# Probing the Reactivity of Adsorbed NO Species by the CO and H<sub>2</sub> Pulse during NO Decomposition on Cu-ZSM-5

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The reactivity of adsorbed NO and the nature of Cu sites on under-, over-exchanged, and silane-treated Cu– ZSM-5 have been probed by the CO and H<sub>2</sub> pulse during NO decomposition at 673 K. Cu<sup>+</sup>(NO) was identified to be the active adsorbate responsible for NO decomposition to N<sub>2</sub>O and O<sub>2</sub> as well as to N<sub>2</sub> and O<sub>2</sub>. Pulsing CO and H<sub>2</sub> into the NO flow facilitates the reduction of Cu<sup>2+</sup> to Cu<sup>+</sup> and increases Cu<sup>+</sup>(NO) concentration, resulting in an enhancement of N<sub>2</sub>O formation rate on under-exchanged Cu–ZSM-5–83/silane-treated Cu– ZSM-5–523 and an acceleration of N<sub>2</sub> and O<sub>2</sub> formation rates on over-exchanged Cu–ZSM-5–127 and -523. The difference in the product formation among these catalysts is attributed to the isolation of Cu sites on the silane-treated Cu–ZSM-5–527 and under-exchanged Cu–ZSM-5–83 catalyst as well as the presence of Cu-dimer sites (Cu–O–Cu) on the over-exchange Cu–ZSM-5–83 catalyst. In contrast to the widely postulated steps for N<sub>2</sub> formation via N<sub>2</sub>O, the profiles of N<sub>2</sub>, N<sub>2</sub>O, O<sub>2</sub>, and IR observable adsorbates during the CO and H<sub>2</sub> pulse suggest that N<sub>2</sub> can be formed without involvement of N<sub>2</sub>O during NO decomposition.

#### Introduction

Cu–ZSM-5 has been known to exhibit the highest activity for NO decomposition. The ability of the copper sites on Cu– ZSM-5 to undergo oxidation/reduction<sup>1-10</sup> distinguishes Cu– ZSM-5 from other NO reduction catalysts. Despite its susceptibility to water- and sulfur-poisoning, Cu–ZSM-5 has been studied in detail.<sup>11–21</sup> A detailed understanding of the NO decomposition mechanism would aid in designing novel catalysts with similar active sites that are resistant to water- and sulfur-poisoning.

Extended X-ray adsorption fine structure (EXAFS), ultraviolet visible (UV-vis) photoluminescence, electron paramagnetic resonance (EPR), density functional theory (DFT), and quantum and statistical mechanical calculations have proposed the existence of more than one type of  $Cu^+$  and  $Cu^{2+}$  species in Cu-ZSM-5.<sup>22-27</sup> In situ infrared (IR) studies have established that NO adsorbs as  $Cu^+(NO)$  at 1814 cm<sup>-1</sup>,  $Cu^{2+}(NO)$  at 1905  $cm^{-1}$ , NO<sup>+</sup> at 2124  $cm^{-1}$ , bridging and chelating  $Cu^{2+}(NO_3^{-})$ at 1624 and 1565 cm<sup>-1</sup>, respectively,<sup>11-16</sup> under reaction conditions over Cu-ZSM-5.28,29 The level of exchanged Cu strongly influences the NO decomposition activity.11 Underexchanged Cu-ZSM-5 produced primarily N2O while overexchanged Cu-ZSM-5 produced mainly N<sub>2</sub>, giving higher NO decomposition activity than under-exchanged catalysts. Despite the difference in the NO decomposition activity/selectivity and Cu-exchange level, all of the Cu-ZSM-5 catalysts produce the same type of adsorbed NO species with different intensities. Although IR in combination with transient techniques has shown that Cu<sup>+</sup>(NO) and bridging Cu<sup>2+</sup>(NO<sub>3</sub><sup>-</sup>) are active species participating in the catalytic cycle of NO decomposition,<sup>28,29</sup> it was not able to distinguish the difference in the reactivity of adsorbed NO and their reaction pathways on the under- and over-exchanged catalysts.

The involvement of  $Cu^+(NO)$  and bridging  $Cu^{2+}(NO_3^-)$  in the redox cycle of NO decomposition suggests that dynamic behavior of their formation and conversion may be further studied by introducing a reducing agent such as CO and  $H_2$ during the NO decomposition reaction.<sup>30</sup> The introduction of CO and  $H_2$ , which has been demonstrated to promote the NO decomposition reaction is expected to perturb the copper sites under the dynamic reduction/oxidation cycle.<sup>29</sup> The present study reports results of using CO and  $H_2$  pulses to probe the reactivity of adsorbed NO and the nature of Cu sites on under-, overexchanged, and silane-treated Cu–ZSM-5 catalysts which show significantly different NO decomposition activities and selectivities. The objectives of this study are to reveal the difference in the nature of Cu sites as well as their adsorbates' reactivity and pathways on these different Cu–ZSM-5 catalysts.

#### **Experimental Section**

Catalyst Preparation. Three levels of copper-exchanged Cu-ZSM-5 were used in the present study. Cu-ZSM-5-127, where 127 indicates the % copper exchange (2 x moles of Cu/ moles of Al), and Cu-ZSM-5-523, with a 523% copperexchange, were both prepared separately by the repeated ionexchange of 3 g Cu–ZSM-5–83 (Sandia National Laboratory) in a 0.07 M copper acetate solution at a pH of 7. The ionexchange process was repeated twice for preparing Cu-ZSM-5-127 whereas the process was repeated three times for preparing Cu-ZSM-5-523. After the ion-exchange process, the catalysts were dried in air overnight at 373 K. Inductively coupled plasma (ICP) emission spectroscopy established a Si/ Al ratio of 24.4 for Cu-ZSM-5-127 and 24.6 for Cu-ZSM-5-523; a Cu/Al ratio of 0.635 for Cu-ZSM-5-127 and 2.615 for Cu-ZSM-5-523. Prior to all reaction studies, unless specified otherwise, the catalysts were pretreated in He at 773 K for 2 h for auto-reduction.

**Reaction System.** The reaction system consisted of an in situ infrared (IR) reactor cell,<sup>30</sup> a Nicolet Magna 550 Fourier transform infrared (FTIR) spectrometer, and a Pfeiffer PRISMA mass spectrometer (MS). A gas distribution system delivered

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Figure 1. IR spectra of adsorbed NO at 373, 473, and 673 K.

the reactant and inert gases to the reactor cell containing the catalyst. One hundred mg of each catalyst was pressed into 3-4 thin pellets, each weighing 25 mg, by a hydraulic press at 4000–5000 psi. One of the pellets was placed in the path of the IR beam of the reactor cell and the others were broken down into flakes and placed in the close vicinity of the IR beam path. The MS determined the changes in the concentration of the reactants and products, while the FTIR monitored the changes in the concentration of the adsorbates during the pulse study.

Pulsing CO and H<sub>2</sub> into the Steady-State NO Flow. Pulsing 1 cm<sup>3</sup> of an isotope of CO, <sup>13</sup>CO, into 5% NO in He flow (2.5  $cm^3/min NO + 47.5 cm^3/min He)$  over Cu-ZSM-5-127 at 673 K was carried out to establish the effect of CO in promoting N<sub>2</sub>, N<sub>2</sub>O, and CO<sub>2</sub> formation. Use of <sup>13</sup>CO distinguishes the MS profile of  $N_2$  from that of <sup>13</sup>CO and the profile of <sup>13</sup>CO<sub>2</sub> from that of N<sub>2</sub>O. 1 cm<sup>3</sup> of CO was pulsed into 5% NO in He flow, similar to the <sup>13</sup>CO pulse studies, over Cu–ZSM-5–83, -523, and its silane-treated catalysts at 673 K. 1 cm<sup>3</sup> pulses of H<sub>2</sub> were also introduced, separately, into 5% NO in He over all of these Cu-ZSM-5 catalysts at 673 K. To determine the state of copper species in Cu-ZSM-5 during the H<sub>2</sub> pulse studies, a separate study involving the introduction of 1 cm<sup>3</sup> of H<sub>2</sub> and a trace amount of CO ( $H_2/CO = 9/1$ ) into 5% NO in He at 673 K was conducted on Cu-ZSM-5-127. All of the pulses were introduced into the NO flow by a six-port GC valve. Under each condition, three pulses were made. Since the results are reproducible, only one set of IR and MS results are reported here.

SiH<sub>4</sub>-Treated Cu–ZSM-5. Auto-reduced Cu–ZSM-5 catalysts, exhibiting pulse and steady-state NO decomposition activity, were subjected to silane (SiH<sub>4</sub>) treatment. Silane treatment consisted of (a) exposing auto-reduced Cu–ZSM-5–523 catalysts to 10% CO in He at 303 K to chemisorb CO on Cu<sup>+</sup>/Cu<sup>2+</sup> sites to avoid them from interacting with SiH<sub>4</sub>, (b) flowing 1% SiH<sub>4</sub> in He over the CO-adsorbed Cu–ZSM-5 catalysts at 303 K for 5 min, and (c) holding the reactor in a batch mode at 373 K for 1 h.

# Results

**Steady-State NO Decomposition.** Figure 1 shows IR spectra of adsorbed NO taken during steady-state NO flow over Cu– ZSM-5–83, -127, -523, and silane-treated 523 catalysts. Despite the difference in Cu content and their activity/selectivity, these catalysts produced Cu<sup>+</sup>(NO) at 1814 cm<sup>-1</sup>, Cu<sup>2+</sup>(NO) at 1905 cm<sup>-1</sup>, NO<sup>+</sup> at 2124 cm<sup>-1</sup>, bridging and chelating Cu<sup>2+</sup>(NO<sub>3</sub><sup>-</sup>) at 1625 and 1560 cm<sup>-1</sup>, respectively.<sup>11-16</sup> Appreciable NO conversion was observed at 673 K for all catalysts except the silane-treated catalysts. Both over-exchanged Cu– ZSM-5 catalysts show activity for the decomposition of NO to N<sub>2</sub> and O<sub>2</sub>, whereas under-exchanged catalyst exhibits activity for decomposing NO to N<sub>2</sub>O and O<sub>2</sub>.

<sup>13</sup>CO Pulse Studies. Figure 2a shows the IR spectra collected during the 1 cm<sup>3</sup>-<sup>13</sup>CO pulse over Cu–ZSM-5–127. Prior to the introduction of the <sup>13</sup>CO pulses, flowing 5% NO produced Cu<sup>+</sup>(NO) at 1814 cm<sup>-1</sup>, Cu<sup>2+</sup>(NO) at 1905 cm<sup>-1</sup>, NO<sup>+</sup> at 2123 cm<sup>-1</sup>, bridging nitrato- species at 1625 cm<sup>-1</sup>, and chelating nitrato-species at 1560 cm<sup>-1</sup>. Introduction of the <sup>13</sup>CO pulse into the steady-state NO flow over Cu–ZSM-5–127 produced changes in the adsorbate as well as reactant/product concentrations. The most noticeable changes in IR spectra due to the <sup>13</sup>-CO pulse are the depletion of all the adsorbed NO species and the formation of Cu<sup>+</sup>(<sup>13</sup>CO) at 2106 cm<sup>-1</sup>, Cu<sup>+</sup>(<sup>13</sup>CO)<sub>3</sub> at 2150 cm<sup>-1</sup>, <sup>13</sup>CO<sub>ads</sub> at 2057 cm<sup>-1</sup>,<sup>29</sup> and <sup>13</sup>CO<sub>2</sub> at 2282 cm<sup>-1</sup>.

The variations in adsorbate intensity with time are plotted along with concentration profiles of reactants/products in Figure 3a-d. It should be noted that MS profiles of gaseous species spread wider than IR profiles of adsorbed species due to the dispersion effect of the gaseous flow. The increase in the N<sub>2</sub>, O<sub>2</sub>, and CO<sub>2</sub> formation as well as reappearance of Cu<sup>+</sup>(NO) with a significantly higher intensity than prior to the <sup>13</sup>CO pulse (shown in Figure 3c) revealed that the major function of CO is to serve as a reductant, reducing Cu<sup>2+</sup> to Cu<sup>+</sup> and significantly enhancing the NO conversion and the NO decomposition rate.



Figure 2. IR spectra collected during the (a) 1 cm<sup>3</sup> of <sup>13</sup>CO pulse into 5% NO stream over auto-reduced Cu-ZSM-5-127 at 673 K and (b) 1 cm<sup>3</sup> of CO pulse into 5% NO stream over auto-reduced Cu-ZSM-5-83 at 673 K.



**Figure 3.** (a) MS intensity profiles of reactor effluent and (b), (c), and (d) IR peak intensity profiles of adsorbates obtained during 1 cm<sup>3</sup> of  $^{13}$ CO pulse into 5% NO stream over auto-reduced Cu-ZSM-5-127 at 673 K; (e) MS intensity profiles of reactor effluent and (f), (g), (h) IR peak height profiles of adsorbates obtained during 1 cm<sup>3</sup> of CO pulse into 5% NO stream over auto-reduced Cu-ZSM-5-83 at 673 K.

It is important to note that a significant fraction of O from NO desorb as  $O_2$  instead of reacting with CO to form  $CO_2$ . This

increased formation of both  $N_2$  and  $O_2$  is an evidence of COpromoting NO decomposition to  $N_2$  and  $O_2$ .



Figure 4. Reaction scheme for the CO pulse into NO flow.

One unique advantage of using <sup>13</sup>CO as a probe is that the N<sub>2</sub> profile can be distinguished from that of <sup>13</sup>CO. Figure 3a shows that the N<sub>2</sub> profile led that of <sup>13</sup>CO<sub>2</sub>, which further led those of <sup>13</sup>CO/O<sub>2</sub>/N<sub>2</sub>O. The lead/lag relationships of the MS profiles of gaseous species and IR profiles of adsorbed species allow elucidation of the sequence of adsorbate and product formation. The source of nitrogen for the formation of N<sub>2</sub> during the <sup>13</sup>CO pulse could be from any of those adsorbed NO species, i.e., Cu<sup>+</sup>(NO), Cu<sup>2+</sup>(NO), and Cu<sup>2+</sup>(NO<sub>3</sub><sup>-</sup>), because N<sub>2</sub> formation corresponded to the rapid decreases in adsorbed NO intensity. The N<sub>2</sub> profile leading that of CO<sub>2</sub> and N<sub>2</sub>O further revealed that (i) decomposition of adsorbed NO and combination of N–N to form N<sub>2</sub> proceeded faster than the reaction of CO with O to produce CO<sub>2</sub> and (ii) N<sub>2</sub> does not have to be formed via N<sub>2</sub>O.

The  $Cu^+(NO)$  could also be replaced by adsorbed CO as indicated by the decrease in  $Cu^+(NO)$  intensity corresponding to the rise of adsorbed CO intensity in Figure 3d

$$Cu^{+}(NO) + CO \leftrightarrow Cu^{+}(CO) + NO$$
 (1)

As the <sup>13</sup>CO pulse traveled through the reactor, the IR intensity of adsorbed <sup>13</sup>CO on Cu<sup>+</sup> sites declined concurrently with gaseous <sup>13</sup>CO, whereas Cu<sup>+</sup>(NO) intensity increased, further substantiating the reversibility of the reaction (eq 1). The rise in the Cu<sup>+</sup>(NO) intensity profile was followed by increases in Cu<sup>2+</sup>(NO) and Cu<sup>2+</sup>(NO<sub>3</sub><sup>-</sup>) as shown in Figure 3b and c. The similar sequence of Cu<sup>+</sup>(NO), Cu<sup>2+</sup>(NO), and Cu<sup>2+</sup>(NO<sub>3</sub><sup>-</sup>) formation, Cu<sup>+</sup>(NO)  $\rightarrow$  Cu<sup>2+</sup>(NO)  $\rightarrow$  Cu<sup>2+</sup>(NO<sub>3</sub><sup>-</sup>), has also been observed during initial exposure of Cu–ZSM-5–127 to a steady-state NO flow at 673 K.<sup>28</sup>

The proposed scheme for the conversion of these NO species, incorporated with their reactions with CO, is illustrated in Figure 4 for explaining the observed dynamic behavior of adsorbates as well as N<sub>2</sub> and O<sub>2</sub> formation during the <sup>13</sup>CO pulse. The basis for a number of the proposed steps and for postulated Cu–O–Cu and Cu–O<sub>2</sub>–Cu sites will be further discussed and substantiated by results of our study<sup>32</sup> and literature.<sup>25,27,33</sup>

During the CO pulse, adsorbed oxygen produced from NO may follow two pathways: one reacting with CO to give  $CO_2$  and the other one following step (iii) and (v) in Figure 4 for oxygen desorption to give  $O_2$ . These two distinct oxygen pathways are manifested by the difference in the maximum point

of CO<sub>2</sub> and O<sub>2</sub> profiles in Figure 3a. Adsorbed oxygen that forms CO<sub>2</sub> may be associated with Cu<sup>2+</sup> and (Cu-O<sub>2</sub>-Cu)<sup>2+</sup> (i.e., Cu dimer sites) because the increase in the CO<sub>2</sub> profile corresponds to the decrease in both Cu<sup>2+</sup>(NO) and Cu<sup>2+</sup>(NO<sub>3</sub><sup>-</sup>) profiles and vice versa. DFT calculation suggests that the reaction of  $(Cu-O_2-Cu)^{2+}$  with CO is highly favorable thermodynamically.<sup>27</sup> Adsorbed oxygen that forms the peak in the O<sub>2</sub> MS profile may be directly resulted from decomposition of Cu<sup>+</sup>(NO) via the catalytic cycle in Figure 4. These two different oxygen pathways may be resolved by use of isotope-labeled NO such as N<sup>18</sup>O as a tracer. As adsorbed CO species are depleted, oxygen from decomposed NO began accumulating on the catalyst surface, converting Cu<sup>+</sup> sites to Cu<sup>2+</sup> sites,<sup>6</sup> building up Cu<sup>2+</sup>(NO<sub>3</sub><sup>-</sup>) species on the surface (step (iv)) and returning to their initial intensities.

**CO** Pulse Studies. Due to the high cost of <sup>13</sup>CO and clear evidence of promotion of N<sub>2</sub> and O<sub>2</sub> formation from the <sup>13</sup>CO pulse, it is convenient to use CO as a probe rather than <sup>13</sup>CO because they have the same chemical reactivity. In addition, the overlapping between CO and N<sub>2</sub> MS profiles did not further complicate interpretation of results since mechanistic steps involved in N<sub>2</sub> formation cannot be differentiated from IR and MS results of the <sup>13</sup>CO pulse.

Figure 2a and b compare IR spectra of adsorbed species during the <sup>13</sup>CO and CO pulse into the steady-state NO flow over Cu–ZSM-5–127 and –83. Cu–ZSM-5–127 gave a higher NO decomposition activity and a more intense IR intensity of adsorbed NO than Cu–ZSM-5–83 prior to the <sup>13</sup>CO (<sup>12</sup>CO) pulse. The use of the <sup>12</sup>CO (i.e., CO) pulse produced Cu<sup>+</sup>(CO)<sub>3</sub> at 2192 cm<sup>-1</sup>, Cu<sup>+</sup>(CO) at 2157 cm<sup>-1</sup>, and CO<sub>ads</sub> at 2108 cm<sup>-1</sup> on Cu–ZSM-5–83. These adsorbed CO species correspond to those adsorbed <sup>13</sup>CO on Cu–ZSM-5–127.

Figure 3a–d and e–h reveal the similarities and differences in MS and IR profiles for Cu–ZSM-5–127 and –83. Although the Cu<sup>+</sup>(CO) intensity on Cu–ZSM-5–83 is about 60% of those on Cu–ZSM-5–127, the amount of O<sub>2</sub> produced from Cu– ZSM-5–127 is about 32 times more than that from Cu–ZSM-5–83. This observation (i) indicates that the presence of Cu<sup>+</sup> site is a requirement for an active NO decomposition catalyst and (ii) suggests that low concentration of Cu sites on underexchanged Cu–ZSM-5 may limit the possibility for the forma-



Figure 5. IR spectra collected during the 1 cm<sup>3</sup> of CO pulse into 5% NO stream over (a) 100 mg auto-reduced Cu-ZSM-5-523 and (b) over silane-treated Cu-ZSM-5-523 at 673 K.

tion of  $(Cu-O-Cu)^{2+}/(Cu-O_2-Cu)^{2+}$  sites to facilitate  $O_2$  desorption.

Figure 5a and b compare IR spectra of adsorbed species during the CO pulse into the steady-state NO flow over Cu-ZSM-5-523 and its silane-treated counterpart. Both catalysts produced nearly the same intensity for adsorbed CO, revealing that Cu sites on both catalysts are accessible to CO adsorption. Silane treatment did not block Cu site on Cu-ZSM-5 for CO adsorption. Thus, the low intensity of Cu<sup>2+</sup>(NO<sub>3</sub><sup>-</sup>) on the silanetreated catalyst can be attributed to the silane blocking the pathway for the formation of  $(Cu-O_2-Cu)^{2+}$ , a postulated site for  $Cu^{2+}(NO_3^{-})$ . The key differences in Cu-ZSM-5-523and its silane-treated catalyst, unveiled in Figure 6a-d and e-h, are the formation of a small amount of CO<sub>2</sub> on the silane-treated catalyst [Figure 6b and (f)] as well as its low NO decomposition activity and low rate of O<sub>2</sub> formation [Figure 6a and e]. Despite its low NO decomposition activity, the silane-treated Cu-ZSM-5-523 catalyst gave almost the same Cu<sup>+</sup>(NO)/Cu<sup>+</sup>(CO) intensity and the same level of intensity increase for Cu<sup>+</sup>(NO) as the Cu-ZSM-5-523 during the CO pulse. Although the silanation did not block Cu<sup>+</sup> sites, it inhibited the NO decomposition and  $O_2$  formation. This observation further (i) confirms that the presence of  $Cu^+$  site is not the only requirement of an active NO decomposition catalyst and (ii) supports that silanation blocks the site for O<sub>2</sub> desorption.

Figure 7 plots the amount of CO<sub>2</sub> produced and IR intensity of Cu<sup>+</sup>(CO) during the CO pulse as well as Cu<sup>2+</sup>(NO<sub>3</sub><sup>-</sup>)/ Cu<sup>+</sup>(NO) during the steady-state NO decomposition on under-, over-exchanged, and silane-treated Cu<sup>-</sup>ZSM-5. The parallel behavior in Cu<sup>2+</sup>(NO<sub>3</sub><sup>-</sup>) and Cu<sup>+</sup>(CO) intensities indicates that all the Cu<sup>2+</sup>(NO<sub>3</sub><sup>-</sup>) species are converted to Cu<sup>+</sup>(CO) during the CO pulse. The increase in amount of CO<sub>2</sub> produced with Cu level suggests the amount of (Cu<sup>-</sup>O<sub>2</sub>-Cu)<sup>2+</sup> sites increased in the order silane-treated Cu–ZSM-5–523 < Cu–ZSM-5– 83 < Cu–ZSM-5–127 < Cu–ZSM-5–523 since the reaction of  $(Cu-O_2-Cu)^{2+}$  with CO to produce CO<sub>2</sub> is highly favorable thermodynamically.<sup>27</sup> Lack of CO<sub>2</sub> formation over silane-treated catalysts suggests that silane may interact with the bridged oxygen of the Cu–O<sub>2</sub>–Cu sites, blocking the reaction with adsorbed CO.

H<sub>2</sub>/CO and H<sub>2</sub> Pulse Studies. Figure 8a shows the IR spectra collected during a 1 cm<sup>3</sup> H<sub>2</sub>/CO (H<sub>2</sub>/CO = 9/1) pulse into 5% NO in He stream over Cu-ZSM-5-127 at 673 K. A trace amount of CO (0.1 cm<sup>3</sup>) was added in the  $H_2$  (0.9 cm<sup>3</sup>) pulse to determine the state of Cu sites during the H<sub>2</sub> pulse. Changes in the adsorbate concentrations and reactor effluent concentrations are plotted with time in Figure 9a-c. The formation of  $Cu^+(CO)$  was accompanied with decreases in  $Cu^{2+}(NO_3^-)$  and  $Cu^{2+}(NO)$ , confirming that the H<sub>2</sub>/CO pulse leads to the reduction of  $Cu^{2+}$  to  $Cu^{+}$ , which chemisorbs CO as  $Cu^{+}(CO)$ . The absence of CO<sub>2</sub> formation indicates that Cu<sup>2+</sup> was reduced to Cu<sup>+</sup> by H<sub>2</sub> instead of CO. The major products resulting from the H<sub>2</sub> pulse are H<sub>2</sub>O and NH<sub>3</sub> as evidenced by the infrared bands of adsorbed OH and NH<sub>3</sub> species [Figures 8a and 9c]. Furthermore, the H<sub>2</sub> pulse caused an increase in the rate of NO decomposition as evidenced by increases in N<sub>2</sub> and O<sub>2</sub> formation. As the H<sub>2</sub> pulse left the reactor, NO adsorbate concentrations gradually returned in the sequence  $Cu^+(NO)$ ,  $Cu^{2+}(NO)$ , and Cu<sup>2+</sup>(NO<sub>3</sub><sup>-</sup>), resembling those observed during the CO pulse. Although Cu<sup>2+</sup>(NO) and Cu<sup>2+</sup>(NO<sub>3</sub><sup>-</sup>) returned to their initial level, Cu<sup>+</sup>(NO) was brought to a slightly higher intensity than its initial level. This interesting behavior was also observed on Cu-ZSM-5-523 and its silane treated counterpart as shown in Figure 10a and b, respectively.

Figure 8b shows the infrared spectra of adsorbed species during the  $H_2$  pulse over Cu–ZSM-5–83. The variations of IR



**Figure 6.** (a) MS intensity profiles of reactor effluent and (b), (c), and (d) IR peak intensity profiles of adsorbates obtained during  $1 \text{ cm}^3$  of CO pulse into 5% NO stream over auto-reduced Cu-ZSM-5-523 at 673 K; (e) MS intensity profiles of reactor effluent and (f), (g), (h) IR peak height profiles of adsorbates obtained during  $1 \text{ cm}^3$  of CO pulse into 5% NO stream over silane-treated Cu-ZSM-5-523 at 673 K.



Figure 7. CO<sub>2</sub> formation and IR intensity.

of adsorbed species on Cu–ZSM-5–83 were not as pronounced as those on Cu–ZSM-5–127 in Figure 8a and Cu–ZSM-5– 523 in Figure 10a. The MS profiles in Figure 9d show the H<sub>2</sub> pulse increased NO conversion and gave two hump responses of N<sub>2</sub>, N<sub>2</sub>O, H<sub>2</sub>O, and NH<sub>3</sub>, indicating the different reactivities of adsorbed N and O on Cu–ZSM-5–83.

H<sub>2</sub> Pulse Studies on Auto-Reduced and Silane-Treated Cu–ZSM-5–523. Figure 10 compares the IR intensity profiles of adsorbed NO species and MS profiles of NO and its decomposition products during the 1 cm<sup>3</sup> of H<sub>2</sub> pulse into 5%

NO in He flow over (a) auto-reduced Cu–ZSM-5–523 and (b) silane-treated Cu–ZSM-5–523 at 673 K. The H<sub>2</sub> pulse produces more N<sub>2</sub> than N<sub>2</sub>O on Cu–ZSM-5–523 while it produces more N<sub>2</sub>O than N<sub>2</sub> on the silane treated catalysts. Since silane treatment inhibits Cu<sup>2+</sup>(NO<sub>3</sub><sup>-</sup>) formation, the effect of the H<sub>2</sub> pulse on the Cu<sup>2+</sup>(NO<sub>3</sub><sup>-</sup>) intensity was not pronounced.

## Discussion

The major effect of the CO and H<sub>2</sub> pulses over underexchanged Cu-ZSM-5-83, over-exchanged Cu-ZSM-5-127, -523, and silane-treated Cu-ZSM-5-523 catalysts is to accelerate the reduction of Cu<sup>2+</sup> to Cu<sup>+</sup>. Although acceleration of the reduction process increases the number of Cu<sup>+</sup> sites for Cu<sup>+</sup>(CO) during the initial stage of the CO pulse and for Cu<sup>+</sup>(NO) for the later stage of the CO pulse, the extent of increase in product formation rate and selectivity depends on the composition of the Cu-ZSM-5 catalysts. Cu-ZSM-5-83 and SiH<sub>4</sub>-treated Cu-ZSM-5-523 exhibit high selectivity for N<sub>2</sub>O formation during NO decomposition. An increase in Cu<sup>+</sup> sites due to the CO/H<sub>2</sub> pulses resulted in a significant increase in the rate of N<sub>2</sub>O formation. In contrast, an increase in Cu<sup>+</sup> sites during the CO/H<sub>2</sub> pulses over Cu-ZSM-5-127 and -523, which are highly selective for N<sub>2</sub> and O<sub>2</sub> formation, led to a marked increase in N<sub>2</sub> and O<sub>2</sub> formation rate. The correlated increase in N2 and N2O formation rates with Cu<sup>+</sup>(CO) and Cu<sup>+</sup>(NO) intensity suggests that Cu<sup>+</sup>(NO) is the active adsorbate responsible for NO decomposition to N<sub>2</sub>O and N<sub>2</sub>. The key questions to be addressed are as follows: (i) Is N2O an intermediate product (or precursor) for the NO decomposition to  $N_2$  and  $O_2$ ? (ii) What is the nature of Cu sites for NO decomposition to N<sub>2</sub>O or N<sub>2</sub>?



**Figure 8.** IR spectra collected during (a) the 1 cm<sup>3</sup> of  $H_2/CO$  (9/1) pulse into 5% NO stream over auto-reduced Cu-ZSM-5-127 at 673 K and (b) 1 cm<sup>3</sup> of  $H_2$  pulse into 5% NO stream over auto-reduced Cu-ZSM-5-83 at 673 K.



**Figure 9.** (a) MS intensity profiles of reactor effluent and (b), (c) IR peak height profiles of adsorbates obtained during 1 cm<sup>3</sup> of H<sub>2</sub>/CO (9/1) pulse into 5% NO stream over auto-reduced Cu-ZSM-5-127 at 673 K; (d) MS intensity profiles of reactor effluent and (e), (f) IR peak intensity profiles of adsorbates obtained during 1 cm<sup>3</sup> of H<sub>2</sub> pulse into 5% NO stream over auto-reduced Cu-ZSM-5-83 at 673 K.

NO decomposition to  $N_2$  and  $O_2$  via the  $Cu^+(NO)_2$  and  $N_2O$  has been proposed as a key pathway in the NO decomposition mechanism.<sup>1,3,6</sup> Nevertheless, results in Figure 3a, 9a, and 10a show that the  $N_2$  profile led that of  $N_2O$  during the <sup>13</sup>CO and  $H_2$  pulses into the NO flow over Cu–ZSM-5–127 and –523, indicating that  $N_2$  formation precedes  $N_2O$  formation.  $N_2$  leading

 $N_2O$  is indicative of NO decomposition to  $N_2$  without involving  $N_2O$  as an intermediate product. Our recent studies have provided IR evidence to show (i) lack of correlation between  $Cu^+(NO)_2$  intensity and  $N_2O$  formation rate<sup>28</sup> and (ii) occurrence of NO and  $N_2O$  decomposition on different type of  $Cu^+$  sites. Theoretical studies have also shown that the formation of  $N_2$ 



**Figure 10.** (a) MS intensity profiles of reactor effluent and (b), (c) IR peak intensity profiles of adsorbates obtained during 1 cm<sup>3</sup> of H<sub>2</sub> pulse into 5% NO stream over auto-reduced Cu-ZSM-5-523 at 673 K; (d) MS intensity profiles of reactor effluent and (e). (f) IR peak height profiles of adsorbates obtained during 1 cm<sup>3</sup> of H<sub>2</sub> pulse into 5% NO stream over silane-treated Cu-ZSM-5-523 at 673 K.

via  $Cu^+(NO)_2/N_2O$  is thermodynamically unfavorable at 773  $K^9$  and found no evidence for the direct decomposition of  $Cu^+(NO)_2$  to  $N_2/N_2O$  and  $O_2$ .<sup>33</sup>

An alternative pathway for explaining N<sub>2</sub> formation from NO is shown in Figure 4 which suggests that the reaction pathway for the decomposition of Cu<sup>+</sup>(NO) to N<sub>2</sub> and N<sub>2</sub>O. Step (i) suggests that two neighboring Cu<sup>+</sup>(NO) species decompose to N<sub>2</sub> and (CuO<sub>2</sub>Cu)<sup>2+</sup>; step (ii) suggests a Eley–Rideal mechanism for the formation of Cu<sup>2+</sup>O<sup>-</sup> and N<sub>2</sub>O. The former would focus on the Cu<sup>+</sup> dimmer sites; the latter on the isolated Cu<sup>+</sup> sites. Species such as hyponitrite have been proposed as intermediates for conversion of NO to N<sub>2</sub>O.<sup>34</sup> Regardless of various proposed intermediates, the facile formation of N<sub>2</sub> as evidenced by the N<sub>2</sub> profile leading those of CO<sub>2</sub>/N<sub>2</sub>O/O<sub>2</sub> in Figure 3a suggests that these adsorbed NO species are highly active on the catalyst surface, facilitating N–N bond formation. N<sub>2</sub>O formation from Cu<sup>+</sup>(NO) leaves adsorbed O, converting Cu<sup>+</sup> to Cu<sup>2+,5</sup> Cu<sup>2+</sup> could adsorb NO as Cu<sup>2+</sup>(O<sup>-</sup>)NO.

Cu $-O_2$ -Cu is a postulated species<sup>5,27,31-33</sup> which is incorporated in the reaction scheme (Figure 4) to distinguish between the sites for catalytic cycles of NO decomposition to N<sub>2</sub> and O<sub>2</sub> as well as to N<sub>2</sub>O and O<sub>2</sub>. Step (iv) suggests (Cu $-O_2$ -Cu)<sup>2+</sup> could either desorb its oxygen as shown in step (iii) or react with NO to form Cu<sup>2+</sup>(NO<sub>3</sub><sup>-</sup>) in step (iv). Bridging NO<sub>3</sub>- on the Cu $-O_2$ -Cu sites can be further decomposed to N<sub>2</sub> and O<sub>2</sub> (step (v)) as evidenced from results of temperature programmed study.<sup>28</sup> Density functional theory calculation further supports that [CuO<sub>2</sub>Cu]<sup>2+</sup> and [CuOCu]<sup>2+</sup> are stable,<sup>25,27,33</sup> suggesting their involvement in interconversion of Cu<sup>+</sup> and Cu<sup>2+</sup> to facilitate the redox cycle of NO and N<sub>2</sub>O decomposition.

Both silane-treated Cu–ZSM-5–127/–523 and underexchanged Cu–ZSM-5–83 exhibit very similar catalytic properties: (i) activity for decomposition of NO to N<sub>2</sub>O instead of N<sub>2</sub>, (ii) low IR intensity for Cu<sup>2+</sup>(NO<sub>3</sub><sup>-</sup>) during the reaction, (iii) low activity for oxygen formation, (iv) and low activity for CO<sub>2</sub> formation during CO pulses. These similarities may be attributed to their lack of the Cu–O–Cu dimer sites. Silanation of the over-exchanged Cu–ZSM-5–523 may disrupt the Cu-O-Cu sites, leading to isolation of Cu<sup>+</sup> sites. In situ infrared study showed that silane reacts with the OH groups on the surface of Cu-ZSM-5 without interacting with Cu<sup>+</sup> sites which were covered with chemisorbed CO during silanation of Cu-ZSM-5.29 Although the chemisorptive properties of Cu<sup>+</sup> remain unaltered as evidenced by the dynamic behavior of Cu<sup>+</sup>(CO) and Cu<sup>+</sup>(NO) shown in Figures 6 and 10, this type of Cu<sup>+</sup> on sliane-treated Cu-ZSM-5-523 (i) loses its activity to catalyze N<sub>2</sub> formation, (ii) shows low activity for catalyzing O<sub>2</sub> formation, and (iii) inhibits bridged Cu<sup>2+</sup>(NO<sub>3</sub><sup>-</sup>) and CO<sub>2</sub> formation. Disruption of these Cu dimer sites would make desorption of oxygen from Cu<sup>2+</sup>O<sup>2-</sup> extremely difficult due to the high positive Gibbs free energy for  $CuO_2 \rightarrow Cu + O_2$ .<sup>9</sup> Low rate of oxygen desorption would cause accumulation of oxygen species, limiting NO dissociation and allowing combination of adsorbed NO and N to produce N<sub>2</sub>O.

### Conclusions

Cu<sup>+</sup>(NO) is the active adsorbate responsible for NO decomposition to N<sub>2</sub>O and O<sub>2</sub> as well as to N<sub>2</sub> and O<sub>2</sub>. Pulsing CO and H<sub>2</sub> into the NO flow facilitates the reduction of Cu<sup>2+</sup> to Cu<sup>+</sup>. Pulsing these reductants caused an increase in Cu<sup>+</sup>(NO) concentration as well as N<sub>2</sub>O formation rate over underexchanged Cu–ZSM-5–83/silane-treated Cu–ZSM-5–523. In contrast, pulsing CO and H<sub>2</sub> into the NO flow on overexchanged Cu–ZSM-5–127 and –523 enhances the formation rates of both N<sub>2</sub> and O<sub>2</sub>. The difference in the product formation among these catalysts may be attributed to the local environment of Cu sites. The low activity of under-exchanged Cu–ZSM-5–523 for the decomposition of NO to N<sub>2</sub> can be explained by their lack of the Cu–O–Cu dimer sites.

In contrast to the widely postulated steps involved in formation of  $N_2$  via  $N_2O$ , the profiles of  $N_2$ ,  $N_2O$ , and  $O_2$  as well as IR observable adsorbates clearly indicates that  $N_2$  formation precedes  $N_2O$  formation on over-exchanged Cu–ZSM-5 catalysts at 673 K.  $N_2$  can be formed without involvement of  $N_2O$  during NO decomposition.

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