Dynamics of NO and N₂O Decomposition over Cu–ZSM-5 under Transient Reducing and Oxidizing Conditions

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N₂O and NO decomposition pathways on Cu-ZSM-5 have been investigated by monitoring the adsorbate dynamics and changes in reactant and product concentrations using infrared spectroscopy (IR) and mass spectrometry (MS) under transient reducing and oxidizing conditions. Transient reducing and oxidizing conditions were produced by the H₂, CO, and O₂ pulses into either N₂O or NO streams. IR and MS studies under the transient conditions revealed that adsorbed O produced from N₂O exhibited different reactivity and dynamics from the adsorbed O produced during NO decomposition. The differences in reactivity and dynamics of the adsorbed O were evidenced by the fact that (i) adsorbed O from N₂O interacted with CO/H₂ to produce two humps in the H₂O and O₂ concentration profiles; adsorbed O from NO reacted with CO/H₂ that led to only one hump in the H₂O and O₂ concentration profile, and (ii) addition of the O₂ pulse led to reaction of O₂ with adsorbed O from NO, resulting in oxidation of Cu^+ in $Cu^+(NO)$ to Cu^{2+} in $Cu^{2+}(NO_3^-)$; addition of O₂ did not lead to any reaction with adsorbed O from N₂O decomposition. N₂O decomposition is proposed to proceed via Cu^+ -ON₂, $Cu^{2+}O^-$, and $Cu^{2+}O^-$ -ON₂ with Cu^+ -ON₂ serving as a precursor for N₂ formation and Cu²⁺O⁻ as a precursor for O₂ formation. NO decomposition proceeds via $Cu^+(NO)$, $Cu^{2+}O^-$, and Cu²⁺(NO₃) with Cu⁺(NO) serving as a precursor for NO dissociation. Cu^+ in $Cu^+(NO)$ is different from that of Cu^+ in Cu^+-ON_2 . The former may be associated with $Al(OH)_{4}^{-}$ of the zeolite, the latter with Si(OH) $_{4}^{-}$. © 2000 Academic Press

Key Words: N₂O decomposition; NO decomposition; Cu–ZSM-5; *in situ* IR; temperature-programmed reaction; step switch; pulse switch; adsorbate dynamics; adsorbate reactivity; transient reducing conditions; transient oxidizing conditions; reaction mechanism; adsorbed O; active sites; site environment.

1. INTRODUCTION

Catalytic nitric oxide (NO) decomposition has been a subject of extensive studies due to its promise for the effective control of NO_x emission (1–3). The attention has

been extended to N_2O decomposition due to the fact that nitrous oxide (N_2O) is not only a by-product of NO decomposition and reduction but also an effective greenhouse gas and ozone-destructing reagent (4–16). Cu–ZSM-5 has been known to exhibit the highest activity for NO decomposition and also high N_2O decomposition activity (17–30). Despite its effectiveness for the NO and N_2O decomposition reaction, Cu–ZSM-5 is not resistant to oxidants, water, or sulfur (27, 28). In the present study, we have focused on investigating the mechanisms of NO and N_2O decomposition on Cu–ZSM-5 so that the knowledge of active adsorbates and sites can be utilized to design and synthesize novel catalysts that would exhibit not only high activity but also deactivation resistance.

Extensive infrared (IR) studies have reported that Cu⁺(NO) (1814 cm⁻¹), Cu²⁺(NO) (1910 cm⁻¹), Cu²⁺O⁻(NO) (1890–1905 cm⁻¹), NO⁺ (2123 cm⁻¹), and bridging and chelating Cu²⁺(NO₃⁻) (1623, 1610, and 1565 cm⁻¹) are the major adsorbates observed during NO decomposition at 77–673 K (21–32). Our recent transient, site-poisoning, and site-promotion studies have revealed that (i) NO⁺ is a spectator, (ii) N₂ and O₂ formation proceeds through separate rate-limiting steps, and (iii) inhibition of adsorbed O migration is the major deactivation pathway for O₂ formation (32). These studies further suggested that Cu⁺ is the active site and that Cu⁺(NO) and Cu²⁺(NO₃⁻) are the active adsorbates that participate in the catalytic cycle of NO decomposition.

In contrast to extensive studies of NO decomposition, very few *in situ* IR studies on N₂O decomposition over Cu–ZSM-5 have been reported. The N₂O decomposition mechanism and its relation to NO decomposition have not been established unambiguously. The current study investigates the mechanisms of both NO and N₂O decomposition over Cu–ZSM-5 by probing the adsorbate reactivity and dynamics as well as the active sites with transient pulsing of H₂, O₂, and CO into the reaction systems. Since both NO and N₂O decomposition reactions are redox reactions that may involve both Cu⁺ and Cu²⁺ sites on Cu–ZSM-5, probing the reactions with a reductant (i.e., H₂ or CO) could lead to the reduction of Cu²⁺ to Cu⁺; probing with



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an oxidant (O₂) could result in the oxidation of Cu⁺ to Cu²⁺, creating a perturbation in the adsorbate concentration and in the product formation processes. In addition, the reductants and oxidant are also expected to react with some of the adsorbates. Changes in adsorbate as well as reactant/product concentrations were monitored by IR and mass spectrometry (MS), respectively. This study revealed the nature of catalytic cycles for N₂O and NO decomposition, distinguished the adsorbates and sites that are active for the N₂O and NO decomposition reactions, and examined the role of oxidizing and reducing reagents in the reactions.

2. EXPERIMENTAL

2.1. Catalyst Preparation

Cu–ZSM-5-523, with a 523% copper exchange, was prepared by the repeated ion exchange of Cu–ZSM-5-83 (83% copper exchange), which was prepared by Johnson Matthey and supplied by the Catalyst bank of Sandia National Laboratories. The percentage copper exchange is defined as the molar ratio of the amount of Cu to that of Al multiplied by 2 [% Cu exchange = 2 (mol of Cu/mol of Al)] (27). Cu–ZSM-5-83 was added to a 0.004 M copper acetate solution at a pH of 7 and stirred for 24 h. The solution was filtered and the solid deposited on the filter paper was washed with distilled water and dried in air at 373 K for 24 h. Inductively coupled plasma (ICP) emission spectroscopy (Galbraith Laboratories, Knoxville, TN) determined Si/Al to be 25 and Cu/Al to be 2.615 in Cu–ZSM-5-523.

2.2. Reactor System

The catalyst, pressed in the form of a self-supporting thin pellet of 15-25 mg, was placed in the in situ IR reactor cell directly in the path of the IR beam (33). Three additional catalyst pellets were crushed into flakes and placed in the reactor outlet that was in the close vicinity of the selfsupporting pellet. The total amount of catalyst placed in the IR cell was 105-110 mg. A Magna (Nicolet Instruments) 550 Fourier transform IR spectrometer (FTIR) recorded the IR spectra and a Pfeiffer Prisma QMG 200 (Pfeiffer Vacuum Technology) MS recorded the changes in the concentration of the reactants and products during the study. No spectra below 1400 cm⁻¹ are presented in this study because below this value a low signal-to-noise ratio was observed; additionally, the use of CaF2 rods and windows cut off IR transmission below 1000 cm^{-1} . The spectral change in the 900 to 1000-cm⁻¹ range associated with extralattic oxygen can only be observed with a very thin Cu-ZSM-5 disk diluted with KBr. The possible complication of KBr and the need to use costly H₂O-resistant and high-temperature IR transmission windows precluded investigation of dynamic behavior of the extralattic oxygen.

2.3. Temperature-Programmed Reaction Studies

Temperature-programmed reaction (TPR) studies involved the exposure of Cu–ZSM-5-523 to a 5% NO in He stream (NO = 2.5 cm^3 /min and He = 47.5 cm^3 /min) at 373 K followed by heating the reactor from 373 to 743 K at a heating rate of 10 K/min. The Cu–ZSM-5-523 catalyst, active for pulse NO and N₂O decomposition, was also exposed to a 5% N₂O in He stream (N₂O = 2.5 cm^3 /min and He = 47.5 cm^3 /min) at 333 K and was subjected to a temperature increase (TPR) from 333 to 773 K at 10 K/min. The FTIR and MS monitored the changes in the adsorbate and gaseous effluent concentration during the TPR studies, respectively.

Prior to the TPR studies, IR spectra of each of the catalyst samples were collected in flowing He at each specific temperature. These spectra were denoted as the background spectra. The background spectrum at the specific temperature was subtracted from the IR spectrum collected at the corresponding temperature during the TPR studies. The resulting IR spectra, shown in this study, hence do not have any contribution from the characteristic vibrations of the catalyst sample or from background spectrum changing with temperature. The background spectra and the spectra obtained during the TPR studies were taken by co-adding 32 scans, which were collected in 4 s. The spectrum at each temperature during the TPR was collected within a 1 K variation in the temperature. Hence, the co-added spectrum collected during the TPR represents the average change in adsorbate intensity during a 1 K increase in temperature.

2.4. Transient Reduction and Oxidation Pulse Studies

One cubic centimeter (1 cm^3) of H₂, O₂, and CO was separately pulsed with a 6-port gas chromatograph (GC) injection valve into a steady-state 5% NO in He flow over Cu–ZSM-5-523 at 673 and 723 K. Introduction of the H₂ and CO (well-known reductants) pulses allowed Cu-ZSM-5-523 to be exposed to a reducing environment for a short period of time while the O₂ pulse exposed the catalyst to an oxidizing environment for a short period of time under NO reaction conditions. The H₂, O₂, and CO pulses were also injected into a 5% N₂O in He flow over Cu-ZSM-5-523 at 673 and 723 K. The H₂, O₂, and CO pulse into NO and N₂O studies involved the introduction of three separate 1 cm³ of $H_2/O_2/CO$ pulses into the 5% NO in He and 5% N₂O in He streams at 673 K over Cu-ZSM-5-523. Each of the three pulses resulted in similar changes in the adsorbate intensity and MS profiles of gaseous reactants and products, indicating good reproducibility. The IR and MS monitored the changes in the adsorbate and reactor effluent concentrations during the H₂, O₂, and CO pulse study under NO and N₂O reaction conditions, respectively. Along with the IR spectra and MS profiles, the variation in the peak intensity (peak height) of the adsorbate species was also tabulated and displayed with respect to time.

2.5. NO/N₂O Co-Adsorption and Reaction Studies

 NO/N_2O co-adsorption and reaction studies were carried out by pulsing 1 cm³ of N_2O into 5% NO over autoreduced Cu–ZSM-5-523 at 673 and 723 K and pulsing 1 cm³ of NO into 5% N_2O over Cu–ZSM-5-523 at 323, 673, and 723 K. Introducing a small amount of N_2O into NO flow and a small quantity of NO into N_2O flow is expected to result in the perturbation of the sites and the adsorbates present on the sites. Monitoring the adsorbate dynamics and concentration profiles of reactants and products during these pulse studies would shed light on the role of N_2O in the NO decomposition pathway and also aid in determining whether NO and N_2O decomposition on Cu–ZSM-5 occur on the same sites.

2.6. Fragmentation of NO, N₂, CO, CO₂, N₂O, and NO₂

The MS profiles of the gaseous species were distinguished from each other by the m/e ratios: m/e = 30 for NO, m/e =28 for N₂, m/e = 32 for O₂, m/e = 44 for N₂O, m/e = 46 for NO₂, m/e = 12 for CO, m/e = 22 for CO₂, m/e = 18 for H₂O, and m/e = 17 for NH₃. The contributions of the N₂O fragment to NO (m/e = 30) and N₂ (m/e = 28) profiles, of NO₂ to NO (m/e = 30), and of H₂O (m/e = 18) to NH₃ (m/e = 17) were accounted for in the present study. Calibration factors for each gaseous species, except H₂O and NH₃, were obtained by pulsing known amounts of the gases into the MS. The calculated calibration factors were utilized for converting the MS intensities of the reactants and products to their respective molar rates.

3. RESULTS

3.1. NO and N₂O TPR

Figure 1 shows the IR spectra and the change in the concentrations of the reactor effluent obtained during the 5% NO in He TPR from 373 to 773 K (10 K/min) over Cu-ZSM-5-523. Flowing 5% NO at 373 K produced adsorbed N₂ at $2158\,cm^{-1},$ $Cu^{Z+}(NO)$ at 1900 $cm^{-1},$ bridging $Cu^{2+}(NO_3^-)$ at 1623 and 1612 cm⁻¹, and chelating $Cu^{2+}(NO_3^-)$ at 1567 cm⁻¹ as shown in Fig. 1a. Increase in temperature from 373 to 743 K led to changes in both the adsorbate and reactor effluent concentrations: NO decomposition to N_2O and O_2 commenced at 473 K (Fig. 1b) where Cu²⁺(NO) showed a substantial drop in its IR intensity, $Cu^{2+}(NO_3^-)$ exhibited a slight decrease in its intensity, and $Cu^+(NO)$ emerged. The Cu⁺(NO) intensity paralleled the rate of N₂O formation with the depletion of $Cu^+(NO)$ coinciding with that of N₂O, suggesting that NO adsorbed on Cu⁺ may serve as a precursor for N₂O formation. Selective NO decomposition to N₂ and O₂ occurred at 753 K where no IR observable



FIG. 1. IR spectra and MS profiles collected during the temperatureprogrammed reaction (TPR) over Cu–ZSM-5-523 in a 5% NO in He stream from 373 to 753 K.

adsorbates were detected, indicating that the rate of desorption of adsorbates and the rate of product formation from adsorbates are significantly higher than the adsorbate formation rate.

The IR spectra and changes in the concentration of the reactor effluent obtained during the 5% N₂O in He TPR over Cu-ZSM-5-523 from 333 to 773 K are shown in Fig. 2. Exposure of Cu-ZSM-5-523 to 5% N₂O at 333 K led to the appearance of prominent IR bands at 2287 and 2240 ${
m cm}^{-1}$ and a weak band at 1623 cm^{-1} along with the gaseous N₂O bands. The assignment of the adsorbate N₂O bands in the 2200- to 2300-cm⁻¹ region has not been established unambiguously on Cu-ZSM-5 while the 1623-cm⁻¹ band was previously assigned to the bridging $Cu^{2+}(NO_3^-)$ species based on the NO adsorption studies on Cu-ZSM-5 (31, 32). The present study attempts to assign bands in the 2200 to 2300-cm⁻¹ region based on the obervations reported during N₂O adsorption studies on transition metal zeolites, metal oxides, and metals. The high electron density at the terminal N and O atoms allows N₂O to bond to the zeolites,



FIG. 2. IR spectra and MS profiles collected during the temperature-programmed reaction (TPR) over Cu–ZSM-5-523 in a 5% $\rm N_2O$ in He stream from 333 to 773 K.

metal oxides, and metals via either the N or O end. The band at 2224 cm⁻¹ corresponds to the N–N vibration; the 1285-cm⁻¹ band signifies the N–O vibration for N₂O in the gas phase (34). N₂O adsorbed on ZnO and ZrO₂ via the O end, giving bands at 2237-2242 and 1233-1255 cm⁻¹ (34-39), on the α -chromia surface via N, giving bands at 2305 and 1339 cm^{-1} , and via O, leading to bands at 2238 and 1237 cm⁻¹ (40), and on NaA, CoA, NiA, and CuA via N, producing bands at 2258–2272 and 1282–1304 cm^{-1} , and via O, giving bands at 2223–2250 and 1240–1282 cm⁻¹ (41). It has also been reported that N₂O bonds to the Cu(I) cations on CuA via N, producing bands at 2230-2250 and 1289 cm⁻¹, and via O, leading to bands at 2223 and 1282 cm^{-1} (41). Hence, as a general rule, bands observed in the 2224-, to 2260 and 1200- to 1285-cm⁻¹ (lower than 1285 cm⁻¹) regions have been assigned to N₂O adsorbed via O while the bands in the 2224- to 2300 and 1285- to 1350-cm⁻¹ regions have been assigned to N₂O adsorbed via N. Based on these studies, the band observed in the present study at 2287 cm^{-1} is assigned to the N-bound N_2O on Cu^+ (Cu^+ – N_2O) and the 2240-cm⁻¹ band to the O-bound N_2O on Cu^+ (Cu^+ - ON_2). The corresponding N–O vibrations in the lower frequency region of 1235–1310 cm⁻¹ could not be observed in the present study as they were overlapped by the presence of gaseous N_2O bands in the same region and were low in intensity when compared to the N–N vibrations.

A temperature increase from 333 to 423 K depleted Cu⁺-ON₂ at 2240 cm⁻¹ and decreased Cu⁺-N₂O species at 2287 cm⁻¹ and led to an increase in the bridging $Cu^{2+}(NO_3^{-})$ species at 1623 cm⁻¹ while there was no change in the concentration of the gaseous reactants and products. An additional temperature increase led to the eventual depletion of Cu^+ – N_2O at 573 K, the formation of adsorbed N_2 at 473 K and its depletion at 623 K, start of N₂O decomposition and N₂ formation at 573 K, and start of O₂ formation at 643 K. High rates of N₂O decomposition were achieved at 773 K where no IR observable adsorbates were detected. The N₂O IR-TPR results have, for the first time, showed that N₂O adsorbs on Cu-ZSM-5 via both N and O as Cu⁺-N₂O and Cu^+ - ON_2 as well as a bridging $Cu^{2+}(NO_3^-)$ species at 333 K and have also confirmed that N₂O starts to decompose to N₂ and O₂ at 573 K and reaches a conversion of 100% at 773 K over Cu-ZSM-5.

The TPR results show that Cu–ZSM-5-523 exhibits a higher decomposition activity for N₂O than NO; N₂O decomposition during TPR produces greater amounts of N₂ and O₂ compared to NO decomposition in the same temperature range; O₂ desorption (523 K) starts at a lower temperature during NO decomposition than that of N₂O (643 K). The different O₂ desorption temperatures suggest that different forms of adsorbed O were produced from NO and N₂O adsorption and surface reactions.

3.2. H₂ Pulse Studies

Figures 3 and 4 show the IR spectra, MS profiles of gaseous reactants and products, and adsorbate peak intensity profiles collected during the first 1 cm³ of the H₂ pulse into a 5% NO in He stream over Cu-ZSM-5-523 at 673 K. It should be noted that the IR spectra taken during the pulse were collected every 3.6 s and the IR intensity profiles of the adsorbates during the entire duration of the pulse are plotted in Fig. 4. The spectra shown in Fig. 3 do not represent all the collected spectra but illustrate the selected few that show the prominent changes during the H₂ pulse switch. Exposure of Cu-ZSM-5-523 to 5% NO at 673 K, prior to the H₂ pulse, led to the formation of bridging and chelating $Cu^{2+}(NO_3^-)$ at 1623 and 1567 cm⁻¹, $Cu^+(NO)$ at 1814 cm⁻¹, Cu²⁺(NO) at 1907 cm⁻¹, and adsorbed NO⁺ at 2123 cm⁻¹ as shown in Fig. 3 as well as produced a 8.7% NO conversion as illustrated in Table 1. Introduction of 1 cm^3 of H₂ (a) decreased Cu⁺(NO), Cu²⁺(NO), bridging and chelating $Cu^{2+}(NO_3^{-})$, and adsorbed NO^+ , (b) increased NO conversion and N₂, O₂, and N₂O formation, and (c) led to the formation of H_2O (gas) at 3505 cm⁻¹ (42) and



FIG. 3. IR spectra taken during the first 1 cm³ of H₂ pulse into a 5% NO stream over Cu–ZSM-5-523 at 673 K.

adsorbed NH₃ species at 3360. The adsorbed NH₃ species at 3360 can be assigned to NH₃ bound to Cu, based on the IR spectra of NH₃ species bound to various Cu, Co, Pt, Mn, and Ni complexes, which give bands in the 3327- to 3345-cm⁻¹ range (42). Figure 4 shows that the initial decrease of all the NO adsorbate species and gaseous NO was followed by an increase in Cu⁺(NO) and N₂, N₂O, and O₂ formation during the continued decrease of Cu²⁺(NO), bridging Cu²⁺(NO₃⁻), and NO⁺. The increase in Cu⁺(NO), to an intensity higher than that prior to the H₂ pulse, accompanied with a decrease in the intensity of the Cu²⁺ species (Cu²⁺(NO) and Cu²⁺(NO₃⁻)) reflects an increase in the number of Cu⁺ sites that may be promoting NO conversion and giving high rates of N₂, O₂, and N₂O formation. The adsorbate and reactant/product concentrations returned to

TABLE 1

NO and N₂O Conversion Prior to 1 cm³ of H₂, CO, and O₂ Pulses into 5% NO and 5% N₂O in He Flow over Autoreduced Cu–ZSM-5-523 (W/F = 0.12 g s cm⁻³) at 673 K

	% Conversion		
	H_2	СО	O ₂
NO	8.7	12.8	8.7
N_2O	9.6	8.9	7.9

their respective original intensities as the pulsed H₂ exited the reactor cell.

The IR spectra in Fig. 3 and IR peak intensity profiles in Fig. 4d indicate a sharp increase and decrease of H_2O (gas) while the MS profiles (Fig. 4b) showed the gaseous H_2O lagging behind the rest of the gaseous species significantly. The lag in the MS profile could be a result of the delay of H_2O (gas) in entering the MS analysis chamber from the IR cell due to adsorption/desorption of H_2O on the walls of the reactor system lines entering the MS.

The role of H_2 in NO decomposition can be summarized as causing the reduction of $Cu^{2+}(NO_3^-)$ and $Cu^{2+}(NO)$ to Cu^+ , NH_3 , and H_2O , promotion of O_2 desorption and formation, and an increase in the number of Cu sites, leading to increases in the NO decomposition rate. The H_2 pulse results also reveal that the Cu^{2+} for $Cu^{2+}(NO)$ is different from that of $Cu^{2+}(NO_3^-)$ as they are affected to a different extent by H_2 addition. Cu^+ –NO parallels N_2O formation similar to that observed during NO TPR.

The first 1 cm³ of H₂ pulse into a 5% N₂O stream over Cu–ZSM-5-523 led to changes in the IR intensities of the adsorbate species as well as MS profiles of the gaseous reactants and products as shown in Figs. 5 and 6. Prior to the H₂ pulse, the 5% N₂O flow over Cu–ZSM-5-523 produced gaseous N₂O at 2235 cm⁻¹ and bridging and chelating Cu²⁺(NO₃⁻) at 1622 and 1560 cm⁻¹ as shown in Fig. 5 as well as led to a 9.6% N₂O conversion (Table 1). Pulsing 1 cm³ of H₂ led to the complete depletion of bridging and chelating

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FIG. 4. MS intensity profiles of reactor effluent and peak intensity profiles of adsorbate species collected during the first 1 cm³ of H_2 pulse into a 5% NO stream over Cu–ZSM-5-523 at 673 K.

 $Cu^{2+}(NO_3^-)$, the formation of adsorbed OH species at 3629 and 3583 cm⁻¹ (43, 44), an increase in NO conversion and N_2 formation, and a decrease in O₂ formation. The adsorbed OH species (3629 and 3583 cm⁻¹) reached their maxima at two separate instances during the H₂ pulse as shown in Fig. 6e. Gaseous H₂O (Fig. 6b) also exhibited two humps in the concentration profiles similar to the adsorbed OH species. Careful examination of lead/lag relationships between $Cu^{2+}(NO_{3}^{-})$, NO, O₂, and OH profiles suggests that the first OH peak in Fig. 6e may be due to the reaction of $Cu^{2+}(NO_3^-)$ with adsorbed hydrogen and the second due to the reaction of O produced from N₂O adsorption and O present on ZSM-5 with adsorbed H₂. The presence of H₂ inhibits the recombination of the adsorbed O species to form O_2 as seen by the decrease in O_2 formation in Fig. 6a. The adsorbed O species instead react with H to adsorbed OH species. The formation of adsorbed OH also prevents the re-oxidation of Cu^+ to Cu^{2+} sites, inhibiting the formation of the bridging and chelating $Cu^{2+}(NO_3^{-})$ species. The observation of OH is a manifestation of the O⁻ ion, which has been found to involve homolytic splitting of hydrogen (45) and partial oxidation of methane (46). As the pulsed H₂ exited the reactor, the adsorbed OH species completely disappeared while the bridging and chelating $Cu^{2+}(NO_3^-)$ and all the gaseous reactants/products returned to their original concentrations.

The most obvious role of H_2 in both NO and N_2O decomposition is the reduction of Cu^{2+} to Cu^+ and promotion of N_2 formation. The distinction in the effect of H_2 on the product formation is the difference in the reactivity of adsorbed oxygen produced from these two reactions. Oxygen from NO tends to undergo desorption to produce gaseous O_2 while oxygen from N_2O tends to react with adsorbed H_2 to produce H_2O .

3.3. O₂ Pulse Studies

Figures 7 and 8 show the IR spectra, change in concentration of reactants and products, and variation in adsorbate peak intensity collected during the first 1 cm³ of O₂ pulse into a 5% NO in He stream over Cu-ZSM-5-523 at 673 K. The adsorbate spectra prior to the O₂ pulse were essentially identical to those prior to the H_2 pulse as shown in Fig. 3. The O_2 pulse (a) decreased $Cu^+(NO)$ and N_2O formation, (b) increased bridging and chelating $Cu^{2+}(NO_3^{-})$, NO conversion, and NO₂ formation, and (c) did not affect $Cu^{2+}(NO)$, N₂ formation, and NO⁺ as shown in Figs. 7 and 8. These observations can be explained by oxidation of adsorbates and surface from Cu^+ to Cu^{2+} due to addition of O_2 . A decrease in $Cu^+(NO)$ with N₂O further supports the postulation that $Cu^+(NO)$ could serve as a precursor for N_2O formation. Furthermore, the mirror image intensity profiles of $Cu^+(NO)$ and bridging and chelating $Cu^{2+}(NO_3^-)$ reflect the oxidation of Cu⁺ sites to Cu²⁺, leading to the conversion of part of $Cu^+(NO)$ to bridging and chelating $Cu^{2+}(NO_3^-)$ during O₂ addition. The decrease in NO concentration and increase of NO_2 is a result of the reaction of NO with O_2 to produce NO₂ as well as a consequence of the co-adsorption of NO and O_2 to produce the $Cu^{2+}(NO_3^{-})$ species.

In contrast to the pronounced effect of O_2 on NO decomposition, the O_2 pulse into 5% N_2O at 673 K did not cause any variation in adsorbate and product concentration. The lack of changes in the adsorbate and product concentration can be attributed to the lack of interaction between the adsorbed O from O_2 and the adsorbed O species produced from N_2O decomposition.

3.4. CO Pulse Studies

Figures 9 and 10 show the IR spectra, MS profiles of reactants and products, and the variation of adsorbate peak intensities with time collected during the first 1 cm³ of CO pulse into a 5% NO in He stream over Cu–ZSM-5-523 at 673 K. The CO pulse into 5% NO produced changes in both the adsorbate and reactor effluent concentrations. CO entry



FIG. 5. IR spectra taken during the first 1 cm³ of H₂ pulse into a 5% N₂O stream over Cu–ZSM-5-523 at 673 K.

depleted bridging and chelating $Cu^{2+}(NO_3^-)$, increased NO conversion and N₂, O₂, and N₂O formation, and led to the formation of CO₂ at 2345 cm⁻¹, Cu⁺(CO) at 2157 cm⁻¹, $Cu^+(CO)_3$ at 2192 cm⁻¹, and adsorbed CO at 2108 cm⁻¹ (20, 28, 32). Cu⁺(NO) initially decreased upon CO addition but increased to an intensity higher than that prior to CO pulse during the continued decrease of bridging and chelating $Cu^{2+}(NO_3^{-})$. The formation of $Cu^+(CO)$ and $Cu^+(CO)_3$ and depletion of $Cu^{2+}(NO_3^-)$ indicates the reduction of Cu^{2+} to Cu^+ ; depletion of $Cu^{2+}(NO_3^-)$ and $Cu^+(NO)$ upon CO entry reflects the reaction of adsorbed (NO_3^-) species with CO; an increase in NO conversion and O₂ formation in the presence of $Cu^+(CO)$ confirms that Cu^+ plays a vital role in NO decomposition. The major roles of CO are to reduce Cu²⁺ to Cu⁺, increasing NO decomposition, to react with adsorbed nitrato species on Cu^{2+} , and to adsorb as $Cu^+(CO)$ and $Cu^+(CO)_3$.

Figures 11 and 12 show the IR spectra, MS profiles of reactants and products, and the variation of adsorbate peak intensities with time collected during the first 1 cm³ of CO pulse into a 5% N₂O in He stream over Cu–ZSM-5-523 at 673 K. Pulsing of 1 cm³ of CO decreased bridging and chelating Cu²⁺(NO₃⁻), increased N₂O conversion and N₂ and O₂ formation, and produced CO₂ (gas) at 2345 cm⁻¹, Cu⁺(CO) at 2157 cm⁻¹, and adsorbed CO at 2140 cm⁻¹. The decrease in bridging and chelating nitrato species combined with the formation of Cu⁺(CO) and promotion of N₂ and O₂ formation suggest that the introduction of CO reduced

the Cu^{2+} sites to Cu^+ , which promotes the N₂O decomposition to N₂ and O₂. The O₂, produced during the CO pulse (Fig. 12a), exhibited two humps in the concentration profiles, suggesting that the CO pulse promoted the desorption of two different types of adsorbed O species.

The CO pulse onto Cu–ZSM-5-523 at 673 K promotes N_2 and CO₂ formation during the NO and N_2O decomposition reactions. CO addition also promoted O_2 formation with the desorption of two kinds of adsorbed O species during N_2O decomposition and one type of O_2 during NO decomposition. The bridging and chelating Cu²⁺(NO₃⁻), produced during NO and N_2O decomposition reactions, decreased upon pulsing of CO, indicating the reduction of the Cu²⁺ sites to Cu⁺, which adsorbed CO similarly as Cu⁺(CO) and CO_{ads} under both NO and N_2O decomposition conditions as evidenced in Figs. 9 and 11.

3.5. NO/N₂O Adsorption

Figure 13 shows the IR spectra, MS profiles of the reactants and products, and the variation of adsorbates peak intensities with time collected during a 1 cm³ of N₂O pulse into a 5% NO stream over Cu–ZSM-5-523 at 673 K. An N₂O pulse into 5% NO led to a decrease in Cu⁺(NO) and NO⁺, increase in bridging and chelating Cu²⁺(NO₃⁻) and in N₂ and O₂ formation, and little change in Cu²⁺(NO) and NO as shown in Figs. 13a–13d. N₂O adsorbs onto the Cu⁺ sites, leading to a decrease in Cu⁺(NO). The decrease in



FIG. 6. MS intensity profiles of reactor effluent and peak intensity profiles of adsorbate species collected during the first 1 cm³ of H_2 pulse into a 5% N₂O stream over Cu–ZSM-5-523 at 673 K.

Cu⁺(NO) is accompanied by an increase in N₂ and O₂ formation but with no significant change in NO concentration, suggesting that the additional N₂ and O₂ formed is from the N₂O decomposition reaction rather than due to the promotion of NO decomposition. Furthermore, IR spectra and MS profiles of the reactor effluents obtained (not shown) from a separate study involving 1 cm³ of N₂O pulse into He at 673 K produced identical adsorbates with the same intensity and the same N₂O, N₂, and O₂ MS profiles as shown in Fig. 13. In summary, the addition of N₂O into a 5% NO in He stream at 673 K does not affect either the NO conversion to N₂ and O₂ or the pulsing activity of N₂O to N₂ and O₂.

One cubic centimeter of NO pulse into a 5% N_2O in He stream at 673 K (not shown) produced no changes in N_2O (gas) in the IR spectrum, increased bridging and chelating $Cu^{2+}(NO_3^-)$, led to the formation of NO^+ , $Cu^+(NO)$, and $Cu^{2+}(NO)$, and caused no changes in the reactant and product concentrations. To observe the changes in N_2O



FIG. 7. IR spectra taken during the first 1 cm 3 of O₂ pulse into a 5% NO stream over Cu–ZSM-5-523 at 673 K.



FIG. 8. MS intensity profiles of reactor effluent and peak intensity profiles of adsorbate species collected during the first 1 cm³ of O_2 pulse into a 5% NO stream over Cu–ZSM-5-523 at 673 K.



FIG. 9. IR spectra taken during the first $1~{\rm cm}^3$ of CO pulse into a 5% NO stream over Cu–ZSM-5-523 at 673 K.



FIG. 10. MS intensity profiles of reactor effluent and peak intensity profiles of adsorbate species collected during the first 1 cm³ of CO pulse into a 5% NO stream over Cu–ZSM-5-523.



FIG. 11. IR spectra taken during the first 1 cm³ of CO pulse into a 5% N_2O stream over Cu–ZSM-5-523 at 673 K.



FIG. 12. MS intensity profiles of reactor effluent and peak intensity profiles of adsorbate species collected during the first 1 cm³ of CO pulse into a 5% N₂O stream over Cu–ZSM-5-523.



FIG. 13. (a) IR spectra, (b) MS intensity profiles of reactor effluent, and (c) and (d) peak intensity profiles of adsorbate species collected during the first 1 cm³ of N_2O pulse into a 5% NO stream over Cu–ZSM-5-523 at 673 K.

adsorbates (Cu⁺–N₂O and Cu⁺–ON₂) during the NO pulse into 5% N₂O, a similar study was conducted at 323 K where the N₂O adsorbates were observed clearly. Figure 14 shows the IR spectra, MS profiles of the reactants and

products, and the variation of adsorbate peak intensities with time collected during a 1 cm³ of NO pulse into a 5% N₂O stream over Cu–ZSM-5-523 at 323 K. Introduction of 1 cm³ of NO led to a decrease in Cu⁺–N₂O,



FIG. 14. (a) IR spectra, (b) MS intensity profiles of reactor effluent, and (c) and (d) peak intensity profiles of adsorbate species collected during the first 1 cm³ of NO pulse into a 5% N₂O stream over Cu–ZSM-5-523 at 323 K.

no change in Cu^+ - ON_2 , N_2O_{ads} (2219 cm⁻¹), and bridged $Cu^{2+}(NO_3^{-})$, and the formation of $Cu^{+}(NO)$, $Cu^+(NO)_2$, and $Cu^{2+}(NO)$ as shown in Figs. 14a–14d. Distinct responses of the Cu⁺-N₂O and Cu⁺-ON₂ species (Fig. 14b) to NO addition suggest that they are adsorbed on different Cu⁺ sites. Near-mirror-image responses of Cu⁺- N_2O and $Cu^+(NO)$ (Fig. 14b) indicate that N_2O adsorbs as Cu^+ – N_2O on the same site as the one on which NO adsorbs as $Cu^+(NO)$. Cu^+-N_2O , which is depleted upon NO addition (Figs. 14a and 14b), is expected to do the same during the NO pulse into 5% N₂O at 673 K. The NO pulse into 5% N₂O, however, did not inhibit or promote N₂O decomposition, confirming that Cu^+-N_2O does not play a role in the N₂O decomposition pathway; i.e., Cu^+ -N₂O is a spectator adsorbate species. The spectator Cu^+ - N_2O may be adsorbing on the same site as that of $Cu^+(NO)$ that is the active adsorbate during NO decomposition on Cu-ZSM-5, suggesting that NO and N₂O decomposition occurs via separate active sites and adsorbates.

4. DISCUSSION

4.1. N₂O Decomposition

 N_2O decomposition has been proposed to proceed via the following steps (11):

$$\begin{split} N_2O + S &\leftrightarrow N_2O\text{-}S\\ N_2O\text{-}S &\to N_2 + O\text{-}S\\ 2O\text{-}S &\leftrightarrow O_2 + 2S. \end{split}$$

where S is the active catalytic site. Although the proposed steps provide a reaction pathway for N_2O decomposition, they do not present information on the structure of active adsorbates and the nature of active sites and offer little theoretical basis in assisting the design of improved N_2O decomposition catalysts. The key to developing a working reaction mechanism, which would aid in the design of novel highly active catalysts, is the knowledge of active adsorbates reside. One objective of this study is to elucidate the type of adsorbed N_2O involved in N_2O decomposition from the results of *in situ* IR studies during a CO, O_2 , and H_2 pulse into N_2O .

IR results in Fig. 2 show that N_2O adsorbs on the Cu– ZSM-5 surface sites via N and O as Cu^+-N_2O (2287 cm⁻¹) and Cu^+-ON_2 (2240 cm⁻¹), respectively, as shown in reactions [1] and [2].

$$Cu^+ + N_2O \leftrightarrow Cu^+ - N_2O$$
 [1]

$$Cu^+ + N_2O \leftrightarrow Cu^+ - ON_2.$$
 [2]

The distinction in catalytic properties between Cu^+-N_2O and Cu^+-ON_2 can be differentiated by their responses to the NO pulse at 323 K (Fig. 14). Figures 14b and 14c show that Cu⁺–N₂O and Cu⁺–NO exhibit near-mirrorimage responses to the NO pulse, suggesting that Cu⁺– N₂O and Cu⁺–NO share the same Cu⁺ sites and that Cu⁺– N₂O + NO \leftrightarrow Cu⁺–NO + N₂O is a reversible process. The process also appeared to occur at 673 K as evidenced by the decrease in Cu⁺–NO during the N₂O pulse into the NO flow as shown in Fig. 13.

Figures 14a and 14b also show that Cu^+-ON_2 , unlike Cu^+-N_2O , was not affected by the introduction of the NO pulse at 323 K. Furthermore, the NO pulse into 5% N₂O at a reaction temperature of 673 K was found to have no effect on the N₂O decomposition rate and product selectivity, indicating that NO does not adsorb onto the active N₂O decomposition sites but may adsorb and replace adsorbates present on sites not participating in the N₂O decomposition reaction. The replacement of Cu^+-N_2O by Cu^+-NO at 323 K combined with the absence of the NO effect on N₂O decomposition at 673 K suggests that Cu^+-N_2O is a spectator adsorbate species during the N₂O decomposition reaction. This inference would possibly, but not necessarily, point to Cu^+-ON_2 as a possible active adsorbate for N₂O decomposition.

Decomposition of N_2O to N_2 and O_2 is envisioned to occur as indicated in the following pathways:

$$Cu^+ - ON_2 \rightarrow Cu^{2+}O^- + N_2$$
[3]

$$Cu^{2+}O^{-} \rightarrow Cu^{+} + \frac{1}{2}O_{2}.$$
 [4]

Reaction [3], the proposed pathway for N₂ formation, is in line with the observation that depletion of Cu⁺–ON₂ was followed by the formation of adsorbed N₂ during N₂O TPR (Fig. 2a). The reduction of Cu²⁺ to Cu⁺ led to the formation of O₂ from Cu²⁺O⁻ as illustrated in reaction [4]. Quantum chemical and statistical mechanical calculations have estimated the Gibbs free energy (ΔG) of reaction [4] to be -24.2 kcal/mol at 773 K (47). An alternate pathway for N₂ formation has also been envisioned to occur as shown in reaction [5], which is expected to compete with reaction [3]. Although density functional theory calculations (48) indicate that the energy barriers to reactions [3] and [5] are comparable, observation of Cu⁺–ON₂ (Fig. 14) and absence of Cu²⁺O⁻–ON₂ in the present study point to reaction [3] as the possible route for N₂ formation.

$$Cu^{2+}O^{-}-ON_{2} \rightarrow Cu^{2+}OO^{-}+N_{2}.$$
 [5]

Reactions [3] and [4] may also be linked as consecutive pathways in the N₂O decomposition mechanism as shown in Scheme 1. Scheme 1 also includes the pathway for $Cu^{2+}(NO_3^-)$ formation (reaction [6]):

$$Cu^{2+}O_{2}^{-} + Cu^{+}O_{2} \rightarrow Cu^{2+}(NO_{3}^{-}) + Cu^{+}N$$
 [6]

$$Cu^+ - N + Cu^+ - N \rightarrow Cu^+ + N_2$$
^[7]



SCHEME 1

Both steps [6] and [7] remain in a speculative stage. Step [6] is postulated according to recent results of step switch results of He to 5% N₂O at 323 K (49) that show that the formation of Cu⁺–ON₂ preceded that of Cu²⁺(NO₃⁻), suggesting that Cu⁺–ON₂ may act as a precursor for Cu²⁺(NO₃⁻) formation. The slow development of Cu²⁺(NO₃⁻) can also be observed during the H₂ and CO pulse into N₂O flow (Figs. 6 and 12) in which Cu²⁺(NO₃⁻) was first removed by the H₂ and CO pulse and then gradually returned to the initial intensity.

The most interesting results of the H_2/CO pulse studies are the formation of two H_2O/OH concentration peaks during the H_2 pulse (Fig. 6) and the formation of two O_2 peaks during the CO pulse (Fig. 12). These observations suggest the presence of at least two types of oxygen on the catalyst surface under N_2O decomposition conditions. These oxygen species can interact with adsorbed hydrogen, leading to OH and H_2O formation during the H_2 pulse, while a significant fraction of these oxygen species cannot be accessed by CO and simply desorb as O_2 upon reduction of Cu^{2+} to Cu^+ during the CO pulse.

Oxygen in $Cu^{2+}(NO_3^-)$ may contribute to CO_2 formation since a sharp decrease in $Cu^{2+}(NO_3^-)$ intensity corresponded to a rapid increase in CO_2 and $Cu^+(CO)$ intensities (Figs. 11 and 12). Furthermore, CO reacted with Cu^{2+} , leading to the reduction of Cu^{2+} to Cu^+ . Since the zeolite framework oxygen must stay intact and cannot be removed by CO, the oxygen desorbed during the CO pulse must come from extra framework lattice oxygen (ELO). The oxygen species may associate with Cu in several different forms, which will be further discussed in Section 4.3.

4.2. NO Decomposition

The adsorbates observed during NO TPR are Cu⁺(NO), Cu²⁺(NO), bridging and chelating Cu²⁺(NO₃⁻), and NO⁺. The role of these adsorbates in NO decomposition may be elucidated from their relationships to N₂, N₂O, and O₂ formation during TPR and H₂/O₂/CO pulse studies.

4.2.1. N_2O formation. The Cu⁺(NO) profile correlates well with the gaseous N₂O profile during NO TPR (Figs. 1a and 1b), the H₂ pulse into NO (Figs. 3, 4a, and 4b), and the O₂ pulse into NO (Figs. 7, 8a, and 8b). These results suggest that Cu⁺(NO) may be a precursor for N₂O formation, which may be written as shown in reactions [8] and [9]:

$$Cu^+ + NO \leftrightarrow Cu^+(NO)$$
 [8]

$$Cu^{+}(NO) + Cu^{+} - N \rightarrow 2Cu^{+} + N_2O.$$
 [9]

The correlation between $Cu^+(NO)$ and N_2O formation profiles, however, was not observed on poisoned catalysts (32). This could be due to the lack of NO dissociation to adsorbed N on these catalysts, which would prevent N_2O formation but would not affect the surface concentration of $Cu^+(NO)$. The N_2O produced from reaction [9] can follow the pathway shown in Scheme 1 to produce N_2 and O_2 . $Cu^+(NO)$ can also serve as a precursor for the formation of $Cu^{2+}(NO_3^-)$ as shown in reaction [10]:

$$Cu^+(NO) + O_2 \leftrightarrow Cu^{2+}(NO_3^-).$$
 [10]

The formation of $Cu^{2+}(NO_3^-)$ from $Cu^+(NO)$ is evidenced by the decrease in $Cu^+(NO)$ and increase in $Cu^{2+}(NO_3^-)$ during the O₂ pulse into NO (Figs. 7 and 8).

4.2.2. NO dissociation. Cu^+ has been considered as a site for the dissociation of NO. The results from CO and H_2 pulse studies (Figs. 3, 4, 9, and 10) show that the formation of N₂, N₂O, and O₂ was enhanced in the reducing environment where Cu⁺ is the prevailing copper site as evidenced by the high intensities of Cu⁺(CO) and Cu⁺(NO). Cu⁺(NO) may be involved in NO dissociation as shown in reaction [11]:

$$Cu^{+}(NO) + Cu^{+} \rightarrow Cu^{+} - N + Cu^{2+}O^{-}.$$
 [11]

It must be noted that there is no direct evidence for the occurrence of reaction [11]. Alternate pathways for NO dissociation have been proposed to proceed as indicated in reactions [12]–[14]:

$$Cu^{+}(NO)_{2} \rightarrow Cu^{2+}O^{-} + N_{2}O$$
 [12]

$$Cu^+-ON + NO \rightarrow Cu^{2+}O^- + N_2O$$
 [13]

$$2ZCu + 2NO \rightarrow ZCuOCuZ + N_2O.$$
 [14]

High Gibbs free energy of reaction (ΔG) at 773 K (47) and the lack of correlation between Cu⁺(NO)₂ and N₂O formation (31) suggested that reaction [12] is unlikely to be the pathway for the NO bond dissociation. Although the Obonded Cu⁺–ON is not observed in the present study, the



highly reactive nature of such species (51) may not allow its detection and the reaction of Cu⁺-ON with NO (reaction [13]) may be a plausible route for NO dissociation. The NO dissociation pathway may also involve the oxocation species (50), ZCuOCuZ (Z represents the Al(OH) $_4^-$ group of the zeolite; O donates extralattice oxygen, ELO.), as illustrated in reaction [14]. NO dissociation via the $(NO)_2$ precursor and N₂O intermediate is the most widely postulated pathway in NO decomposition (21-23, 26). However, the significant differences in the N₂, O₂, OH, and H₂O profiles during the H_2 pulse in Figs. 3–6 revealed that N_2O is not a major precursor for the decomposition of NO to N_2 and O2. The NO dissociation pathway without N2O involvement remains to be investigated. In summary, Cu⁺ is needed for the dissociation of NO and the unique high activity of Cu-ZSM-5 for NO decomposition is due to its ability to sustain Cu in the Cu⁺ state. The identity of adsorbates participating in NO dissociation cannot be determined by the *in situ* IR technique.

4.2.3. O_2 formation. The formation of O_2 during NO decomposition has been proposed to occur as shown in reactions [15]–[18] (31, 32, 47, 52).

$$Cu^{2+}O^{-} \rightarrow Cu^{+} + \frac{1}{2}O_{2}$$
 [15]

$$CuO_2Cu \leftrightarrow 2Cu^+ + O_2$$
 [16]

$$CuO_2Cu \leftrightarrow CuOCu + \frac{1}{2}O_2$$
 [17]

$$Cu^{2+}(NO_3^-) \leftrightarrow Cu^+ + NO + O_2.$$
 [18]

Quantum mechanical and statistical calculations (47) have confirmed that reaction [14], with a Gibbs free energy of reaction (ΔG) of -24.1 kcal/mol at 773 K, is thermodynamically favorable. Density functional studies (52) indicated that two Cu²⁺O⁻ species can combine to form the dioxocation, *Z*CuO₂Cu*Z*, which would further decompose to regenerate Cu⁺ and produce O₂ (reactions [15] and [16]). Results from our previous NO TPD studies (31, 32) have shown that another alternative for O_2 formation is through the decomposition of bridged $Cu^{2+}(NO_3^-)$ to Cu^+ and NO and O_2 (reaction [18]). The bridged $Cu^{2+}(NO_3^-)$ could be formed via two routes: (i) reaction of NO with $Cu^{2+}O_2^-$, which is formed by the combination of a mobile O species with $Cu^{2+}O^-$ produced from NO dissociation, and (ii) interaction of NO with a CuO_2Cu species since such a species would offer the possibility of two copper sites acting as a bridge for the nitrate ligand. The dissociation of NO and formation of N_2 , N_2O , and O_2 during the NO decomposition reaction are summarized in Scheme 2 and Table 2.

4.3. Cu^+ Sites for Cu^+ - ON_2 , Cu^+ - N_2O , and Cu^+ (NO)

IR results from the present study revealed the dynamic behavior of the NO and N₂O adsorbates but provide little information on the nature of Cu⁺ sites and its chemical/physical environment. The nature of the Cu⁺ site may be elucidated from the recent results of density functional calculations for NO and N₂O adsorption (53) on two types of Cu⁺ sites: (i) Cu⁺(Al(OH)₄⁻) ($Z_{Al}Cu^+$), i.e., the Cu⁺ site associated with Al, and (ii) Cu⁺(Si(OH)₄⁻) ($Z_{Si}Cu^+$), i.e., the Cu⁺ site associated with Si. Binding energy calculations from this study indicate that the adsorption of NO onto $Z_{Al}Cu^+$ is more favorable than NO onto $Z_{Si}Cu^+$. Hence, NO is envisioned to adsorb onto $Z_{Al}Cu^+$ as shown in reaction [19]:

$$Z_{Al}Cu^+ + NO \leftrightarrow Z_{Al}Cu^+ - NO.$$
 [19]

Comparison of the calculated binding energies (53) for adsorbed N₂O on various Cu⁺ sites also revealed that N₂O adsorbs as Cu⁺–ON₂ on $Z_{Si}Cu^+$ more favorably than on $Z_{Al}Cu^+$. NO pulse into 5% N₂O results (Fig. 14) from the present study show that Cu⁺–N₂O and Cu⁺(NO) adsorb on the same Cu⁺ site. These results combined with the density

TABLE 2

NO decomposition	N ₂ O decomposition	
$\begin{tabular}{lllllllllllllllllllllllllllllllllll$	$\begin{array}{c} Adsorption \\ Cu^+ + N_2O \leftrightarrow Cu^+ - N_2O \\ Cu^+ + N_2O \leftrightarrow Cu^+ - ON_2 \end{array}$	
$\label{eq:constraint} \begin{array}{l} NO \mbox{ dissociation} \\ Cu^+(NO) + Cu^+ \rightarrow Cu^+ - N + Cu^{2+}O^- \\ Cu^+ - ON + NO \rightarrow Cu^{2+}O^- + N_2O \end{array}$		
$\begin{array}{c} N_2O \text{ and } N_2 \text{ formation} \\ Cu^+(NO) + Cu^+ - N \leftrightarrow 2Cu^+ + N_2O \\ Cu^+ - ON + NO \rightarrow Cu^{2+}O^- + N_2O \\ Cu^+ + N_2O \leftrightarrow Cu^+ - ON_2 \\ Cu^+ - ON_2 \rightarrow Cu^{2+}O^- + N_2 \\ Cu^+ - N + Cu^+ - N \rightarrow 2Cu^+ + N_2 \end{array}$	$\begin{array}{l} N_2 \ formation \\ Cu^+ \text{-}ON_2 \nleftrightarrow Cu^{2+}O^- + N_2 \end{array}$	
$\begin{array}{c} O_2 \text{ formation} \\ Cu^{2+}O^- \leftrightarrow Cu^+ + \frac{1}{2}O_2 \\ CuO_2Cu \rightarrow 2Cu^+ + O_2 \\ Cu^{2+}(NO_3^-) \leftrightarrow Cu^+ + NO + O_2 \end{array}$	$\begin{array}{c} O_2 \text{ formation} \\ Cu^{2+}O^- \leftrightarrow Cu^+ + \frac{1}{2}O_2 \\ Cu^{2+}O_2^- \leftrightarrow Cu^+ + O_2 \end{array}$	
$\begin{array}{c} Cu^{2+}(NO_{3}^{-}) \text{ formation} \\ Cu^{+}(NO) + O_{2} \leftrightarrow Cu^{2+}(NO_{3}^{-}) \\ Cu^{2+}O^{-} + O \rightarrow Cu^{2+}O_{2}^{-} \\ Cu^{2+}O_{2}^{-} + NO \rightarrow Cu^{2+}(NO_{3}^{-}) \end{array}$	$\begin{array}{c} Cu^{2+}(NO_{3}^{-}) \text{ formation} \\ Cu^{2+}O^{-}+Cu^{+}-ON_{2} \leftrightarrow Cu^{2+}O^{-}-ON_{2} \\ Cu^{2+}O^{-}-ON_{2} \leftrightarrow Cu^{2+}O_{2}^{-}+N_{2} \\ Cu^{2+}O_{2}^{-}+Cu^{+}-ON_{2} \leftrightarrow Cu^{2+}(NO_{3}^{-})+Cu^{+}-N \end{array}$	

Proposed NO and N₂O Decomposition Mechanisms over Cu-ZSM-5

Note. S: cationic site on ZSM-5; S-O-NO⁺ is indicated as NO⁺ in the present study. *Z*CuOCu*Z* or *Z*CuO₂Cu*Z* can replace all single Cu⁺ sites in both mechanisms.

functional calculations suggest that Cu^+ for $Cu^+(NO)$ and Cu^+ for Cu^+-N_2O may be associated with Z_{Al} ; the Cu^+ for Cu^+-ON_2 may be associated with Z_{Si} , supporting the fact that NO and N_2O decomposition may occur on Cu^+ sites present in different environments.

4.4. Nature of Oxygen in NO and N₂O Decomposition

The formation of O_2 has been envisioned to occur as shown in Scheme 1 during N_2O decomposition and as illustrated in Scheme 2 during NO decomposition over Cu– ZSM-5. The distinct difference in reactivity of adsorbed O produced from N_2O and NO decomposition is summarized in Table 3. N_2O decomposition is expected to produce N_2 and O^- upon N_2O dissociation. ESR studies (11) have proved unambiguously that oxygen adsorbs as a reactive $O^$ species during the N_2O decomposition reaction. O^- from N_2O is expected to combine with another O^- to desorb as gaseous O_2 and reduce Cu^{2+} to Cu^+ . Furthermore, the $O^$ has been shown to migrate and transform to a more strongly bonded O^{2-} (reaction [20]) in oxide catalysts under high temperatures, depending on the type and concentration of transition-metal ion associated with the catalyst (11):

$$O^- + e^- \leftrightarrow O^{2-}$$
. [20]

It is expected that O^{2-} is more difficult to desorb than O^{-} due its strong association with metal sites. This strongly

associated O^{2-} could be the adsorbed O species produced from NO decomposition and O_2 addition since the O_2 pulse into NO significantly inhibited NO decomposition. The formation of additional O^{2-} , produced from the adsorption of the pulsed O_2 , along with the already present O^{2-} from NO decomposition should lead to the inhibition of O_2 desorption and NO decomposition. Density functional studies (48, 50) show that the O^{2-} species may be associated with Cu(II)– O^{2-} –Cu(II), which can further be interconverted to

TABLE 3

Differences in Reactivity of Adsorbed O from N₂O and NO Decomposition

Experiment	O from N ₂ O decomposition	O from NO decomposition
CO pulse (Figs. 10 and 12)	Two hump O ₂ profile	One hump O ₂ profile
H ₂ pulse (Figs. 3–6)	Two hump H ₂ O/ OH profile	One hump H ₂ O profile; formation of N ₂ O; desorption of O ₂
O ₂ pulse (Figs. 7 and 8)	No effect	Oxidization of Cu^+ in $Cu^+(NO)$ to Cu^{2+} in $Cu^{2+}(NO_3^-)$; inhibition of NO decomposition
NO and N ₂ O pulses into He (Refs. 30 and 49)	O2 did not lag behind N2 and NO	O ₂ profile lags behind N ₂ , N ₂ O, and NO

Cu(II)– $O_2^{2^-}$ –Cu(II). Lack of spectroscopic information on the oxocation and adsorbed oxygen species did not allow verification of the types of the oxygen species, which were postulated based on density functional calculations. However, the postulation of different forms of oxygen, O⁻ and O²⁻, from N₂O decomposition is indeed consistent with the observation of two O₂ and H₂O peaks during the CO and H₂O pulse studies (Figs. 6 and 12).

The activity of the Cu–ZSM-5 catalyst for NO and N₂O decomposition is closely related to its ability to desorb oxygen from the catalyst surface, allowing it to maintain the majority of its Cu sites in the Cu⁺ state. The importance of the Cu⁺ state is illustrated in Figs. 9 and 11, which show that Cu⁺(CO) is the dominant species during a CO pulse into NO and N₂O. In contrast to the dominance of the Cu⁺ state in Cu–ZSM-5 under NO and N₂O decomposition conditions, Cu²⁺ is the major species on the CuO/Al₂O₃ catalyst (accompanied by a trace amount of Cu⁰ and Cu⁺) which exhibits little activity for both reactions (49). The unique capability of Cu–ZSM-5 can be attributed to the nature of the interaction between Cu⁺ and the zeolite framework; such interactions cannot be probed by our infrared techniques.

5. CONCLUSIONS

Addition of CO, H_2 , and O_2 into the steady-state flow of NO and N_2O over Cu–ZSM-5 not only produces transient reducing and oxidizing conditions but also leads to changes in the reactivity and dynamics of adsorbates. NO and N_2O decomposition produces differently adsorbed O species: adsorbed oxygen produced from N_2O decomposition (i) reacts with the pulsed H_2 to produce two humps in the H_2O profile, (ii) interacts with the pulsed CO to desorb O_2 with two humps, and (iii) did not interact with adsorbed O produced from the O_2 pulse; adsorbed O produced from NO decomposition interacts with the pulsed CO and H_2 to (i) desorb O_2 and H_2O with a single peak in concentration and (ii) interact with adsorbed O from the O_2 pulse to inhibit NO decomposition.

 N_2O decomposition is proposed to proceed via Cu^+ - ON_2 , $Cu^{2+}O^-$, and $Cu^{2+}O^-$ - ON_2 with Cu^+ - ON_2 serving as a precursor for N_2 formation and $Cu^{2+}O^-$ as a precursor for O_2 formation. NO decomposition proceeds via Cu^+ (NO), $Cu^{2+}O^-$, and $Cu^{2+}(NO_3^-)$ with Cu^+ (NO) serving as a precursor for NO dissociation. Cu^+ in Cu^+ (NO) is different from that of Cu^+ in Cu^+ - ON_2 . The former may be associated with $Al(OH)_4^-$ of the zeolite, the latter with $Si(OH)_4^-$.

The lack of O_2 inhibition effect on N_2O decomposition and the differences in the reactivity of adsorbed O from N_2O and NO decomposition suggest that future studies for the development of novel NO decomposition catalysts should aim for the conversion of the adsorbed O^{2-} produced from NO decomposition to the type of adsorbed O (O⁻) resembling those produced from N_2O decomposition.

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