) and unreacted acetone (215 and 30 ppm). The conversion of acetone to imine **6** was nearly complete upon raising the sample temperature to 523 K. Small amounts of **7** (54 ppm in 2-$^{13}C$ isotopmer) and **8** (174 and 166 ppm in 2-$^{13}C$ isotopomer) were also formed after heating at 523 K. The $^{15}N$ spectrum was the average of 20 000 scans acquired at 298 K without heating and showed the formation of protonated imine **6** (−190 ppm).

Acetone and ammonia were unreactive on zeolite NaY (spectra not shown), but these adsorbates showed rich chemistry on zeolite HY, especially at higher loadings and temperatures. Acetone and its products have α hydrogens and hence undergo aldol condensation reactions. Because of the complex equilibria present for this system, including reversible formation of imines, the NMR spectra alone cannot be used to infer the mechanism of these condensation reactions, but the products themselves were easily identified.

This system presents some interesting challenges in sample preparation. One of our original concerns was that, even with shallow-bed adsorption, there might be segregation of the two reactants or dependence on the order of adsorbate loading. Since acetone can dimerize on acidic zeolites near room temperature, we either adsorbed the ammonia first or adsorbed a gas phase mixture of the two reagents. Figure 6 shows selected spectra from our exploration of different adsorption protocols for this demanding system. Figure 6a shows the spectrum obtained after simultaneously adsorbing a gas phase mixture; clearly, even this method resulted in some degree of inhomogeneity in the distribution of reactants, as suggested by formation of small amounts of diacetone alcohol and dimers such as **7**. The $^{15}N$ spectrum in Figure 6 is of the same sample as Figure 6a; as expected, there are two $^{15}N$ signals corresponding to primary amine groups as well as signals from imine **6** and unreacted ammonia/ammonium. Figure 6b shows that the sequential adsorption procedure produced slightly greater loading inhomogeneities at room temperature than the simultaneous protocol. Finally, Figure 6c shows that it was possible to form a significant amount of imine from acetone at room temperature without any secondary products, and suggests the reason for dimer formation at room temperature with the other protocols. A derivative of the shallow-bed CAVERN device that provides a much larger surface area at the expense of low-temperature operation was used in the adsorption of an excess of ammonia at room temperature. This sample was then gently heated and evacuated to remove some of the excess ammonia without converting the

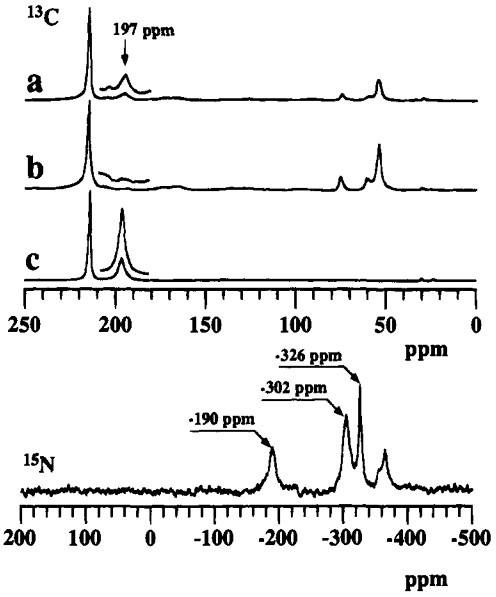
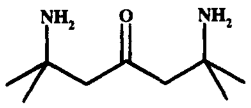


**Figure 6.** Selected $^{13}C$ and $^{15}N$ spectra of [2-$^{13}C$]acetone and [$^{15}N$]-ammonia on HY, showing the effects of various adsorption protocols. All the spectra were acquired at 298 K without heating. Bloch decay spectra are shown except for the $^{15}N$ spectrum, which was acquired using cross-polarization. (a) A gas phase mixture of 0.5 equiv of [2-$^{13}C$]-acetone and 0.6 equiv of [$^{15}N$]ammonia was adsorbed onto zeolite HY, and the spectrum shows the formation of imine **6** (197 ppm), diacetone alcohol (75 ppm), and amines (54 and 59 ppm) such as **7**. The accompanying $^{15}N$ spectrum shows imine **6** (−190 ppm) and amines (−302 and −326 ppm). (b) The sequential adsorption protocol was used with the same loadings as in a. The $^{13}C$ spectrum shows that no imine **6** formed, and the aldol condensation reaction was more important. (c) The ammonium−Y adsorption protocol was used with 0.4 equiv of [2-$^{13}C$]acetone. The spectrum shows that nearly 50% of acetone was converted to imine **6**, and no aldol condensation products were detected.

ammonium to Bronsted sites; this protocol was also expected to promote diffusion of ammonia throughout the zeolite crystallites and thus provide titration of all Bronsted sites. The $NH_4Y$ catalyst thus prepared was then exposed to acetone at room temperature, and Figure 6c was obtained. The absence of secondary products in Figure 6c suggests that the formation of small amounts of secondary products with the other protocols resulted from incomplete titration of Bronsted sites at room temperature. Theoretical and experimental studies[20,21] indicate that ammonia weakly associates with ammonium complexes in zeolites, and it is suggested that this could impede the uniform titration of the Bronsted sites, which can be effected with mild heating.



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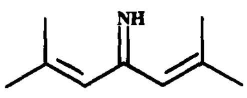

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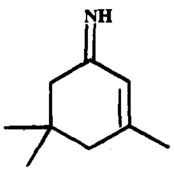
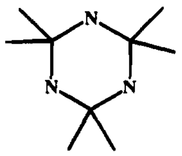


**11**

A number of high-temperature experiments were performed in order to identify some of the products of the acetone/ammonia reaction. Figure 7 shows parallel experiments for the two $^{13}C$ isotopomers of acetone. At moderate temperatures, the dominant products included **8** and **9**. At 523 K, **9** began to deaminate to form **10**; **10** subsequently cyclized to form **11**, which deaminated and rearranged to form aromatics such as mesitylene (see caption for assignments). The yields of various products differed with different adsorption protocols; however, the same products were always identified at high temperatures. Pyridine derivatives were not detected, although they might be expected to form at temperatures higher than those used here.

The aqueous ammonia solution chemistry literature suggests that observation of *gem*-amino−hydroxy intermediates is more challenging for ketones than aldehydes. Furthermore, some of the early reports of *gem*-amino−hydroxyl species mistakenly identified the cyclic trimeric forms of those species, which tend to form with warming.[11] We were able to reproduce the observation of a small peak at 81 ppm during the low-temperature reaction of acetone and ammonia on HY, and this chemical shift is identical to that reported in solution for 2-aminopropan-2-ol (**4**), the ammonia adduct of acetone.[22] Parts a and b of Figure 8 show a result obtained by adsorbing acetone on ammonia-treated HY at 163 K and then heating to 193 K; the 81 ppm peak was clearly visible with CP, but it was absent from the Bloch decay spectrum, suggesting either that there was very little of it or that it has a very long $^{13}C$ $T_1$. A peak was also visible at 65 ppm, and when the sample was heated to 213 K, this peak remained, but the 81 ppm peak was lost. A peak at 65 ppm is in the appropriate range for the cyclic trimer **12**.



**12**

We suggest that there is enough room in the supercage of ammonia-treated HY for **12** to form, but not the corresponding trimer of the ammonia adduct of benzaldehyde. Although we are confident that the peaks at 81 and 65 ppm in Figure 8 are real, we would be uncomfortable proposing assignments for them without the thorough characterization work for the much more stable *gem*-amino−hydroxy intermediate from benzaldehyde (**3**).

Finally we report that some of the acetone/ammonia on HY samples showed significant evidence of molecular dynamics that could potentially confound NMR measurements performed at room temperature following off-line sample heating, but provide additional information to a true in situ variable-temperature NMR protocol. Figure 9 shows a case in point; these spectra were acquired in order of decreasing temperature, and this corresponds to top to bottom in that figure. All of the lines are narrow in the $^{13}C$ MAS Bloch decay spectrum measured at 433 K. In particular, the large signals at 174 and 166 ppm due to **8** are well-resolved, and smaller signals due to **11** (184, 179, and 34 ppm) were also apparent. When this sample was cooled to room temperature, as might be done for in situ protocols with off-line heating, the signals for the unsaturated products were broadened substantially to yield a single downfield feature centered at ca. 170 ppm. The 34 ppm signal of **11** is "NMR invisible" at 298 K. This type of broadening can occur in NMR as a result of chemical exchange on an intermediate time scale or by any of several dynamical processes that interfere with

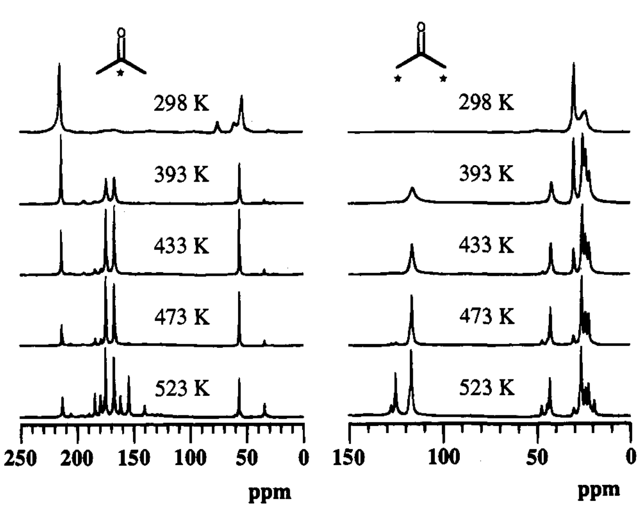


**Figure 7.** In situ $^{13}C$ MAS NMR studies of acetone and ammonia on zeolite HY. The [2-$^{13}C$]acetone/ammonia sample was the same as reported in Figure 6b, and the same sequential adsorption protocol was used for the preparation of [1,3-$^{13}C$]acetone/ammonia sample. The 298 K spectra show the formation of diacetone alcohol (75 ppm in 2-$^{13}C$) and amine **7** (54 ppm in 2-$^{13}C$). Upon heating to 393 K, **8** (174 and 166 ppm in 2-$^{13}C$; 22 and 116 ppm in 1,3-$^{13}C$) and **9** (214 and 56 ppm in 2-$^{13}C$; 42 and 25 ppm in 1,3-$^{13}C$) started to form. More **8** formed upon raising the sample temperature to 473 K. At 523 K, **9** deaminated to form **10** (161 and 154 ppm in 2-$^{13}C$; 125 ppm in 1,3-$^{13}C$), which subsequently cyclized to form **11** (184, 179, and 34 ppm in 2-$^{13}C$; 118 and 47 ppm in 1,3-$^{13}C$). The formation of mesitylene was indicated by the resonances at 140 ppm in 2-$^{13}C$ spectrum and 128 ppm in 1,3-$^{13}C$ spectrum at 523 K.

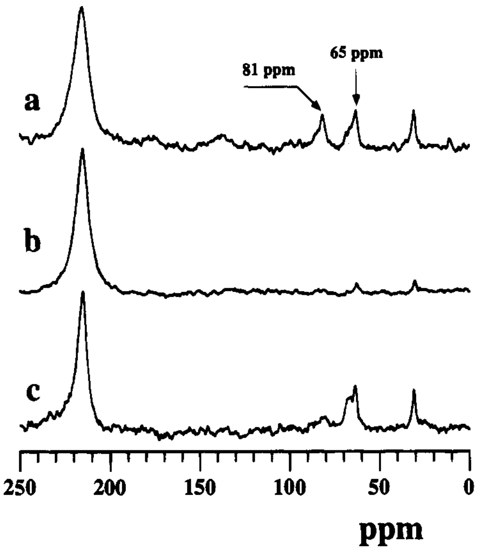


**Figure 8.** In situ $^{13}C$ NMR study of the reactions of [2-$^{13}C$]acetone and [$^{15}N$]-ammonia on HY following the sequential adsorption protocol at 163 K. The loadings were 1.0 equiv for ammonia and 0.5 equiv for acetone. (a) CP spectrum acquired at 193 K, suggesting the formation of **4** (81 ppm). The resonances around 65 ppm are probably due to the oligomerization products of **4**, and the 30 ppm peak is the natural-abundance signal of acetone. (b) This Bloch decay spectrum at 193 K shows that the amount of **4** was very small. (c) This CP spectrum at 213 K shows that the 81 ppm resonance disappeared upon gentle heating.

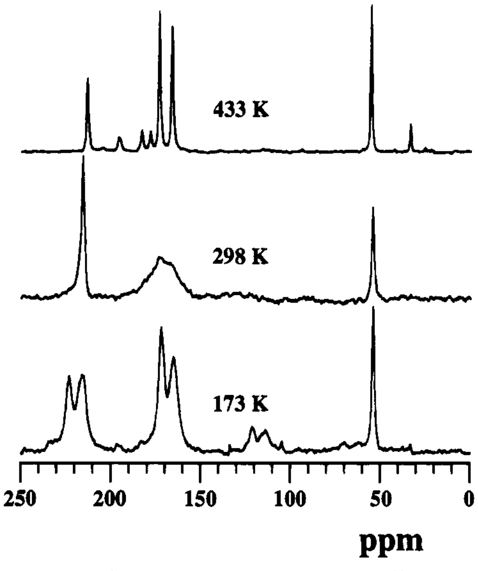


**Figure 9.** Selected $^{13}C$ Bloch decay spectra of [2-$^{13}C$]acetone/[$^{15}N$]-ammonia on zeolite HY, showing the dynamics of imines **8** and **11**. This was the same sample as reported in Figure 6a. The spectrum acquired at 433 K shows sharp peaks for imine **9** (174 and 166 ppm) and **11** (184, 179, and 34 ppm), and these peaks broadened substantially at 298 K. Upon further decreasing the sample temperature to 173 K, the spectrum acquired with a spinning speed of 4600 Hz showed two well-resolved isotropic peaks for **8** and their spinning sidebands (see text).

coherent averaging by $^1H$ decoupling[23] or sample rotation.[24] This sample was then cooled to 173 K, and the Bloch decay spectrum at that temperature showed that the signals for **8** were significantly sharpened at the lower temperature, but those of **11** were still broad. Spinning sidebands were also evident for **8** at 173 K, while those features were averaged by molecular motion at higher temperatures. This suggests one explanation for the dramatic effect of temperature on resolution in Figure 9. If large-amplitude motions of **8** occurred on a time scale of $v_r^{-1}$, where $v_r$ is the spinning speed of the rotor, this would maximize broadening as a result of the conflicting averaging mechanisms. Figure 9 suggests that the reorientation of **8** occurred on a time scale of ca. 220 $\mu$s at 298 K for the sample studied. At higher temperatures, the time scale of this motion was reduced such that the conflict of averaging mechanisms was removed, and this motion was effectively isotropic as revealed by the loss of sideband intensity. At temperatures well below ambient, the conflict was again removed by reducing the time scale of molecular reorientation well below $v_r^{-1}$, and sidebands became evident as a result of restricted reorientation on this time scale.

## Discussion

**The *gem*-Amino−Hydroxy Intermediate.** Literature reports of the reaction of aldehydes with ammonia date back to 1835,[25] but the first unambiguous observation of the formation of 2-aminopropan-2-ol (**4**) from acetone in solution had to wait until 1985.[22] The most studied reaction is that between acetaldehyde and ammonia; the *gem*-amino−hydroxy has a $^{13}C$ shift of 75.4 ppm in solution. Upon warming, it cyclotrimerizes to form 2,4,6-trimethylhexahydro-1,3,5-triazene (analogous to **12**), which has a $^{13}C$ shift of 67.2 ppm. Acetone reacts in liquid $NH_3$ at 215 K to form **4** with an observed $^{13}C$ shift of 80.6 ppm; Figure 8 shows an 81 ppm peak which disappeared to

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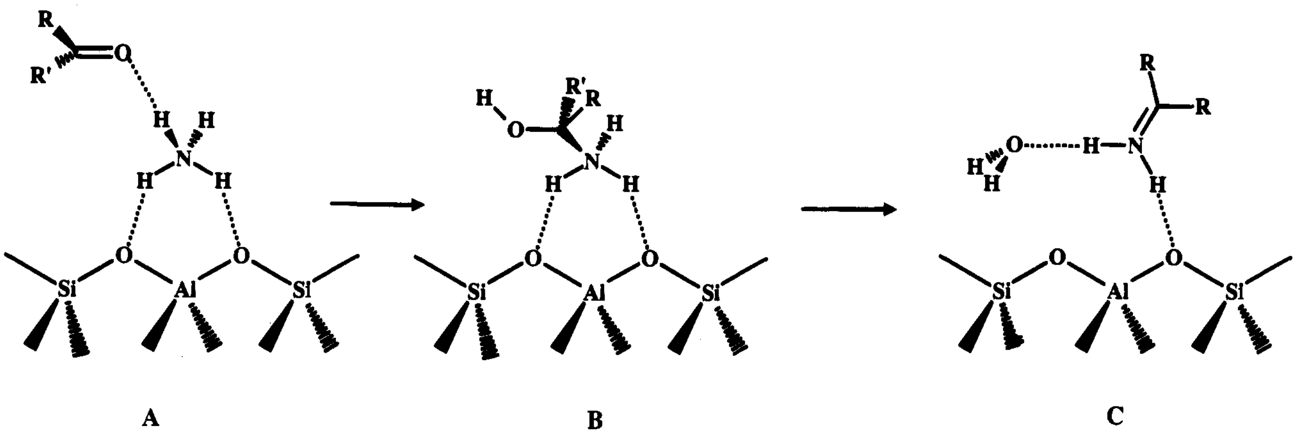
**Scheme 2**

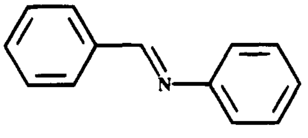


form a 67 ppm peak upon heating. The chemical shift of 78 ppm observed for **3** in zeolite Y is very close to that observed for the *gem*-amino–hydroxy from acetaldehyde in liquid $NH_3$. Cyclotrimerization of **3** did not occur in the zeolite, and would not be expected to, because the size of the supercage would prohibit this reaction with phenyl substituents. We are not aware of any $^{15}N$ measurement of a *gem*-amino–hydroxy species in solution, but our observed shift of −320 ppm for **3** in zeolite Y is consistent with primary amines.[26]

The outstanding agreement between our observed $^{13}C$ shifts and the literature on $NH_3$ solution studies combined with other evidence reported in Figure 4 constitute unambiguous evidence for the formation of *gem*-amino–hydroxy species in zeolites as intermediates in imine formation.

Analogous tetrahedral intermediates also form in the reactions of aldehyde with hydroxylamine hydrochloride in buffered aqueous solutions. It is worth remembering that the most direct evidence for these intermediates was the flow solution NMR work of Fyfe and co-workers.[27]

**Protonation Shifts.** Several recent papers have used measured protonation shifts of adsorbates in zeolites to argue that the zeolites studied here are less strongly acidic than 100% sulfuric acid.[7,28,29] Those studies drew on very extensive measurements in standard acid solutions to calibrate the relationship between chemical shift and acidity. Unfortunately, the literature does not abound with similar measurements for imines, and protonation shifts ($^{15}N$ and $\alpha$-$^{13}C$) are actually quite small for most primary amines.[26] However, a few general statements can be made. The $^{13}C$ shift of imine **6** was reported to be 201.6 ppm in superacid solution.[30] We were unable to find its shift in $CDCl_3$, but a value of 160 ± 7 ppm was estimated using the predictive feature of the SPECINFO database.[31] Its measured value in zeolite HY was 197 ppm, a shift consistent with significant protonation, but perhaps less so than in superacids. The $^{15}N$ shifts of imines are very sensitive to the degree of protonation;[32] for example, the imine **13** has an $^{15}N$ shift of −54.1 ppm in $CDCl_3$, but it shifts far upfield to −193.6 in $CF_3COOH$. These data rationalize the major peak observed at −216 ppm for protonated **5** in HY and may help assign the smaller peaks at −69 and ca. −100 ppm in the $^{15}N$ spectrum of Figure 4 as **5** in less acidic environments. The corresponding $^{13}C$ shift for the model compound **13** is less strongly affected by protonation; 161.4 ppm in $CDCl_3$ vs 165.6 in superacid.[30] This helps rationalize the two $^{13}C$ signals observed for **5** at 168 and 173 ppm in spectra like Figure 3, but the differences in molecular structure of **5** vs **13** preclude a quantitative interpretation in terms of acid strength arguments.



**13**

**Adsorbate Structures.** It is not possible from the NMR measurements alone to propose a detailed description of the reaction coordinate for imine formation, but a combination of the results reported here and previously published work suggests reasonable structures for the reactants, intermediates, and products in zeolite Y.

The structure of $NH_3$ adsorbed onto the Bronsted sites of a zeolite has been of much recent experimental and theoretical study.[20,21,33,34] The consensus view is that proton transfer to form a free $NH_4^+$ or a cation singly-bonded to the conjugate base site is energetically unfavorable. For proton transfer to occur, one must consider structures in which multiple hydrogens are bonded to two or three framework oxygens at the conjugate base sites. Experimental studies[7,35] have shown that carbonyl compounds such as acetone are hydrogen bonded to Bronsted sites through one of the unshared pairs. In the case of more basic adsorbates such as $\alpha,\beta$-unsaturated ketones, there may be appreciable transfer of the proton to the oxygen of the adsorbate.[7,36−38] No calculations have been published on the zeolite cluster/ammonia/acetone system, so deducing the structure of the reactants in the zeolite involves a little speculation. The gas phase proton affinity of $NH_3$ is ca. 10 kcal higher than

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that of acetone,[39] but this could understate the preference of the Bronsted site for ammonia vs acetone, because gas phase measurements do not model specific interactions like the multiple hydrogen bonding deduced for the ammonium/zeolite cluster structures. Because $NH_4^+$ can multiply bond to the framework, and because proton transfer from the zeolite to acetone is known to be incomplete, we propose structure **A** in Scheme 2 for the reactants in zeolite Y. This structure shows an $NH_4^+$ doubly-bonded to the zeolite conjugate base sites and hydrogen-bonded to the carbonyl. This structure rationalizes the downfield shift of the carbonyl group (which is not quite so large as without coadsorbed ammonia),[7] the reduced activity for aldol chemistry, and the greater mobility of the carbonyl compounds in $NH_3$-treated vs untreated zeolites. Active roles for ammonium and the conjugate base sites of the zeolite may also be inferred by the unreactivity of the $NH_3$/acetone/NaY system.

Structure **B** in Scheme 2 is our view of the intermediate; the protonated amino group is still doubly-bonded to the zeolite sites, and the hydroxyl group could also be stabilized by hydrogen bonding, depending on loading and/or site density.

One model of the imine product is shown in Scheme 2, structure **C**. We show the protonated imine singly-bonded to the zeolite cluster and also hydrogen-bonded to the co-product water, but other hydrogen-bonding geometries are also possible for this system. Coordination of the protonated imine to the zeolite and/or water rationalizes the observation that the $^{13}C$ isotropic shifts in the zeolite are not as far downfield as they are in superacid solutions.

## Concluding Remarks

Simple aldehydes and ketones can react with ammonia on zeolites to form imines. In the case of benzaldehyde on zeolite HY, this reaction proceeds through a persistent *gem*-amino–hydroxy intermediate. The apparent stability of this species in the zeolite greatly exceeds expectations based on analogous solution chemistry. It is hoped that this observation highlights the fact that zeolites are media for organic reactions with properties distinct from the solution and gas phases.

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