Magnetic resonance studies of reactions of urea and nitric oxide on FeZSM-5, HZSM-5 and silicalite

Conrad A. Jones, Donald Stec, Sarah C. Larsen*

Department of Chemistry, University of Iowa, Chemistry Building, Iowa City, IA 52242, USA

Abstract

Urea is a potential reducing agent for the selective catalytic reduction (SCR) of NO_x. In this study, ^{13}C and ^{15}N solid state magic angle spinning nuclear magnetic resonance (MAS NMR) experiments were used to investigate the reactions of labeled urea (^{13}C and ^{15}N) alone and with nitric oxide (NO) and oxygen on FeZSM-5 (Fe/Al = 0.11), HZSM-5 and silicalite (purely siliceous form of ZSM-5) after thermal treatments at different temperatures. The hydrolysis of labeled urea to carbon dioxide and ammonia on FeZSM-5 and HZSM-5 after thermal treatments at elevated temperatures was observed using ^{13}C and ^{15}N MAS NMR. Reactions of NO, urea and oxygen on HZSM-5, FeZSM-5 and silicalite were also monitored with ^{13}C and ^{15}N MAS NMR. On both HZSM-5 and FeZSM-5, urea, NO and oxygen reacted to form nitrogen, carbon dioxide and ammonia. On silicalite, urea, NO and oxygen reacted to form CO_2, ammonia and a side product with an imine functionality. No nitrogen was formed on silicalite. EPR spectroscopy was used to investigate the environment of the iron in FeZSM-5.
© 2003 Elsevier B.V. All rights reserved.

Keywords: EPR; Solid state NMR; Zeolites; Urea; SCR; HZSM-5; FeZSM-5; Silicalite

1. Introduction

Zeolites are three-dimensional, crystalline, aluminosilicate, molecular sieves that contain pores of molecular dimensions. Zeolites are used in applications, such as catalysis, ion exchange, purification, separation, and drying. Many transition metal exchanged zeolites, such as CuZSM-5, CoZSM-5, and FeZSM-5, have been used as catalysts for the selective catalytic reduction (SCR) of NO_x [1,2]. Iron-exchanged zeolites (e.g. FeZSM-5) have been shown to be very effective catalysts for the SCR of NO_x with hydrocarbons (SCR-HC) or ammonia (SCR-NH₃) as reductants [3–15]. FeZSM-5 catalysts are also very active at high temperatures even at high levels of water vapor and SO_2 compared to other transition metal exchanged zeolites [3,4,6,8–11,14]. However, the catalytic activity of FeZSM-5 is strongly dependent on exchange procedure (solid state, sublimation, etc.), parent zeolite, and the pretreatment of the zeolite [16]. Catalytic measurements and temperature programmed desorption (TDP) have been used to obtain valuable information about

the kinetics and type of species resulting from NO_x SCR-HC reactions on FeZSM-5 surfaces, as well as conversion of NO to N_2 [3,4,6–10,15–19]. Moreover, spectroscopic methods such as electron paramagnetic resonance (EPR) [19–23] and Mossbauer [24–26] have been used to study the environment of iron cations (Fe^{2+}/Fe^{3+}) in the zeolite and to identify iron oxide aggregates. Fourier transform infrared (FTIR) spectroscopy has been used to identify the species formed on the FeZSM-5 surfaces during the NO_x SCR-HC reaction [7].

Solid state magic angle spinning (MAS) nuclear magnetic resonance (MAS NMR) spectroscopy has been shown to be a very important spectroscopic method for studying catalysts and reactions occurring on the surfaces of catalysts [27]. Solid state NMR can provide structural and mechanistic information, as well as identification of surface species/gas phase species during reactions at varying temperatures [27,28]. Previous solid state NMR experiments probing SCR reactions on transition metal exchanged zeolites have been reported by Larsen and coworkers [28–30].

Nitrogen oxide removal remains an intriguing problem in environmental catalysis [31–35]. Koebel et al. proposed that urea could be a potential reductant for the SCR of NO_x [31]. Unlike ammonia, the handling, storage, and transport of urea are efficient and safe. In addition, urea is nontoxic

* Corresponding author. Tel.: +1-31-9335-1346;
fax: +1-31-9335-1270.
E-mail address: sarah-larsen@uiowa.edu (S.C. Larsen).

even at high concentrations in aqueous solution. Due to these reasons and its extensive study in NO_x removal in diesel engines, urea could possibly replace ammonia as a reductant for SCR. Seker et al. have studied the NO_x reduction by urea over sol–gel Pt/alumina catalysts in which the NO_x conversion temperature is strongly dependent on O_2 and water when urea is present [32].

The potential of urea to be used as a reductant with FeZSM-5 (and HZSM-5) for the SCR of NO_x has not been previously investigated. In this study, the reactions of urea with NO will be probed using solid state NMR spectroscopy. FeZSM-5 was prepared using the sublimation method [11] and was characterized by X-ray diffraction (XRD), inductively coupled plasma atomic emission spectroscopy (ICP-AES), and EPR spectroscopy. Solid state MAS NMR spectroscopy was used to investigate reactions of labeled urea (^{13}C and ^{15}N) and labeled urea/NO/O_2 on FeZSM-5, HZSM-5 and silicalite (purely siliceous form of ZSM-5). ^{13}C NMR and ^{15}N MAS NMR were used to determine the carbon and nitrogen based reactants and products, respectively. With the application of both ^{13}C and ^{15}N NMR, adsorbed species and/or gas species can be identified as well as reaction pathways occurring on the zeolite surfaces at different temperatures.

2. Experimental

2.1. Synthesis and characterization of FeZSM-5 and HZSM-5

HZSM-5 was prepared by adding 10 g of NaZSM-5 (Zeolyst, Si/Al = 20) to 500 ml of 0.1 M NH_4NO_3. The resulting solution was stirred for 24 h at room temperature. This process allowed the Na^+ ions in NaZSM-5 to exchange with the ammonium ions (NH_4^+). After stirring for 24 h, the solution was filtered and then placed in an oven at 80 °C for 2 h. The final step was to calcine the sample at 400 °C for 24 h under compressed air flow to decompose the NH_4 into NH_3 and a Bronsted acid site. FeZSM-5 (Fe/Al = 0.11) was prepared via the sublimation method according to Lobree et al. [11]. This was done by grinding 0.4 g of $FeCl_3 \cdot 6H_2O$ and 5.0 g of the HZSM-5 in a mortar and pestle in a glove bag under nitrogen at room temperature. The resulting yellow mixture was then placed into a quartz calcination tube that was placed in a furnace and was heated for 4 h under argon flow to 310 °C, the sublimation temperature of $FeCl_3 \cdot 6H_2O$. The orange–red sample was filtered, washed with deionized water, and dried overnight at 80 °C in an oven. Silicalite was synthesized in-house from a clear gel solution with the following composition: 3TPAOH:0.16NaOH:25Si:2000H_2O:100EtOH, where TPAOH is tetrapropylammonium hydroxide following a modified literature procedure [36]. Tetraethylorthosilicate (TEOS) was the silicon source. The clear gel was heated in a teflon-lined autoclave at 165 °C for 72 h. The silicalite

was then washed with deionized water, dried in air and calcined to remove the template.

The XRD pattern for FeZSM-5 matched that of a ZSM-5 standard XRD pattern and did not show the presence of any iron oxides. The Fe/Al exchange value was determined by inductively coupled plasma atomic emission spectroscopy to be 0.11. The EPR spectrum was obtained at 120 K using the Bruker EMX61 spectrometer (X-band) with a microwave frequency of 9.44 GHz.

2.2. Preparation of samples for NMR

Approximately 0.2 g of zeolite (FeZSM-5, HZSM-5 and silicalite) was impregnated ex situ with an aqueous solution of labeled urea (^{13}C, 99% and ^{15}N, 98%, Cambridge Isotopes). FeZSM-5 samples were prepared with urea/Fe ratios of 4:1 while HZSM-5 samples were prepared with a urea/H^+ ratio of 1:1 (the loadings for the two samples relative to aluminum content were urea/Al = 1 and 0.44 for H and FeZSM-5, respectively). Samples with adsorbed urea were allowed to dry at room temperature and were placed into pyrex sample tubes that were degassed on a vacuum rack. To prepare samples containing labeled urea and nitric oxide (NO) (Matheson Gas Products), the nitric oxide was introduced to the zeolite samples with adsorbed urea by immersing the sample tubes in liquid nitrogen after degassing. Then, samples were taken off the vacuum rack and sealed using a torch while the sample was immersed in liquid nitrogen. The sealed samples were then heated for 1 h at the desired temperatures. An Omega (CN-76000) programmable temperature controller controlled the reaction temperatures. Samples were allowed to cool to room temperature and placed in Chemagnetics 7.5 mm (o.d.) pencil rotors for magic angle spinning NMR measurements.

2.3. Solid state MAS NMR procedures

MAS NMR spectra were obtained using a 7 T wide bore Bruker cryomagnet equipped with a TecMag Discovery console which corresponds to a Larmour frequency of 75.470 and 30.425 MHz for ^{13}C and ^{15}N, respectively. A Chemagnetics double-channel 7.5 mm pencil MAS probe was used to spin rotors for all sealed samples. The spinning speed was approximately 4.0 kHz single pulse direct excitation was used for ^{13}C and ^{15}N. The $\pi/2$ pulse width was 6.0 μs for ^{13}C; the $\pi/2$ pulse width was 4.5 μs for ^{15}N. Recycle delay was 2 s and a line broadening of 50 Hz was used for both ^{13}C and ^{15}N. The number of scans for ^{13}C and ^{15}N MAS NMR was 4000 and 25,000 scans, respectively. Solid adamantine mixed with KBr (38.5 ppm) and saturated $^{15}NH_4^{15}NO_3$ solution (0 ppm for NO_3^-) were used as external chemical shift standards for ^{13}C and ^{15}N, respectively. All of the chemical shifts for ^{13}C and ^{15}N are reported relative to TMS and CH_3NO_2, respectively. All ^{13}C and ^{15}N spectra were obtained at room temperature.
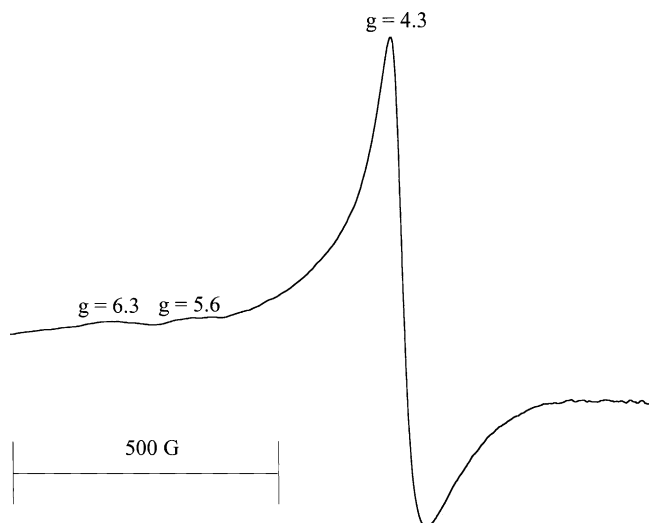
Fig. 1. EPR spectrum of untreated FeZSM-5 (Fe/Al = 0.11) taken at 120 K.

3. Results and discussion

3.1. EPR study of FeZSM-5

The EPR spectrum of hydrated FeZSM-5 (Fe/Al = 0.11) obtained at 120 K is shown in Fig. 1. EPR signals with g-values of 4.3, 5.6, and 6.3 were observed in the spectrum. Similar EPR signals have been observed for iron-exchanged zeolite samples prepared by other groups [16,20,22]. Based on the results reported in the literature, the $g = 4.3$ signal is attributed to Fe^{3+} in tetrahedral coordination; the peaks at 5.6 and 6.4 are be assigned to Fe^{3+} cations in distorted tetrahedral coordinations [16,20,22]. Based on a comparison of the catalytic activity of samples prepared by various exchange methods, Long and Yang concluded that the Fe^{3+} in tetrahedral coordination ($g = 4.3$ signal) is responsible for the catalytic activity of FeZSM-5 for the SCR of NO_x with NH_3 [16]. This is the dominant signal for the FeZSM-5 sample used in this study as shown by the EPR spectrum in Fig. 1.

3.2. Adsorbed urea on FeZSM-5 and HZSM-5

An aqueous solution of labeled urea was prepared and placed in the NMR probe to determine the ^{13}C and ^{15}N chemical shifts of urea in solution. The ^{13}C chemical shift for the urea in solution was observed at 164 ppm, corresponding to the $^{13}C=O$ bond, while the ^{15}N chemical shift was observed at -300 ppm, corresponding to an amine group ($-R\ ^{15}NH_2$). Table 1 gives relevant chemical shifts for the species observed in these experiments.

Fig. 2 shows the ^{13}C MAS NMR spectra of labeled urea adsorbed on FeZSM-5 after pretreatment at 25, 150 and 250 °C in a sealed sample tube followed by cooling to room temperature for spectra acquisition and Fig. 3 shows the corresponding ^{15}N MAS NMR spectra. At room temperature,

Table 1
^{13}C and ^{15}N MAS NMR chemical shifts

Species	^{13}C (ppm)	^{15}N (ppm)	Reference
Urea (aq. solution)	164	−300	This work
Urea adsorbed on FeZSM-5	162	−298	This work
Urea adsorbed on HZSM-5	160	−300	This work
CO_2	123	–	[37]
NH_3, NH_4^+	–	−350 to −380	[38,39]
N_2	–	−72	[28–30,45]

peaks are observed at 162 and -298 ppm in the ^{13}C and ^{15}N MAS NMR spectra, respectively, and are assigned to the carbonyl carbon and the amine nitrogens of adsorbed urea, respectively, through a comparison with the NMR chemical shift values listed in Table 1. In the ^{15}N MAS NMR spectrum, there is also a small peak present at -360 ppm, indicating the presence of ammonia or ammonium ion. After heating to 150 °C (and subsequently 250 °C) and cooling back to room temperature for spectral acquisition, a peak is present at 125 ppm in the ^{13}C MAS NMR spectrum and is assigned to $^{13}CO_2$ [37]. Similarly in Fig. 3, only one peak at -360 ppm is observed in the ^{15}N NMR spectrum. This peak is assigned to NH_4^+ based on a comparison with the NH_4^+ chemical shift in solution (-360 ppm) and with the results of other ^{15}N NMR studies of NH_3 adsorbed on zeolites with Bronsted acid sites [38–40]. In previous ^{15}N NMR studies of NH_3 adsorbed on zeolites, several different NH_3 and NH_4^+ species were identified based on the extent of hydrogen bonding and the ammonia concentration [38,39]. The ^{15}N
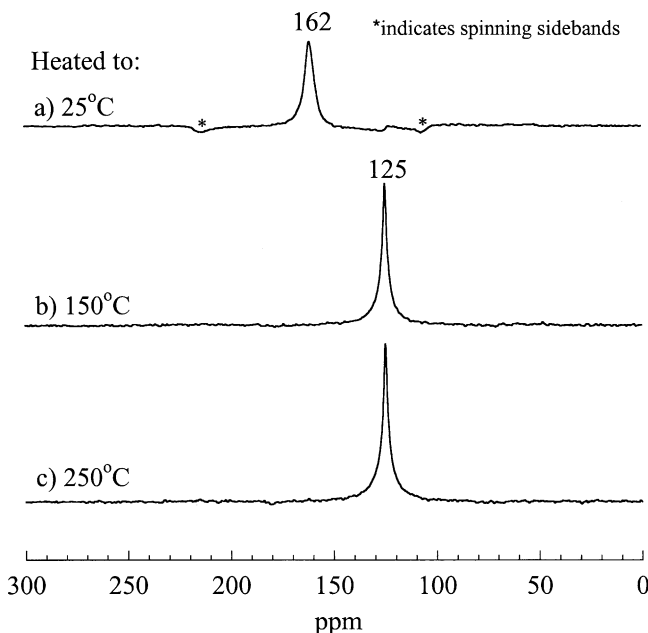

Fig. 2. ^{13}C single pulse MAS NMR of labeled urea (^{13}C and ^{15}N) adsorbed on FeZSM-5 (Fe/Al = 0.11) before and after heating to indicated temperatures. Asterisks denote spinning sidebands. Spectra were acquired at room temperature after the sealed sample was heated to: (a) 25 °C; (b) 150 °C; and (c) 250 °C. Number of scans acquired (NS) was 4000. Line broadening = 50 Hz.
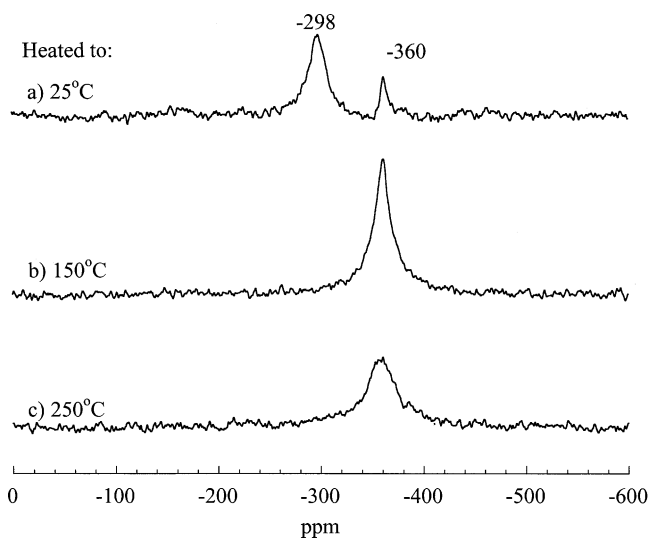
Fig. 3. ^{15}N single pulse MAS NMR of labeled urea (^{13}C and ^{15}N) adsorbed on FeZSM-5 (Fe/Al = 0.11) before and after heating to indicated temperatures. Spectra were acquired at room temperature after the sealed sample was heated to: (a) 25 °C; (b) 150 °C; and (c) 250 °C. Number of scans acquired (NS) was 25,000. Line broadening = 50 Hz.

NMR chemical shift for NH_4^+ coordinated to the zeolite, HY, was observed to range from −353 to −357 ppm, which is strongly shifted to lower fields relative to gas phase NH_3 (−400 ppm). Pfeifer and coworkers [39] state that the ^{15}N NMR peak due to ammonia adsorbed on Lewis acid sites will be shifted further downfield relative to the NH_4^+ peak (approximately −360 ppm) and since no peaks were observed in the ^{15}N NMR spectrum in Fig. 3 downfield of the NH_4^+, it was concluded that none of the signals were due to ammonia adsorbed on Lewis acid sites. After heating to 150 °C, the peaks at 162 ppm and −298 ppm for ^{13}C and ^{15}N have disappeared suggesting that the urea is totally decomposed.

Upon closer inspection of the ^{15}N NMR spectra in Fig. 3, it is apparent that the intensity of the ammonia peak decreases as the pretreatment temperature increases from 150 to 250 °C. The full width half maximum (FWHM) of the ammonia peak increases from ∼300, 600, 900 Hz as the pretreatment temperature was varied from 25, 150, 250 °C, respectively. In previous FTIR studies by Long and Yang, the data suggested that two ammonia species were formed on FeZSM-5, physisorbed NH_3 and NH_4^+ chemisorbed on Bronsted acid sites [41]. The peak observed at −360 ppm in Fig. 3 is assigned to adsorbed NH_4^+. The change in the spectral line broadening as a function of pretreatment temperature is attributed to a change in hydrogen bonding of the adsorbed NH_4^+ species with other NH_3 groups as reported by Lunsford and coworkers [38]. The overall integrated area of the spectra shown in Fig. 3a–c are the same which is consistent with the fact that the samples were prepared in sealed pyrex tubes.

As shown in Figs. 4 and 5, similar results were obtained for samples of labeled urea adsorbed on HZSM-5 after thermal pretreatments at the same temperatures. The ^{13}C NMR
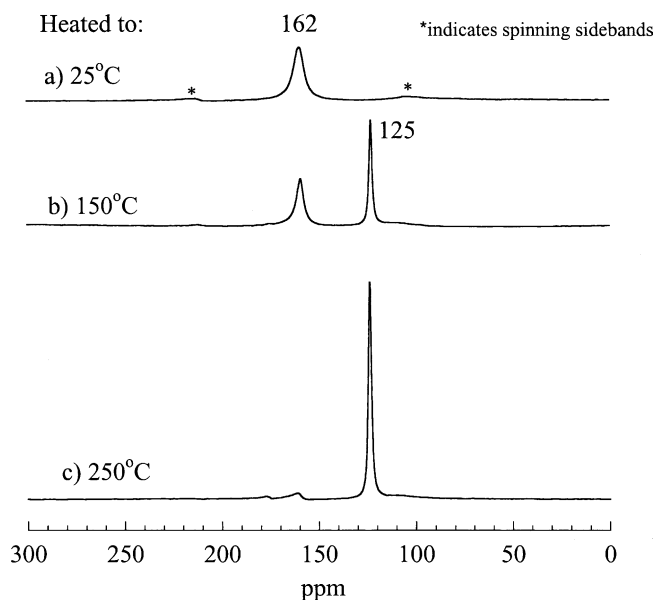

Fig. 4. ^{13}C single pulse MAS NMR of labeled urea (^{13}C and ^{15}N) adsorbed on HZSM-5 before and after heating to indicated temperatures. Asterisks denote spinning sidebands. Spectra were acquired at room temperature after the sealed sample was heated to: (a) 25 °C; (b) 150 °C; and (c) 250 °C. Number of scans acquired (NS) was 4000. Line broadening = 50 Hz.

spectra shown in Fig. 4 have peaks due to urea (162 ppm) and CO_2 (125 ppm) as discussed above. Some urea remains even after heating to 250 °C. The ^{15}N NMR spectra in Fig. 5 are slightly different than the ^{15}NMR spectra shown in Fig. 3. Peaks at −300, −367 and −360 ppm are observed in the spectra shown in Fig. 5 after pretreatment at 25, 150 and 250 °C, respectively. The peaks at −300 and −360 ppm are assigned to adsorbed urea and adsorbed NH_4^+, respectively,
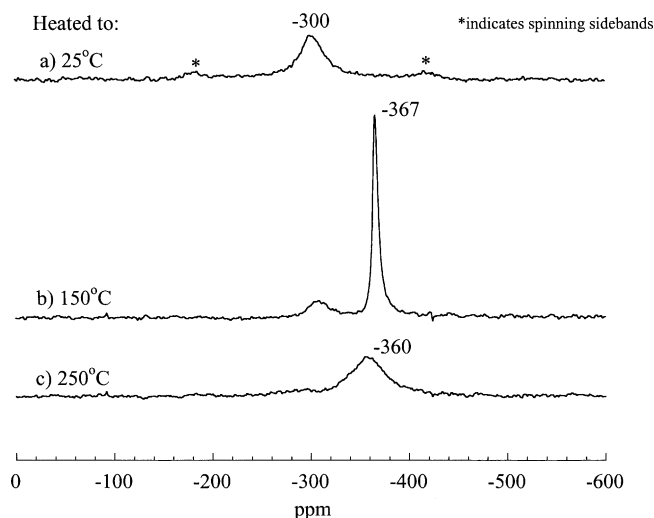

Fig. 5. ^{15}N single pulse MAS NMR of labeled urea (^{13}C and ^{15}N) adsorbed on HZSM-5 before and after heating to indicated temperatures. Asterisks denotes spinning sidebands Spectra were acquired at room temperature after the sealed sample was heated to: (a) 25 °C; (b) 150 °C; and (c) 250 °C. Number of scans acquired (NS) was 25,000. Line broadening = 50 Hz.

as discussed above. The peak at -367 ppm is assigned to a mobile form of NH_3 according to Pfeifer and coworkers [39]. The interpretation is that the urea reacts to form a mobile form of ammonia (-367 ppm) which after further heat treatment reacts at Bronsted acid sites to form adsorbed NH_4^+ (-360 ppm). The urea does not completely hydrolyze on HZSM-5 but it is unclear whether this is due to different surface coverages or to the presence of iron sites in FeZSM-5 that facilitate decomposition of the urea.

The following overall reaction has been previously proposed for the hydrolysis of urea [31,32].

$$(NH_2)_2CO(s) + H_2O(g) \rightarrow 2NH_3(g) + CO_2(g) \qquad (1)$$
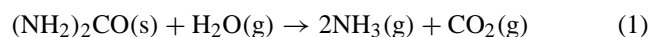
Since the zeolite samples used in our experiments were not dehydrated prior to the adsorption of urea, some water is present in the samples to hydrolyze the urea as shown in the reaction above. This reaction is believed to proceed according to a stepwise reaction of urea to form isocyanic acid and ammonia and then the reaction of isocyanic acid and water to form ammonia and CO_2. However, isocyanic acid (137 ppm for ^{13}C and -357 ppm for ^{15}N) [37] was not observed by NMR in the experiments reported here, presumably because the reaction proceeded rapidly to ammonia and CO_2. The presence of ^{13}C and ^{15}N MAS NMR signals confirms the hydrolysis of urea to form ammonia and carbon dioxide according to (1). The fact that urea readily decomposes to form ammonia is a positive indication that these zeolites will be active for the SCR of NO_x with NH_3.

3.3. Reaction of urea, NO and O_2 on FeZSM-5, HZSM-5 and silicalite

The ^{13}C and ^{15}N MAS NMR spectra of a sealed sample of labeled urea (^{13}C and ^{15}N), NO and O_2 adsorbed on FeZSM-5 after thermal pretreatments at different temperatures and subsequent cooling to room temperature for spectral acquisition are shown in Figs. 6 and 7. The NMR spectra are similar to those observed for reactions of urea alone on FeZSM-5, except that in the presence of NO and O_2, N_2 is formed after pretreatments at 150, 250 and 350 °C. Initially peaks due to adsorbed urea (162, -300 ppm for ^{13}C and ^{15}N, respectively) were observed. The urea then reacts to form ammonia, and carbon dioxide after thermal treatment at 150 °C. Further reaction of the ammonia to nitrogen was observed in the ^{15}N NMR spectrum as illustrated by the appearance of a peak at -68 ppm in the NMR spectra acquired after pretreatments at 150, 250 and 350 °C. A decrease in the intensity of the ammonia peak was also observed indicating that the ammonia was reacting with NO to form N_2. Similar spectra (data not shown) were obtained for samples of labeled urea and NO on FeZSM-5 except that only a small amount of nitrogen was formed relative to the reaction in the presence of oxygen.

The NMR results can be explained by the following reactions in which urea hydrolyzes to form ammonia and car-
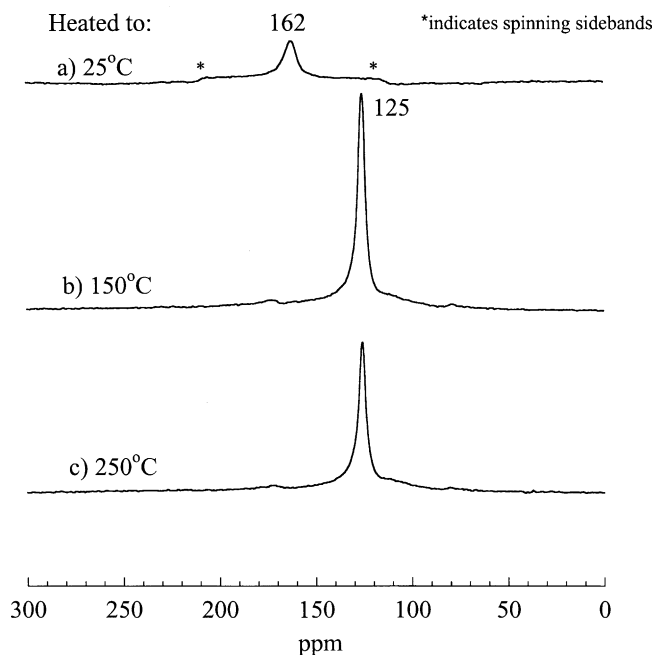

Fig. 6. ^{13}C single pulse MAS NMR of labeled urea (^{13}C and ^{15}N), NO and O_2 adsorbed on FeZSM-5 (Fe/Al = 0.11) before and after heating to indicated temperatures. Asterisks denote spinning sidebands. Spectra were acquired at room temperature after the sealed sample was heated to: (a) 25 °C; (b) 150 °C; and (c) 250 °C. Number of scans acquired (NS) was 4000. Line broadening = 50 Hz.

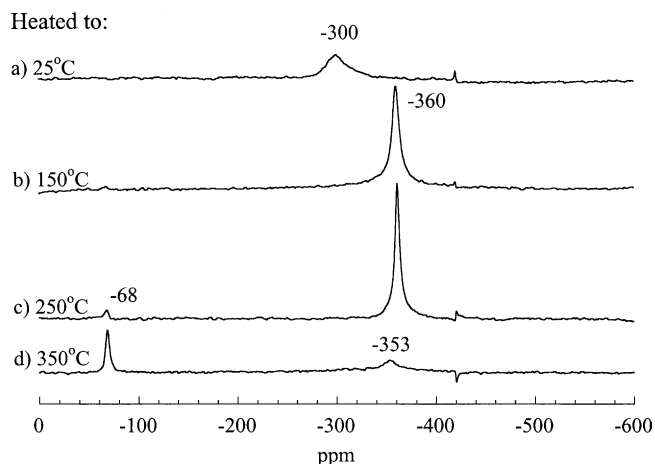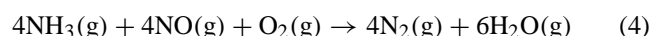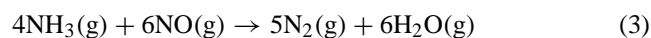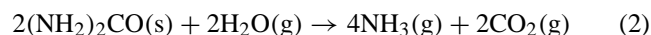bon dioxide and then the ammonia reacts with NO to form nitrogen and water [31].

$$2(NH_2)_2CO(s) + 2H_2O(g) \rightarrow 4NH_3(g) + 2CO_2(g) \qquad (2)$$

$$4NH_3(g) + 6NO(g) \rightarrow 5N_2(g) + 6H_2O(g) \qquad (3)$$

$$4NH_3(g) + 4NO(g) + O_2(g) \rightarrow 4N_2(g) + 6H_2O(g) \qquad (4)$$

Fig. 7. ^{15}N single pulse MAS NMR of labeled urea (^{13}C and ^{15}N), NO and O_2 adsorbed on FeZSM-5 (Fe/Al = 0.11) before and after heating to indicated temperatures. Spectra were acquired at room temperature after the sealed sample was heated to: (a) 25 °C; (b) 150 °C; (c) 250 °C; and (d) 350 °C. Number of scans acquired (NS) was 25,000. Line broadening = 50 Hz.
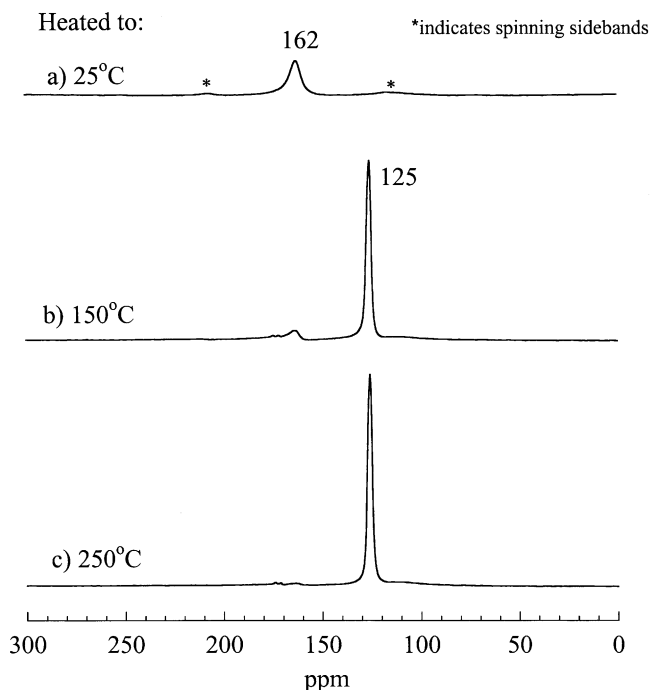
Fig. 8. ^{13}C single pulse MAS NMR of labeled urea (^{13}C and ^{15}N), NO, and O_2 adsorbed on HZSM-5 before and after heating to indicated temperatures. Asterisks denote spinning sidebands. Spectra were acquired at room temperature after the sealed sample was heated to: (a) 25 °C; (b) 150 °C; and (c) 250 °C. Number of scans acquired (NS) was 4000. Line broadening = 50 Hz.

The reaction of ammonia with nitric oxide in the presence of oxygen (reaction (4)) is faster than the reaction in the absence of O_2 (reaction 3) [31].

The ^{13}C and ^{15}N MAS NMR spectra of urea, NO and oxygen on HZSM-5 are shown in Figs. 8 and 9, respectively. The formation of CO_2 (125 ppm) and adsorbed NH_4^+ (−362,
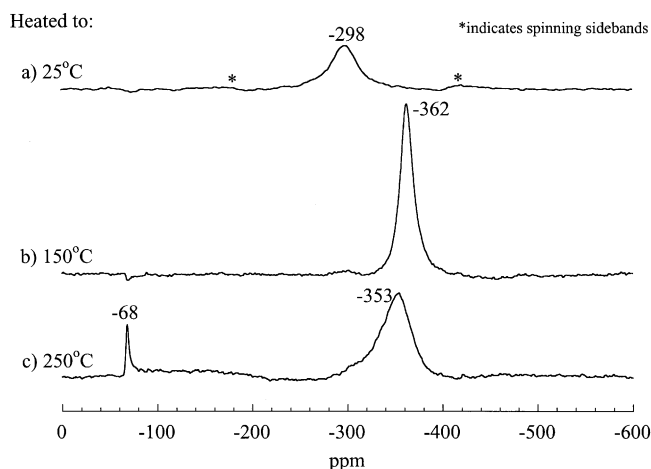

Fig. 9. ^{15}N single pulse MAS NMR of labeled urea (^{13}C and ^{15}N), NO, and O_2 adsorbed on HZSM-5 before and after heating to indicated temperatures. Asterisks denote spinning sidebands. Spectra were acquired at room temperature after the sealed sample was heated to: (a) 25 °C; (b) 150 °C; and (c) 250 °C. Number of scans acquired (NS) was 25,000. Line broadening = 50 Hz.

Fig. 10. ^{13}C single pulse MAS NMR of labeled urea (^{13}C and ^{15}N), NO, and O_2 adsorbed on silicalite before and after heating to indicated temperatures. Asterisks denote spinning sidebands. Spectra were acquired at room temperature after the sealed sample was heated to: (a) 25 °C; (b) 150 °C; and (c) 250 °C. Number of scans acquired (NS) was 4000. Line broadening = 50 Hz.
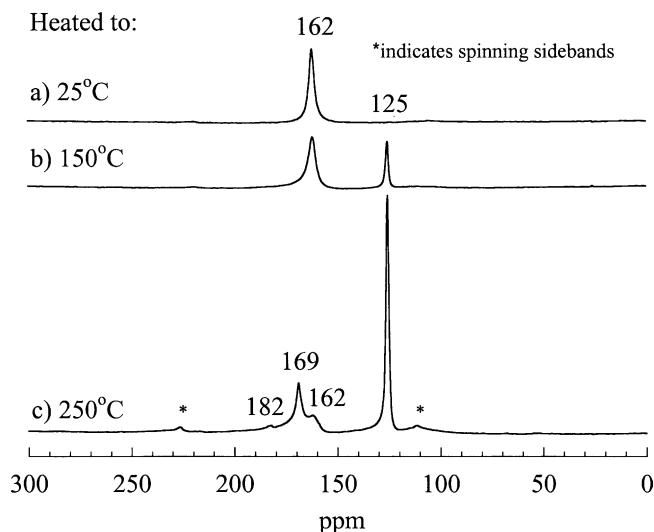
−353 ppm) were observed. Just as for FeZSM-5 samples with urea, NO and O_2, the formation of N_2 was also observed in the ^{15}N NMR spectrum at −68 ppm indicating that these materials can be used for SCR-NH$_3$ with urea.

The ^{13}C and ^{15}N MAS NMR spectra of urea, NO and oxygen on silicalite are shown in Figs. 10 and 11, respectively. The reason for using silicalite, the purely siliceous form of ZSM-5, in this study, was two-fold: (1) to show that SCR of NO with urea to form nitrogen formation only occurs on ZSM-5 zeolites with metal or Bronsted acid sites and (2) to probe the adsorption of ammonia on a zeolite surface that
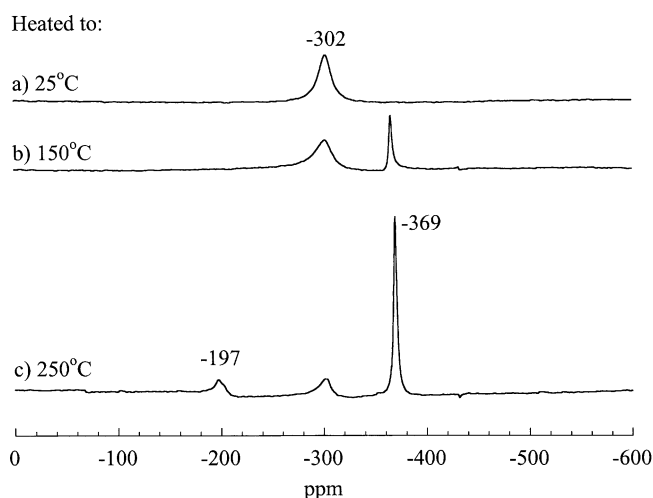

Fig. 11. ^{15}N single pulse MAS NMR of labeled urea (^{13}C and ^{15}N), NO, and O_2 adsorbed on silicalite before and after heating to indicated temperatures. Spectra were acquired at room temperature after the sealed sample was heated to: (a) 25 °C; (b) 150 °C; and (c) 250 °C. Number of scans acquired (NS) was 25,000. Line broadening = 50 Hz.

does not contain Lewis or Bronsted acid sites. The decomposition of urea to CO_2 (125 ppm) is observed in the ^{13}C NMR spectrum after heat treatment at 150 °C. The amount of CO_2 formed relative to the amount of urea is much less than urea decomposition on HZSM-5 and FeZSM-5. New species are observed in the ^{13}C NMR spectrum at 182 and 169 ppm after heat treatment to 250 °C. In the analogous ^{15}N NMR spectra, urea decomposition to ammonia (-369 ppm) is observed after heat treatment at 150 °C. The ammonia peak is much narrower than the comparable peak on H and FeZSM-5 indicating that a mobile NH_3 species is the primary species formed on silicalite. Since silicalite does not contain Bronsted acid sites, the NH_3 cannot form NH_4^+. After pretreatment at 250 °C, a new peak at -197 ppm is observed in the ^{15}N NMR spectrum (Fig. 11c).

The new peaks in the ^{13}C and ^{15}N NMR spectra after reaction at 250 °C suggest the formation of an imine group moiety. In previous work, the chemical shifts for imine compounds adsorbed on HZSM-5 ranged from 189 to 197 ppm for the ^{13}C peak and -190 to -191 ppm for the ^{15}N imine peak [28,42,43]. Fang and coworkers recently investigated reactions of urea on catalysts using IR and Raman spectroscopy and reported the formation of ammelides from the reaction of a C=O bond with ammonia to form C=NH imine groups [44]. Ammelide is from a group of polymeric melamines. Melamine has the chemical formula $(HNC=NH)_3$ and the ^{13}C NMR chemical shift of melamine is 167 ppm. This is very close to the chemical shift of the dominant peak in the ^{13}C NMR spectrum in Fig. 10c suggesting that melamine or closely related compound is being formed. The peak at 182 ppm in the ^{13}C NMR spectrum is most likely due to another closely related imine compound. The peak at -197 ppm in the ^{15}N is in the range expected for an imine nitrogen based on previously observed imine complexes in zeolites [28,42]. Therefore, this peak is assigned to the imine nitrogen of melamine or a closely related complex. The formation of melamine and related compounds has been linked to deactivation in urea SCR reactions [44]. No nitrogen formation is observed on the silicalite sample.

3.4. Implications for the SCR of NO_x with urea

The experimental results reported here indicate that urea decomposes thermally on HZSM-5 and FeZSM-5 to form ammonia (ammonium ion) and CO_2 after pretreatments at 150 and 250 °C. The decomposition of urea is complete after thermal treatments at 250 °C. The decomposition of urea to form ammonia is a promising indication that HZSM-5 and FeZSM-5 will be active catalysts for the SCR of NO with urea.

Yang and coworkers have recently shown that FeZSM-5 is active for the SCR of NO_x with ammonia [12,13,16,41]. Therefore, the next step in the studies reported here was to examine the reaction of urea, NO and oxygen on HZSM-5 and FeZSM-5 to try to observe the formation of N_2, the desired SCR product. The solid state NMR results indicate

that nitrogen is formed after thermal treatments starting at ~150 °C consistent with the SCR of NO by urea. An analogous experiment on silicalite did not show the formation of nitrogen, but rather showed the formation of melamine and related compounds which are believed to deactivate SCR catalysts.

The observed reactivities of the HZSM-5 and FeZSM-5 samples used in this study were very similar. Silicalite was not as active as HZSM-5 or FeZSM-5 for urea decomposition and did not show the formation of nitrogen from urea, NO and O_2. Therefore, based on the results reported here, while it is difficult to differentiate between the activity of H- versus FeZSM-5, it is clear that silicalite is not active for the SCR of NO_x with urea. The similarity of HZSM-5 and Fe-ZSM-5 reactivity could be due to the fact that the FeZSM-5 sample used in these studies has a relatively low iron loading (Fe/Al = 0.11) with the other charge compensating sites being Bronsted sites, which are the exclusive charge-compensating sites present in HZSM-5. Future studies of higher iron loadings could address this issue.

4. Conclusions

The reactions of adsorbed urea and NO on FeZSM-5 and HZSM-5 were investigated using ^{13}C and ^{15}N solid state NMR. The carbon and nitrogen-containing products formed after thermal pretreatments at different temperatures on FeZSM-5 and HZSM-5 were identified. Urea hydrolyzed to form CO_2 and ammonia on HZSM-5 and FeZSM-5. The disappearance of urea and the formation of CO_2 and NH_3 were monitored by ^{13}C and ^{15}N MAS NMR. The ammonia signal in the ^{15}N NMR spectra for both HZSM-5 and FeZSM-5 was attributed to the formation of an ammonium (NH_4^+) species adsorbed on Bronsted acid sites. Reaction of urea, NO and O_2 on HZSM-5 and FeZSM-5 resulted in the formation of CO_2, NH_3 (NH_4^+), and N_2. No nitrogen was formed on silicalite after reaction of urea, NO and O_2. These results suggest that FeZSM-5 (and HZSM-5) may be useful as catalysts for the SCR of NO_x with urea.

References

[1] M. Iwamoto, H. Hamada, Catal. Today 10 (1991) 57.
[2] M. Shelef, Chem. Rev. 95 (1995) 209.

[3] X. Feng, W.K. Hall, J. Catal. 166 (1997) 368.

[4] X. Feng, W.K. Hall, J. Catal. 41 (1996) 46.

[5] V. M. Mastikhin, S.V. Filimonova, J. Chem. Soc., Faraday Trans. 88 (1992).

[6] M. Kogel, R. Monnig, W. Schweiger, A. Tissler, T. Turek, J. Catal. 182 (1999) 470.

[7] H.-Y. Chen, W.M.H. Sachtler, Catal. Lett. 50 (1998) 125.

[8] H.-Y. Chen, W.M.H. Sachtler, Catal. Today 42 (1998) 73.

[9] H.-Y. Chen, T.V. Voskoboinikov, W.M.H. Sachtler, J. Catal. 180 (1998) 171.

[10] L.J. Lobree, I. Hwang, J.A. Reimer, A.T. Bell, Catal. Lett. 63 (1999) 233.

[11] L.J. Lobree, I. Hwang, J.A. Reimer, A.T. Bell, Catal. Lett. 186 (1999) 242.

[12] R.Q. Long, R.T. Yang, J. Catal. 188 (1999) 332.

[13] R.Q. Long, R.T. Yang, J. Am. Chem. Soc. 121 (1999) 5595.

[14] A.Z. Ma, W. Grunert, Chem. Commun. 1 (1999) 71.

[15] R. Joyner, M. Stockenhuber, J. Phys. Chem. B 103 (1999) 5963.

[16] R.Q. Long, R.T. Yang, Catal. Lett. 74 (2001) 201.

[17] T.V. Voskoboinikov, H.-Y. Chen, W.M.H. Sachtler, Appl. Catal. B: Environ. 19 (1998) 279.

[18] K. Hadjiivanov, H. Knozinger, B. Tsyntsarski, L. Dimitrov, Catal. Lett. 62 (1999) 35.

[19] E.-M. El-Maki, R.A. van Santen, W.M.H. Sachtler, J. Catal. 196 (2000) 212.

[20] A.V. Kucherov, T.N. Montreuil, T.N. Kucherova, M. Shelef, Catal. Lett. 56 (1998) 173.

[21] A.V. Kucherov, A.A. Slinkin, Zeolites 8 (1988) 110.

[22] D. Goldfarb, M. Bernardo, K.G. Strohmaier, D.E.W. Vaughan, H. Thomann, J. Am. Chem. Soc. 116 (1994) 6344.

[23] H.-T. Lee, H.-K. Rhee, Catal. Lett. 61 (1999) 71.

[24] W.K. Hall, X. Feng, J. Dumesic, R. Watwe, Catal. Lett. 198 (1998) 13.

[25] M. Mauvezin, G. Delahay, B. Coq, S. Kieger, J.C. Jumas, J. Olivier-Fourcade, J. Phys. Chem. B 105 (2001) 928.

[26] A.M. Volodin, K.A. Dubkov, A. Lund, Chem. Phys. Lett. 41 (2001) 333.

[27] J.F. Haw, in: A.T. Bell, A. Pines (Eds.), NMR Techniques in Catalysis, Marcel Dekker, New York, 1994, pp. 139–194.

[28] J. Wu, S.C. Larsen, J. Catal. 182 (1999) 244.

[29] J. Wu, S.C. Larsen, Catal. Lett. 70 (2000) 43.

[30] C.A. Jones, S.C. Larsen, Catal. Lett. 78 (2002) 243.

[31] M. Koebel, M. Elsener, M. Kleeman, Catal. Today 59 (2000) 335.

[32] E. Seker, N. Yasyerli, E. Gulari, C. Lambert, R.H. Hammerle, Appl. Catal. B: Environ. 37 (2002) 27.

[33] E. Seker, N. Yasyerli, E. Gulari, C. Lambert, R.H. Hammerle, J. Catal. 208 (2002) 15.

[34] E. Seker, E. Gulari, J. Catal. 194 (2000) 4.

[35] M. Koebel, M. Elsener, G. Madia, Ind. Eng. Chem. Res. 40 (2001) 52.

[36] Q. Li, B. Mihailova, D. Creaser, J. Sterte, Micropor. Mesopor. Mater. 40 (2000) 53–62.

[37] G. Fischer, J. Geith, T. Klapotke, B. Krumm, Z. Naturforsch 57 (2002) 19.

[38] W.L. Earl, P.O. Fritz, A.A.V. Gibson, J.H. Lunsford, J. Phys. Chem. 91 (1987) 2091–2095.

[39] D. Michel, A. Germanus, H. Pfeifer, J. Chem. Soc., Faraday Trans. 78 (1982) 237–254.

[40] A. Kyrlidis, S.J. Cook, A.K. Chakraborty, A.T. Bell, D.N. Theorodorou, J. Phys. Chem. 99 (1995) 1505–1515.

[41] R.Q. Long, R.T. Yang, J. Catal. 194 (2000) 80–90.

[42] T. Xu, J. Zhang, J.F. Haw, J. Am. Chem. Soc. 117 (1995) 3171–3178.

[43] A.I. Biaglow, J. Sepa, R.J. Gorte, D. White, J. Catal. 151 (1995) 373–384.

[44] H.L. Fang, H.F.M. DaCosta, Appl. Catal. B: Environ. 46 (2003) 17–34.

[45] V.M. Mastikhin, S.V. Filimonova, I.L. Mudrakovsky, V.N. Romannikov, J. Chem. Soc., Faraday Trans. I 87 (1991) 2247.