^{15}N solid state NMR study of the reactions of propane or propene, ^{15}NO and oxygen on Na-, H-, and CuZSM-5

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The reactions of propane or propene with ^{15}NO in the absence or presence of oxygen on Na-, H-, and CuZSM-5 zeolites have been investigated using ^{15}N solid state nuclear magnetic resonance (NMR) spectroscopy. The nitrogen-containing surface species and gas phase products formed by these reactions under conditions of thermal equilibrium were monitored and identified by ^{15}N NMR. The role of the hydrocarbon reductant, oxygen and the exchangeable cation in the selective catalytic reduction of NO by hydrocarbons (SCR-HC) was examined in this study.

Keywords: solid state NMR, CuZSM-5, SCR-HC, propane, propene, NO

1. Introduction

NO_x (a mixture of NO and NO_2) is produced by high temperature combustion processes and contributes to the formation of acid rain and ground level ozone. The development of new catalysts for the abatement of NO_x has been motivated by increasing public and government concern about NO_x emissions from stationary sources, such as power plants, and mobile sources, such as diesel and lean-burn engines. The selective catalytic reduction of NO by hydrocarbons (SCR-HC), such as propane and propene, in the presence of O_2 has received much attention because of the significance of this reaction for emission control applications [1–3]. It has many advantages over the traditional SCR of NO by NH_3; namely, it avoids the problems associated with NH_3 as a reductant [4].

Numerous studies have shown that CuZSM-5 zeolites are active for SCR-HC of NO [5–9]. However, the mechanism for the SCR-HC reaction remains unclear. Potential nitrogen-containing reaction intermediates have been proposed for the SCR-HC process on CuZSM-5, such as an adsorbed nitrogen oxide complex NO_y ($y \geqslant 2$) [9–13], isocyanates [14], nitrite and nitrate complexes [15], nitro- or nitroso- or oximes compounds [13,16–20] and ammonia [21]. Many aspects, such as the surface species or fragments formed in the process of SCR-HC of NO, need to be further explored.

Beutel et al. previously studied the interaction of the proposed SCR-HC reaction intermediate, acetone oxime, with ^{15}NO on CuZSM-5 using a combination of Fourier transform infrared (FTIR) and mass spectrometry [18]. Isotopic labeling studies indicated that N–N bonds formed via the interaction of gaseous NO with an adsorbed oxime complex [18]. In another FTIR study, Rebrov and coworkers observed the formation of acetone oxime from propane, NO and O_2 [13]. Centi and coworkers used FTIR and ^{13}C nuclear magnetic resonance (NMR) to study the surface species formed during the SCR of NO with propane and propene [22]. Using ^{13}C and ^{15}N solid state magic angle spinning (MAS) NMR, we recently studied reactions of 2-^{13}C and ^{15}N labeled acetone oxime with NO on Cu- and HZSM-5 [23]. Several different reaction pathways for acetone oxime decomposition and reaction with NO on Cu- and HZSM-5 were identified.

The objective of the current work was to use ^{15}N solid state MAS NMR to detect the surface and product species formed by reactions of propane or propene, ^{15}NO and oxygen on Na-, H- and CuZSM-5 zeolites. The direct observation of a proposed intermediate, such as acetone oxime, would provide compelling evidence for the intermediacy of such a species in SCR-HC. In addition, the study will provide information about the roles of exchanged metal cations, hydrocarbon reductants (propane versus propene), and molecular oxygen in the SCR-HC process. All of the NMR experiments were performed on sealed samples that were heated to the specified temperature and then cooled to room temperature for data acquisition.

2. Experimental

2.1. Synthesis and characterization of catalysts

NaZSM-5 zeolite was hydrothermally prepared by a template-free synthesis procedure [24–26]. 3.0 g $Al(OH)_3$ and 6.0 g NaOH were dissolved in 250 ml of deionized water and were added slowly with stirring to 106.5 g of silica

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sol (Ludox 40%). 0.37 g of seed crystals of ZSM-5 were then added to the above gel mixture to promote crystallization. The gel was transferred to Teflon-lined Parr autoclaves, placed in an oven and heated to 180 °C for 48 h. The crystallized zeolites were washed with deionized water and dried overnight at 80 °C. The crystallinity of NaZSM-5 was verified by powder X-ray diffraction (XRD) on a Siemens (D5000) diffractometer. The crystal morphology and size were examined by scanning electron microscopy (SEM) on a HITACHI S-4000 SEM. The Si/Al ratio was determined to be 25 by inductively coupled plasma/atomic emission spectroscopy (ICP/AES) using a Perkin–Elmer Plasma 400.

CuZSM-5 catalyst was prepared by a conventional ion exchange method [26]. A 200 ml aqueous solution of 0.01 M $Cu(NO_3)_2$ was added to 2 g of NaZSM-5 and the mixture was stirred for 24 h at room temperature. The product was filtered, washed with 1 l deionized water, and finally dried in the air. The content of Cu in the CuZSM-5 sample was 2.4 wt% (corresponding to 120% exchanged $((2\times Cu)/Al\times 100\%)$) by ICP/AES. The XRD pattern, Si/Al ratio, and ^{27}Al, ^{29}Si NMR of the CuZSM-5 were identical to those of the parent NaZSM-5. The CuZSM-5 was degassed (1×10^{-3} Torr, 1 Torr = 133.3 Pa) prior to being used in the adsorption and reaction.

HZSM-5 catalyst was prepared by exchanging the Na^+ in NaZSM-5 with NH_4^+ which subsequently decomposed to produce NH_4^+ and the Brønsted acid site. The exchange was achieved by soaking 10 g of NaZSM-5 in 500 ml of 0.1 M NH_4NO_3 for 24 h, drying the product at 80 °C for 2 h. The final step was to heat the product under vacuum (10^{-5} Torr) to 400 °C over 6 h, and then maintaining this temperature for 18 h. The HZSM-5 was characterized using the procedure described above for CuZSM-5.

2.2. Reagents and materials

Nitric-^{15}N oxide (98+% ^{15}N) was obtained from Cambridge Isotopes. Nitric oxide (C.P., 99% min.) and propylene (Polymer Grade) were obtained from Matheson. Propane (Instrument Grade) was purchased from Air Products. The O_2 was obtained from Air Products. Sodium hydroxide (GR) was obtained from EM Science. Aluminum hydroxide hydrate ($Al(OH)_3\cdot xH_2O$) and Ludox (40%) were obtained from Aldrich.

2.3. Preparation of samples

NaZSM-5, CuZSM-5 or HZSM-5, typically 0.3 g, were used in the sample preparation. Prior to the adsorption, the catalysts were first loaded into glass ampoules for pretreatment at 500 °C for NaZSM-5 and CuZSM-5-A, 400 °C for HZSM-5, and room temperature for CuZSM-5-B, all under vacuum (1×10^{-3} Torr) for 3 h. Pretreatment at 500 °C under vacuum will be referred to as the *standard thermal pretreatment*. Throughout this paper, CuZSM-5-A will refer to CuZSM-5 that has undergone standard thermal pretreatment at 500 °C and CuZSM-5-B will refer to CuZSM-5 that has not had any thermal pretreatment. The glass ampoule was a modified version of a design used by Haw and coworkers [27] and has been described in detail elsewhere [23]. The gaseous reactants, in the sequence of propane or propene, ^{15}NO and O_2 and in the ratio of 1 : 1 : 1.5, were introduced into the ampoules on the vacuum rack by immersing the sample in liquid nitrogen. A torch was used to seal the sample. The sealed ampoules were then placed in Chemagnetics 7.5 mm (o.d.) pencil rotors for MAS NMR measurements. Incremental off-line heating of the samples was used and the reaction temperature was controlled by an Omega (CN-76000) programmable temperature controller. All NMR spectra were acquired at room temperature.

Various samples, with the following different combinations of gaseous reactants on NaZSM-5, CuZSM-5 and HZSM-5, were prepared: ^{15}NO alone, propane + ^{15}NO, propane+^{15}NO+O_2, propene+^{15}NO, propene+^{15}NO+O_2. All samples were studied under conditions of thermal equilibrium.

2.4. NMR spectroscopy

The ^{27}Al, ^{29}Si, and ^{15}N MAS NMR spectra were obtained using a wide bore Bruker MSL-300 MHz NMR spectrometer housed in the NMR facility at the University of Iowa, operating at 78.205, 59.621, and 30.425 MHz for ^{27}Al, ^{29}Si, and ^{15}N, respectively. A Chemagnetics double-channel 7.5 mm pencil MAS probe was used to spin rotors loaded with the sealed samples at 4.5–5.0 kHz at the magic angle. Single pulse direct excitation was used for ^{27}Al, ^{29}Si, and ^{15}N, with the $\pi/2$ pulse width 3.5, 6.0, and 7.0 μs, respectively. Recycle delay was 1 s for ^{27}Al, 10 s for ^{29}Si, and 1 s for ^{15}N. A line broadening of 50 Hz was used for ^{15}N spectra, and of 10 Hz for ^{27}Al and ^{29}Si. Tetramethylsilane (TMS) and 1 M $Al(NO_3)_3$ solution were used as chemical shift references for ^{29}Si and ^{27}Al NMR spectra, respectively. Saturated $NH_4{}^{15}NO_3$ (−4 ppm) was used as an external chemical shift standard for ^{15}N and the chemical shift for ^{15}N is reported relative to neat CH_3NO_2. Typically 20 000 scans were averaged for ^{15}N NMR spectra in the experiments. All of the NMR spectra were acquired at 25 °C.

3. Results

3.1. Reactions of propane and ^{15}NO on Na-, H-, and CuZSM-5

The ^{15}N MAS NMR spectra of ^{15}NO and propane adsorbed on Cu-, H-, and NaZSM-5 at room temperature are shown in figure 1 (a)–(d). No peaks were observed in the ^{15}N NMR spectrum (see figure 1(a)) of ^{15}NO and propane adsorbed on CuZSM-5-A. The absence of any ^{15}N NMR signal suggests that nitrogen-containing products are either not present in the sample or are broadened due to paramagnetic interactions with Cu^{2+}. ^{15}NO would not be observed

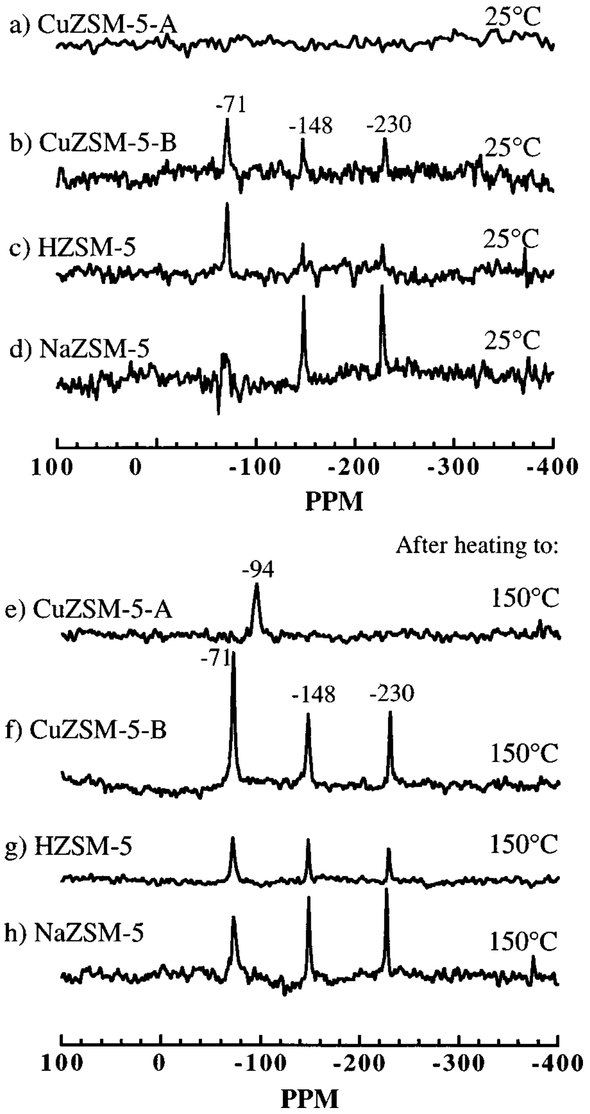

Figure 1. ^{15}N MAS NMR spectra of propane + ^{15}NO at room temperature on (a) CuZSM-5-A, (b) CuZSM-5-B, (c) HZSM-5, and (d) NaZSM-5. ^{15}N MAS NMR spectra of propane + ^{15}NO after heating to 150 °C and cooling to room temperature for data acquisition: (e) CuZSM-5-A, (f) CuZSM-5-B, (g) HZSM-5, and (h) NaZSM-5. NS (number of scans acquired) was: (a) 20 000, (b) 40 000, (c) 28 000, (d) 38 000, (e) 15 000, (f) 20 000, (g) 15 000, and (h) 33 500.

in the NMR spectrum because it is paramagnetic. ^{15}N NMR peaks were observed at −71, −148, and −230 ppm in figure 1 (b)–(d). The single peak at −71 ppm is assigned to N_2 and the two peaks at −147 ppm (central N) and −230 ppm (terminal N) are assigned to N_2O [23,28]. The NMR spectra in figure 1 (b)–(d) indicate that a mixture of N_2 and N_2O was formed on HZSM-5, CuZSM-5-B, and NaZSM-5 after adsorption of propane and ^{15}NO.

The ^{15}N NMR spectra of ^{15}NO and propane adsorbed on Na-, H-, and CuZSM-5 at room temperature, followed by heating to 150 °C and then cooling back to room temperature for data acquisition, are shown in figure 1 (e)–(h). After heating the sample containing ^{15}NO and propane to 150 °C, more N_2 and N_2O were formed on CuZSM-5-B, HZSM-5, and NaZSM-5 compared to the room temperature adsorption. Approximately equal amounts of N_2 (−71 ppm) and N_2O (−147 and −230 ppm) were formed on CuZSM-5-B, H-, and NaZSM-5, as shown in figure 1 (f), (g) and (h).

A peak at −94 ppm was observed in the ^{15}N NMR spectrum of the CuZSM-5-A sample after heating to 150 °C and then cooling for data acquisition (figure 1(e)). The sample was further heated to 350 °C and no changes in the spectrum were observed. There are several possibilities for the assignment of this peak. The −94 ppm peak is most likely due to an adsorbed species since the linewidth of the NMR peak is broader than the linewidth of the NMR peaks of the gas phase N_2 and N_2O species observed in the other spectra. In a previous FTIR study, a signal assigned to N_2 directly coordinated to copper(I) to form the complex, $[Cu(I)–N_2]^+$ was observed [29,30]. EPR and XANES studies have shown that in a hydrated sample of CuZSM-5 the copper is all present as Cu^{2+}, but after the standard thermal pretreatment, Cu^{2+} is autoreduced to Cu^+ [26,31]. However, in a separate experiment in which $^{15}N_2$ was adsorbed on CuZSM-5-A, a single ^{15}N NMR signal was observed at −71 ppm which can be assigned to gas phase N_2.

Another possibility is that the signal is due to an adsorbed nitrogen species, such as acetone oxime adsorbed on CuZSM-5-A. In our previous paper, acetone oxime-^{15}N on CuZSM-5-A produced an ^{15}N NMR peak at −99 ppm [23]. However, in our previous study acetone oxime was completely decomposed at 250 °C. This is in contrast to the present study in which the peak at −94 ppm is stable to 350 °C. In addition, a peak at ~ -90 ppm was observed when only ^{15}NO was adsorbed on CuZSM-5-A. For these reasons, the assignment of the peak at −94 ppm to acetone oxime can be ruled out.

The best assignment for the peak at −94 ppm is to the diamagnetic species, Cu^+NO^+. NO^+ has an ^{15}N NMR chemical shift of ∼1 to −28 ppm depending on the solvent [32,33]. An increase in chemical shielding due to an interaction with copper would be expected. Increases in shielding for the ^{15}N NMR signal have been observed when NO_2^- (nitrite) species are complexed to metal ions [32]. Adelman and coworkers have proposed that NO adsorbs on Cu^{2+} and a charge transfer from NO to Cu produces a diamagnetic Cu^+NO^+ species [19]. Cu^+NO^+ (or $Cu^{\delta+}NO^{\delta+}$, in the case of incomplete charge transfer) has also been observed in several FTIR studies [34–36]. According to the mechanism proposed by Adelman and coworkers, the first step of SCR of NO with propane involves the reaction of NO and O_2 to form NO_2 and a surface species identified as NO_y which then reacts with propane to form nitrosopropane and eventually acetone oxime [37]. The NO^+ molecule formed from the charge transfer then reacts with acetone oxime to form N_2O.

A small peak at −375 ppm is observed in figure 1(h) and is assigned to NH_4^+ [23,38,39]. The chemical shifts for $NH_{3(g)}$ and $NH^+_{4(aq)}$ are −399.9 and −359.9 ppm, respectively, relative to liquid CH_3NO_2 [39]. Therefore, the species observed in NaZSM-5 is most likely closer to NH_4^+ probably due to an interaction with a structural hydroxyl group [39].

3.2. Reactions of propane + $^{15}NO + O_2$ on Na-, H-, and CuZSM-5

When ^{15}NO, propane and O_2 reacted on Na-, H-, and CuZSM-5, the results were quite different than in the absence of O_2. The ^{15}N NMR spectra are shown in figure 2. Initially, no ^{15}N NMR signals were observed on CuZSM-5-A and -B, as shown in figure 2 (a) and (b). N_2 (-74 ppm) and NH_4^+ (-380 ppm) peaks were observed on HZSM-5. Two new peaks at 36 and -2 ppm were observed on NaZSM-5. These peaks can be assigned to a surface-bound nitrogen species. The ^{15}N NMR chemical shift for solid $Na^{15}NO_3$ is -3 ppm [32,40]. Therefore, the peak at -2 ppm is assigned to an adsorbed NO_3 (nitrate) on NaZSM-5. Previously, similar peaks have been observed on zeolites and have been assigned to adsorbed nitrate species [41]. The peak at 36 ppm is due to an adsorbed nitrogen complex, but the exact identity is not clear since many nitrogen-containing compounds have chemical shifts in this region [32]. This species is assigned to methylnitrate (CH_3ONO_2) which has a chemical shift ranging from 37–42 ppm depending on the solvent [32].

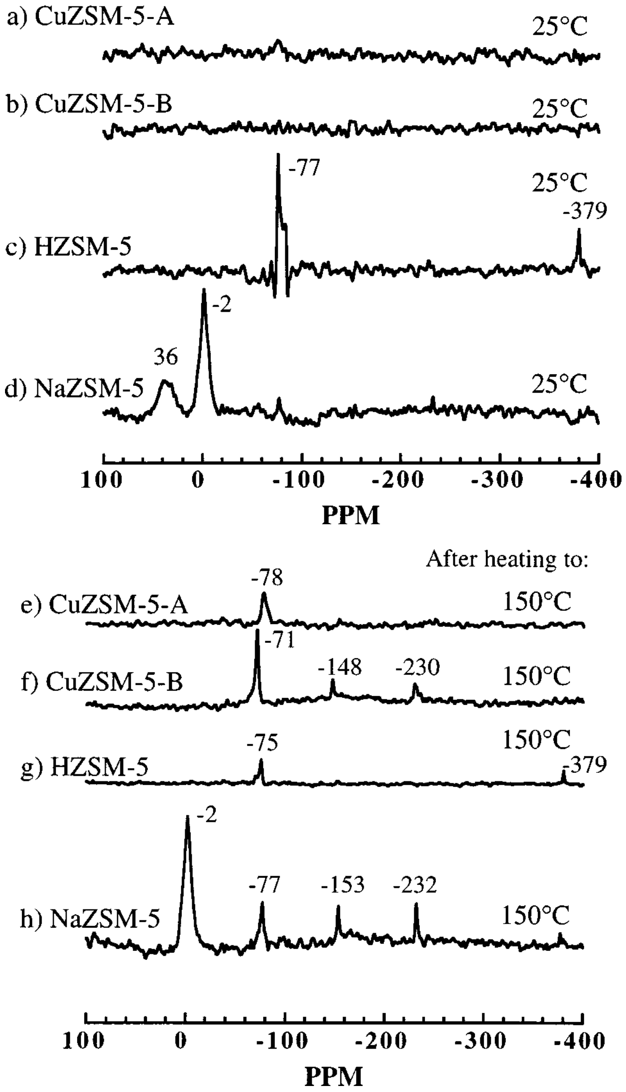

Figure 2. ^{15}N MAS NMR spectra of propane + $^{15}NO + O_2$ at room temperature on (a) CuZSM-5-A, (b) CuZSM-5-B, (c) HZSM-5, and (d) NaZSM-5. ^{15}N MAS NMR spectra of propane + $^{15}NO + O_2$ after heating to 150 °C and cooling to room temperature for data acquisition: (e) CuZSM-5-A, (f) CuZSM-5-B, (g) HZSM-5, and (h) NaZSM-5. NS (number of scans acquired) was: (a) 20 000, (b) 20 000, (c) 14 500, (d) 20 000, (e) 20 000, (f) 20 000, (g) 40 000 and (h) 35 000.

After heating the samples to 150 °C and cooling to room temperature for data acquisition, the ^{15}N NMR spectra changed as shown in figure 2 (e)–(h). The ^{15}N NMR spectrum of the CuZSM-5-A sample showed one peak at -78 ppm and it is assigned to N_2. The spectrum for CuZSM-5-B showed three peaks in the ^{15}N NMR spectrum assigned to N_2 (-71 ppm) and N_2O (-148 and -230 ppm), respectively. The ^{15}N NMR spectrum of propane + $^{15}NO + O_2$ on HZSM-5 (figure 2(g)) showed two peaks at -75 and -379 ppm that can be attributed to N_2 and NH_4^+. The spectrum in figure 2(h) showed peaks assigned to N_2 (-77 ppm), N_2O (-153 and -232 ppm) and a nitrate (NO_3^-) (-2 ppm) species. The species at 36 ppm in figure 2(d) was not present after heating the sample to 150 °C, but the peaks due to N_2 and N_2O increased in intensity. This suggests that the species at 36 ppm was converted into N_2 and/or N_2O. After further heating to 250 °C and then cooling for data acquisition, the loss of the peak at -2 ppm and the growth of the N_2 peak at -77 ppm was observed suggesting that the nitrate species reacted to form N_2.

3.3. Reactions of propene + ^{15}NO on Na-, H-, and CuZSM-5

The reaction of propene and ^{15}NO on Cu-, H-, and NaZSM-5 was monitored by ^{15}N NMR as shown in figure 3. After room temperature reaction, N_2 (-72 ppm) and trace amounts of N_2O (-148 and -232 ppm) were detected on CuZSM-5-B, HZSM-5 and NaZSM-5. No products were detected by ^{15}N NMR on CuZSM-5-A. After heating the samples to 150 °C and cooling to room temperature for data acquisition, a peak at -89 ppm (see figure 3(e)) was observed on CuZSM-5-A. This peak is similar to the peak in figure 1(d) and has several possible assignments as discussed in an earlier section. Four peaks were observed in the ^{15}N NMR spectrum of propene and ^{15}NO on CuZSM-5-B at -72, -148, -232, and -364 ppm (see figure 3(f)). Analogous to the previous assignments, these peaks are assigned to N_2, N_2O, and NH_4^+, respectively. After further heating of the sample to 250 °C, only one peak due to N_2 is observed at -71 ppm. A mixture of N_2 and

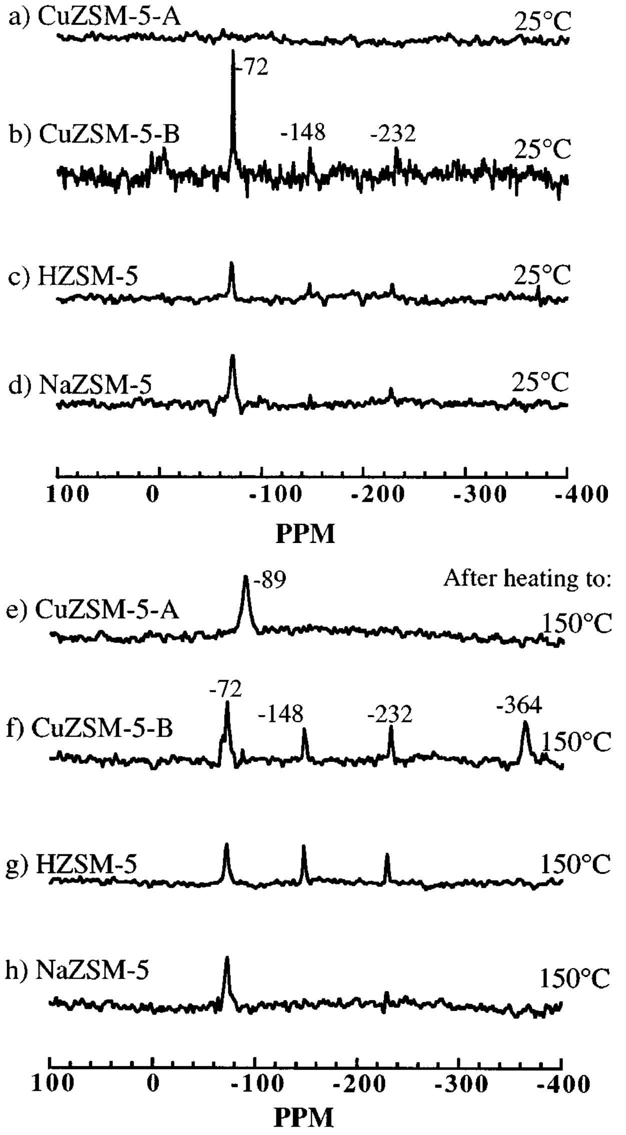

Figure 3. ^{15}N MAS NMR spectra of propene + ^{15}NO at room temperature on (a) CuZSM-5-A, (b) CuZSM-5-B, (c) HZSM-5, and (d) NaZSM-5. ^{15}N MAS NMR spectra of propene + ^{15}NO after heating to 150 °C and cooling to room temperature for data acquisition: (e) CuZSM-5-A, (f) CuZSM-5-B, (g) HZSM-5, and (h) NaZSM-5. NS (number of scans acquired) was: (a) 20 000, (b) 40 000, (c) 20 000, (d) 20 000, (e) 20 000, (f) 20 000, (g) 20 000, and (h) 20 000.

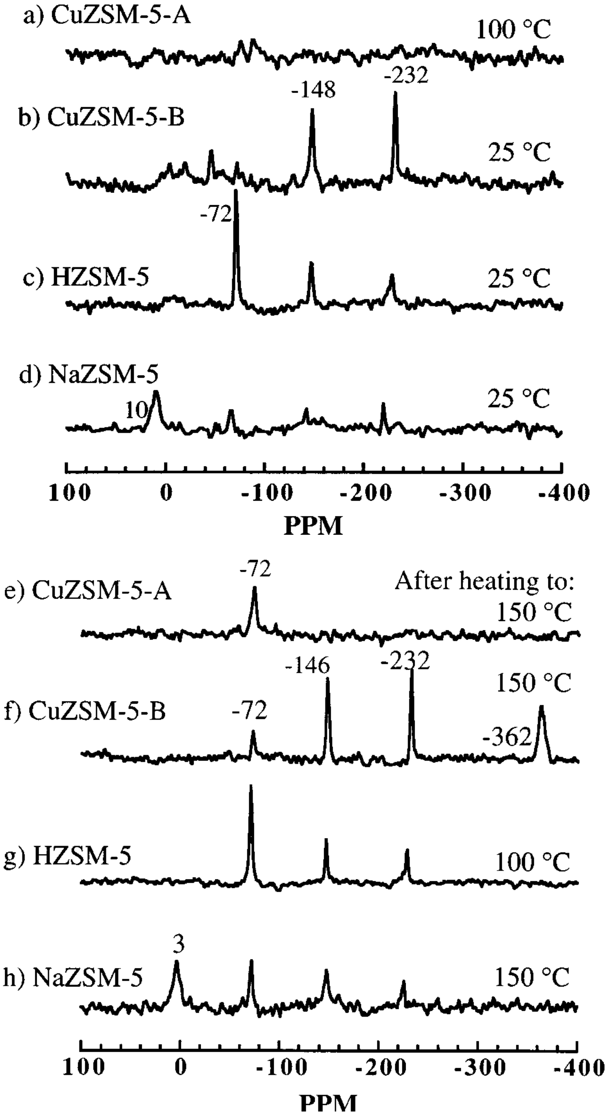

Figure 4. ^{15}N MAS NMR spectra of propene + ^{15}NO + O_2 at room temperature on (a) CuZSM-5-A, (b) CuZSM-5-B, (c) HZSM-5, and (d) NaZSM-5. ^{15}N MAS NMR spectra of propene + ^{15}NO + O_2 after heating to 150 °C and cooling to room temperature for data acquisition on: (e) CuZSM-5-A, (f) CuZSM-5-B, (g) HZSM-5, and (h) NaZSM-5. NS (number of scans acquired) was: (a) 38 862, (b) 40 000, (c) 20 000, (d) 20 000, (e) 20 000, (f) 20 000, (g) 20 000, and (h) 30 000.

N_2O was observed on HZSM-5 (figure 3(g)) and only N_2 was formed on NaZSM-5 (figure 3(h)).

3.4. Reactions of propene + ^{15}NO + O_2 on Na-, H-, and CuZSM-5

The ^{15}N NMR spectra of propene, ^{15}NO and O_2 on Cu-, H-, and NaZSM-5 are shown in figure 4. No ^{15}N NMR peaks were observed up to 100 °C for CuZSM-5-A. Peaks assigned to N_2O were observed in the ^{15}N NMR spectrum of CuZSM-5-B. ^{15}N NMR peaks assigned to N_2 (−72 ppm), N_2O (−146 and −232 ppm) were observed in the spectra of HZSM-5 and NaZSM-5 after room temperature adsorption of propene, ^{15}NO and O_2. For NaZSM-5, an additional peak in the NMR spectrum was observed at 10 ppm and this is assigned to a surface nitrate species, as discussed earlier in this paper. The ^{15}N NMR spectrum of propene, ^{15}NO, and O_2 on CuZSM-5-A after heating to 150 °C and cooling to room temperature for data acquisition has one peak at −72 ppm assigned to N_2 (see figure 4(e)). The analogous ^{15}N NMR spectrum of CuZSM-5-B has four peaks assigned to N_2 (−72 ppm), N_2O (−146 and −232 ppm) and NH_4^+ (−362 ppm) as can be seen in figure 4(f). The ^{15}N NMR spectra of HZSM-5 and NaZSM-5 have peaks attributed to N_2 and N_2O; the ^{15}N NMR spectrum of NaZSM-5 has an additional peak at 3 ppm that can be attributed to an adsorbed nitrate species (vide infra).

4. Discussion

4.1. Effect of the hydrocarbon reductant (propane or propene) on the SCR-HC of NO

The differences in reactivity with propane vs. propene as a reductant for SCR-HC of NO in the absence of O_2 can be evaluated by comparing figures 1 and 3. The ^{15}N NMR spectra for analogous samples (i.e., propene or propane, under the same reaction conditions) were similar for CuZSM-5-A and HZSM-5. Interestingly, peaks were observed at -94 ppm (propane) and -89 ppm (propene) on CuZSM-5-A, which may be attributed to an adsorbed nitrogen species, such as Cu^+NO^+. This peak was only observed in the absence of oxygen and was stable to 350 °C. The stability of this species is presumably because acetone oxime and other oxygen-containing intermediates cannot form in the absence of oxygen and are therefore not available to react with the Cu^+NO^+ species.

Notable differences in the NMR spectra are observed with propane vs. propene as the reductant for the CuZSM-5-B and NaZSM-5 samples, as can be seen in figures 1(f), 3(f), 1(h) and 3(h). With propene as the reductant, N_2, N_2O, and NH_4^+ were observed after heating CuZSM-5-B to 150 °C while only N_2 and N_2O were formed with propane as the reductant. When the CuZSM-5-B sample was heated to higher temperature, the NH_4^+ peak disappeared and the N_2 and N_2O peaks increased in intensity. The other difference was observed for the NaZSM-5 sample. With propane as the reductant, N_2 and N_2O were both formed on NaZSM-5 while with propene as the reductant, only N_2 was formed.

In summary, after reaction with ^{15}NO and a reductant, the product distributions of N_2 and N_2O formed on CuZSM-5-A and on HZSM-5 were independent of the identity of the reductant (propane or propene). In contrast, propene and ^{15}NO reacted on CuZSM-5-B to form NH_4^+, which was not formed at all with propane as the reductant. On NaZSM-5, ^{15}NO and propene reacted to produce N_2 while ^{15}NO and propane reacted to form both N_2 and N_2O.

In the presence of O_2, CuZSM-5-A is still unaffected by the identity of the hydrocarbon reductant (figures 2(e) and 4(e)). It should be noted that with ^{15}NO, O_2, and either propane or propene, N_2 was observed after heating CuZSM-5-A to 150 °C and the ^{15}N NMR peak occurred close to the gas phase value of -72 ppm. Apparently, in the absence of oxygen, the Cu^+NO^+ complex observed at -94 to -89 ppm did not react to form N_2 or N_2O. NaZSM-5 also reacted similarly with either propane or propene as the reductant in the presence of O_2.

For CuZSM-5-B, N_2 and N_2O were formed with ^{15}NO, O_2, and either propane or propene as the reductant, but NH_4^+ was also formed in the presence of propene. This probably has more to do with the reductant, propene, than with the presence of oxygen since NH_4^+ was also observed for propene and ^{15}NO on CuZSM-5-B in the absence of O_2 after heating to 150 °C. For HZSM-5, only N_2 and NH_4^+ were formed with ^{15}NO, O_2, and propane as the reductant, while N_2 and N_2O were formed with ^{15}NO, O_2, and propene as the reductant.

The catalytic activity for SCR-HC with propane or propene as the reductant on CuZSM-5 is very high [22,42]. Gaudin and coworkers used transient techniques and concluded that with propene as the reductant, cracking reactions and adsorption of carbonaceous species occurred at lower temperatures than with propane [42]. The increased reactivity of propene compared to propane is not surprising, since for example, the oligomerization of propene on Brønsted acid sites in zeolites is a well-known reaction. They concluded that a nitrogen-containing surface species was formed between carbon and NO with propane or propene as the reductant. Centi and coworkers also investigated the differences between propene and propane as the reductant for SCR-HC reactions using steady-state and transient catalytic tests and FTIR and ^{13}C NMR [22]. Several differences between the mechanism for SCR-HC on propene vs. propane were listed: (1) the method of hydrocarbon activation, (2) the types of nitrogen oxide species involved in the formation of the nitro–organic intermediate, and (3) the number of carbon atoms in the intermediates due to the presence of competitive oligomerization reactions with propene as the reductant [22].

In the present study, the most notable difference observed with different reductants was the formation of NH_4^+ on CuZSM-5-B with propene as the reductant. NH_4^+ was not observed on CuZSM-5-B with propane as the reductant. The NH_4^+ that was formed then reacted further after heating to 250 °C to form N_2. This is consistent with the mechanism proposed by Centi and coworkers in which ammonia reacts with NO to form N_2 and H_2O. The formation of ammonia is predicted to occur with both propane and propene as reductants; however, the rate of formation of ammonia depends on the rate of its formation as well as the rate of a competive reaction [22]. Another point is that the nitrate surface species that are formed on NaZSM-5 are different with propane vs. propene as reductant. This may indicate that the nitrate species being formed are different and may contain different numbers of carbon atoms in accord with the prediction that propene will oligomerize on NaZSM-5. The most striking similarity observed in the ^{15}N NMR spectra of propane and propene, and ^{15}NO on CuZSM-5-A was the peak at -94 (-89 ppm) that was observed. This peak is attributed to Cu^+NO^+ [18,19].

4.2. Effect of oxygen on the SCR-HC of NO

The main difference observed by ^{15}N NMR when oxygen was added to the system containing propane (or propene) and ^{15}NO on NaZSM-5 was the formation of a nitrate species. A strong peak at -2 ppm was observed on NaZSM-5 with propane, ^{15}NO and O_2. This peak was attributed to a surface-bound nitrate complex that was further converted into N_2 as the sample was heated to 250 °C. A similar species with a chemical shift of 10 ppm was observed on NaZSM-5 after reaction of propene, ^{15}NO and O_2. Nitrate surface species were not observed by ^{15}N NMR of propane (or propene) and ^{15}NO on H- or CuZSM-5. It is possible that the nitrate species were formed on H- and CuZSM-5 but that they more readily reacted to form N_2 and N_2O than on NaZSM-5. The stability of the nitrate species on NaZSM-5 could explain the low activity of NaZSM-5 for the SCR-HC of NO reaction.

4.3. Effect of exchangeable cation on the SCR-HC of NO

In this study, the most notable cation-dependent effects were (1) the formation of nitrate surface species on NaZSM-5, as discussed above, (2) the formation of a surface species tentatively assigned to acetone oxime or a related compound on CuZSM-5-A, and (3) the formation of NH_4^+ on CuZSM-B. The formation of acetone oxime and adsorbed ammonium ion are consistent with the results of previous studies in the literature and support previously proposed mechanisms for SCR-HC on CuZSM-5 [18,19].

4.4. Implications of this work for the SCR-HC of NO$_x$

The goal of the present work was to use ^{15}N NMR to identify surface species formed on Cu-, H-, and Na-ZSM-5 that could be important intermediates in the SCR-HC of NO_x. Reactant molecules were adsorbed on the zeolites, the samples were heated to various temperatures, and then the samples were examined using ^{15}N NMR spectroscopy. The NMR spectra were obtained under conditions of thermal equilibrium and at temperatures well below the catalytically relevant temperatures of ∼400 °C. In general, for the samples examined in this study, heating to higher (more catalytically relevant) temperatures did not produce any changes in the observed ^{15}N NMR features. The exceptions were the samples in which nitrate species or NH_4^+ were formed. Further heating of these samples caused the conversion of the nitrate or NH_4^+ species into N_2 or N_2O as already discussed in this paper. Therefore, while the NMR results presented in this paper do not prove or disprove a mechanism for SCR-HC of NO, valuable evidence supporting the presence of particular surface species is obtained.

^{13}C NMR spectra were not obtained for these samples because of the signal to noise considerations when using unlabeled material. In preliminary ^{13}C NMR experiments under conditions similar to those used in this study, the only carbon species, other than the reductant, that was observed was CO_2.

5. Conclusions

^{15}N MAS NMR was used to study the reactions of propane or propene with ^{15}NO and O_2 on Na-, H-, and CuZSM-5. Gas-phase product species, N_2 and N_2O, were detected and surface-bound nitrogen-containing species were identified, such as NH_4^+, various nitrate species and Cu^+NO^+. The adsorbed nitrate species were only observed on NaZSM-5 after treatment with propane (propene), ^{15}NO and O_2 and it was completely converted into N_2 at ∼250 °C. The effects of the hydrocarbon reductant, the presence of molecular oxygen and the exchangeable cation were discussed.

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References

[1] W. Held, A. Konig, T. Richter and L. Pupper, SAE Paper 900 (1990) 469.
[2] M. Iwamoto and H. Hamada, Catal. Today 10 (1991) 57.
[3] M. Shelef, Chem. Rev. 95 (1995) 209.
[4] H. Bosch and F. Janssen, Catal. Today 4 (1987) 369.
[5] Y. Li and J.N. Armor, Appl. Catal. B 1 (1991) L3.
[6] Y. Li and J.N. Armor, Appl. Catal. B 3 (1994) 239.
[7] R. Burch and S. Scire, Appl. Catal. B 3 (1994) 295.
[8] X. Feng and W.K. Hall, J. Catal. 166 (1997) 368.
[9] Y. Li, T.L. Slager and J.N. Armor, J. Catal. 150 (1994) 338.
[10] F. Witzel, G.A. Sill and W.K. Hall, J. Catal. 149 (1994) 229.
[11] T. Beutel, B.J. Adelman, G.D. Lei and W.M.H. Sachtler, Catal. Lett. 32 (1995) 83.
[12] E.V. Rebrov, A.V. Simakov, N.N. Sazonova, V.A. Rogov and G.B. Barannik, Catal. Lett. 51 (1998) 27.
[13] E.V. Rebrov, A.V. Simakov, N.N. Sazonova and E.S. Stoyanov, Catal. Lett. 58 (1999) 107.
[14] Y. Ukiso, S. Sato, A. Abe and K. Yoshida, Appl. Catal. B 2 (1993) 147.
[15] V.A. Sadykov, S.L. Baron, V.A. Matyshak, G.M. Alikina, R.V. Bunina, A.Y. Rozovskii, V.V. Lunin, E.V. Lunina, A.N. Kharlanov, A.S. Ivanova and S.A. Veniaminov, Catal. Lett. 37 (1996) 157.
[16] C. Yokoyama and M. Misono, J. Catal. 150 (1994) 9.
[17] R.H.H. Smits and Y. Iwasawa, Appl. Catal. B 6 (1995) L201.
[18] T. Beutel, B. Adelman and W.M.H. Sachtler, Catal. Lett. 37 (1996) 125.
[19] B.J. Adelman, T. Beutel, G.-D. Lei and W.M.H. Sachtler, Appl. Catal. B 11 (1996) L1.
[20] B.J. Adelman, T. Beutel, G.-D. Lei and W.M.H. Sachtler, J. Catal. 158 (1996) 327.
[21] F. Poignant, J. Saussey, J.C. Lavalley and G. Mabilon, J. Chem. Soc. Chem Commun. (1995) 89.
[22] G. Centi, A. Galli and S. Perathoner, J. Chem. Soc. Faraday Trans. 92 (1996) 5129.
[23] J. Wu and S.C. Larsen, J. Catal. 182 (1999) 244.
[24] E. Narita, K. Sato, N. Yatabeand and T. Okabe, Ind. Eng. Chem. Prod. Res. Dev. 24 (1985) 507.
[25] V.P. Shiralkar and A. Clearfield, Zeolites 9 (1989) 363.
[26] S.C. Larsen, A. Aylor, A.T. Bell and J.A. Reimer, J. Phys. Chem. 98 (1994) 11533.
[27] L.W. Beck, J.L. White and J.F. Haw, J. Magn. Reson. 99 (1992) 182.
[28] V.M. Mastikhin, I.L. Mudrakovsky and S.V. Filimonova, Chem. Phys. Lett. 149 (1988) 175.
[29] A. Zecchina, S. Bordiga, G. Palomino, D. Scarano, C. Lamberti and M. Salvaggio, J. Phys. Chem. B 103 (1999) 3833.

[30] G. Spoto, S. Bordiga, G. Ricchiardi, D. Scarano, A. Zecchina and F. Geobaldo, J. Chem. Soc. Faraday Trans. 91 (1995) 3285.

[31] D.-J. Liu and H.J. Robota, Catal. Lett. 21 (1993) 291.

[32] M. Witanowski, L. Stefaniak and G.A. Webb, in: *Annual Reports on NMR Spectroscopy*, Vol. 25, ed. G.A. Webb (Academic Press, San Diego, 1993).

[33] B.E. Mann, in: *NMR and the Periodic Table*, eds. R.K. Harris and B.E. Mann (Academic Press, London, 1978) pp. 87–105.

[34] M. Iwamoto, H. Yahiro, N. Misuno, W. Zhang, Y. Mine, H. Furukawa and S. Kagawa, J. Phys. Chem. 96 (1992) 9360.

[35] A. Aylor, S.C. Larsen, J.A. Reimer and A.T. Bell, J. Catal. 157 (1995) 592.

[36] T. Hoost, K. Laframboise and K. Otto, Catal. Lett. 37 (1997) 153.

[37] B.J. Adelman, T. Beutel, G.-D. Lei and W.M.H. Sachtler, Appl. Catal. B 11 (1996) L1.

[38] T. Xu, J. Zhang and J.F. Haw, J. Am. Chem. Soc. 117 (1995) 3171.

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

[40] P.J. Barrie, C.J. Groombridge, J. Mason and E.A. Moore, Chem. Phys. Lett. 219 (1994) 491.

[41] V.M. Mastikhin and S.V. Filimonova, J. Chem. Soc. Faraday Trans. 88 (1992) 1473.

[42] C. Gaudin, D. Duprez, G. Mabilon and M. Prigent, J. Catal. 160 (1996) 10.