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# Role of Cyanide Species in the Reduction of NO by $CH_4$ over Co−ZSM-5

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***In situ* infrared observation during the reduction of NO by $CH_4$ over Co−ZSM-5 reveals the presence of CN species. The reactivity of these species has been probed by exposing them to $NO_2$, $O_2$, or NO while monitoring their rate of disappearance. In a complementary set of experiments, mass spectrometry was used to identify the reaction products as $N_2$ and $CO_2$. At 450°C the rate coefficients for the consumption of CN are $8.5 \times 10^{-5}$, $1.9 \times 10^{-6}$, and $3.3 \times 10^{-7}$ $s^{-1}$ $ppm^{-1}$ for reaction in $NO_2$, $O_2$, and NO, respectively. The reactivity of CN is sufficiently high for these species to be considered reaction intermediates in the formation of $N_2$ and $CO_2$ during the reduction of NO by $CH_4$ in the presence of $O_2$.** © 1997 Academic Press

## INTRODUCTION

Since Li and Armor (1) first reported the effectiveness of Co−ZSM-5 for the reduction of NO by $CH_4$ in the presence of $O_2$, a series of investigations have been undertaken to identify the mechanism by which the reaction occurs (2–8). These efforts have shown that NO reacts with $O_2$, both in the gas phase and over the catalyst, to form $NO_2$, and that adsorbed $NO_2$ is the primary species that reacts with $CH_4$ (2–7). *In situ* infrared observations have established that the most abundant reactive intermediate at reactions temperatures (350–550°C) are nitrito species associated with $Co^{2+}$ cations (2, 6), and isotopic labeling studies in which $CD_4$ is substituted for $CH_4$ strongly indicate that the reaction of gas-phase $CH_4$ with adsorbed $NO_2$ is the rate-limiting step in the overall reduction of NO (8). Based on *in situ* infrared observations, we have recently reported the formation of CN species during the reduction of NO by $CH_4$ over Co−ZSM-5, and have suggested that these species might be involved in the formation of $CO_2$ and $N_2$ via the reaction $CN_s + NO_{2,g} \rightarrow CO_{2,g} + N_{2,g}$ (6). The goal of the present study was to confirm the presence of CN species and to ascertain whether these species are sufficiently active to serve as reaction intermediates. To this end, transient response experiments were carried out in which the dynamics of the reaction of CN species with $NO_2$, $O_2$, and NO were followed by infrared spectroscopy and mass spectrometric analysis of the reaction products.

## EXPERIMENTAL

Co−ZSM-5 was prepared by ion exchange. Approximately 15 g of Na−ZSM-5 obtained from UOP was added to 3.5 liters of a 0.01 *M* cobalt acetate solution. This mixture was stirred at 25°C for 21 h, then at 60°C for 33 h, and finally at 70°C for 19 h (1). The cobalt-exchanged zeolite was filtered and washed with distilled water and then dried overnight in a vacuum oven at 120°C. The Si/Al ratio of the final catalyst is 16.2 and the Co/Al ratio is 0.28.

The cobalt-exchanged zeolite was pressed into a 20- to 50-mg self-supporting wafer and placed into an infrared cell similar to that described by Joly *et al.* (9). Spectra were recorded on a Digilab FTS-50 Fourier transform infrared spectrometer at a resolution of 4 $cm^{-1}$. Typically, 30 scans were coadded to obtain a good signal-to-noise ratio. The total time to acquire a complete set of data is approximately 50 s, and the time indicated in all experiments is the midpoint of the data collection time. A reference spectrum of Co−ZSM-5 in He taken at the reaction temperature was subtracted from each spectrum.

Gases were supplied to the infrared cell from a gas manifold. From Matheson 4.99% NO, 1.03% $NO_2$, 2.14% $CH_4$, and 10.1% $O_2$ in He were obtained. $^{13}CH_4$ and $^{15}NO$ were obtained from Isotec. He, NO, and $CH_4$ were passed through an oxysorb trap, an ascarite trap, and a molecular sieve trap for additional purification. $O_2$ was passed through traps containing ascarite and molecular sieves. Prior to each experiment the catalyst was (1) heated at 500°C in $O_2$ for about 30 min, (2) heated at 500°C in He for about 3 h, and (3) cooled to 450°C in He.

Two sets of experiments were carried out to determine the rate at which adsorbed species react in various gas mixtures. In the first set, the catalyst was placed in the infrared cell and then exposed for 15 min at 450°C to a gas mixture containing 6300 ppm NO and 1.8% $CH_4$ in He, flowing at 100 $cm^3$/min. Next, the cell was purged with He for 30 s. Subsequently, a stream of either pure He or He containing 1% $NO_2$, $O_2$, or NO was passed through the cell while infrared spectra were recorded as a function of time.

To determine the composition of the products formed during the transient experiments, a second set of

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experiments was performed in a quartz microreactor containing 0.1 g of the catalyst. The effluent products were analyzed using a mass spectrometer (UTI 100C). As many as eight masses were monitored each second. This set of experiments was conducted in the same manner as the infrared experiments, with the exception that $^{13}CH_4$ was used instead of $^{12}CH_4$, to minimize the overlap of cracking patterns.

## RESULTS AND DISCUSSION

Figure 1 shows the infrared spectrum of species adsorbed on Co–ZSM-5 in a He stream containing 6300 ppm NO and 1.8% $CH_4$ at 450°C. Five bands are observed at 2270, 2173, 1930, 1885, and 1800 $cm^{-1}$. The band at 1930 $cm^{-1}$ is due to cobalt nitrosyl, and the pair of bands at 1885 and 1800 $cm^{-1}$ are due to cobalt dinitrosyl (6).

Isotopic labeling experiments were performed to aid in the assignment of the features at 2270 and 2173 $cm^{-1}$. After creating the two bands in a mixture of $^{14}NO + {}^{12}CH_4$ the flow was switched to either $^{15}NO + {}^{12}CH_4$ or $^{14}NO + {}^{13}CH_4$. In either case, both bands red-shifted, indicating that they are due to species that contain both N and C. The results are shown in Table 1.

Based on its position the band at 2173 $cm^{-1}$ might be attributed to NCO species adsorbed on $Co^{2+}$ (10). This would also be consistent with the observation by Solymosi *et al.* of a band at 2185 $cm^{-1}$ for NCO species adsorbed on $Cu^{2+}$ cations in Cu–ZSM-5 (11); however, the observed isotopic shifts are inconsistent with those predicted on the assumption that NCO can be treated as a pseudo-diatomic species, viz., N(C–O) or (NC)–O (10). Cyanide species are also known to have stretching frequencies in the vicinity of 2173 $cm^{-1}$ (10). Assuming an assignment of $Co^{2+}$–CN for this band results in predicted shifts of 2139 $cm^{-1}$ for $^{12}C^{15}N$ and 2128 $cm^{-1}$ for $^{13}C^{14}N$, in good agreement with the observed values of 2144 and 2132 $cm^{-1}$, respectively. The assignment of the band at 2173 $cm^{-1}$ to $Co^{2+}$–CN is further supported by the stoichiometry of the products produced during transient reaction studies conducted with $NO_2$, $O_2$, and NO (see below).

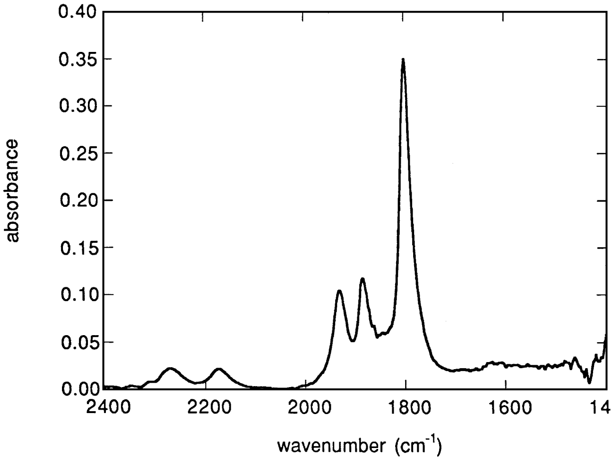

**FIG. 1.** Infrared spectrum observed after passing 6300 ppm NO and 1.8% $CH_4$ over the catalyst at 450°C for 15 min.

**TABLE 1**

**Effects of Isotopic Labeling on the Positions of the Bands Observed at 2270 and 2173 $cm^{-1}$**

| Gas mixture | $\nu$ ($cm^{-1}$) | $\nu$ ($cm^{-1}$) |
|---|---|---|
| $NO + CH_4$ | 2270 | 2173 |
| $^{15}NO + CH_4$ | 2256 | 2144 |
| $NO + {}^{13}CH_4$ | 2237 | 2132 |

The band at 2270 $cm^{-1}$ is assigned to $Al^{3+}$–NCO. Solymosi *et al.* have observed a similar band at 2260 $cm^{-1}$ when Cu–ZSM-5 is exposed to HNCO (11). Assignment of the 2270 $cm^{-1}$ band to NCO is consistent, as well, with the observation of a red shift to 2256 $cm^{-1}$ when the species is $^{15}N$ labeled. The observed shift is in excellent agreement with the predicted shift of 2254 $cm^{-1}$ assuming that NCO is treated as a pseudo-diatomic species (NC)–O. When the NCO group is $^{13}C$ labeled, the frequency shifts to 2237 $cm^{-1}$. This value falls exactly halfway between the predicted values of the frequency, 2254 $cm^{-1}$ assuming a pseudo-diatomic of the form (NC)–O and 2220 $cm^{-1}$ assuming a pseudo-diatomic form of N(C–O).

To ascertain whether $Al^{3+}$–NCO or $Co^{2+}$–CN might be an intermediate in the reduction of NO by $CH_4$, we performed a series of transient experiments. NCO and CN species were formed by reacting NO plus $CH_4$ over the catalyst at 450°C. The bottommost spectrum in Figs. 2a–d shows the intensities of the infrared bands for these species. At time zero, either 1% $NO_2$, $O_2$, or NO in He is passed over catalyst, and the changes in the band intensities for CN and NCO species are recorded as a function of time. In the case of either NO, $O_2$, or He there is an immediate jump in the intensity of the isocyanate band and an associated decrease in the cyanide band. We believe this to be caused by the partial oxidation of CN to NCO due to residual NO or $NO_2$ in the reactor. Assuming that the total amount of CN lost is equal to the gain in NCO, it is possible to calculate the ratio of extinction coefficients for NCO and CN species. By this means we obtain an average value for $\varepsilon_{NCO}/\varepsilon_{CN}$ of ≈7.9. The conclusion that this ratio is greater than 1 is supported by the literature. Isocyanate groups have been found to have extinction coefficients ranging from 1300 to 2000 liters/(mol · cm) whereas cyanide groups have extinction coefficients ranging from 10 to 150 liters/(mol · cm) (12). Moreover, for ethylene monosubstituted with NCO or CN the value of $\varepsilon_{NCO}/\varepsilon_{CN}$ is 38.4 (13).

Figure 2 shows that the cyanide band decays in all gases, and in $NO_2$, it is removed completely on exposure. There is

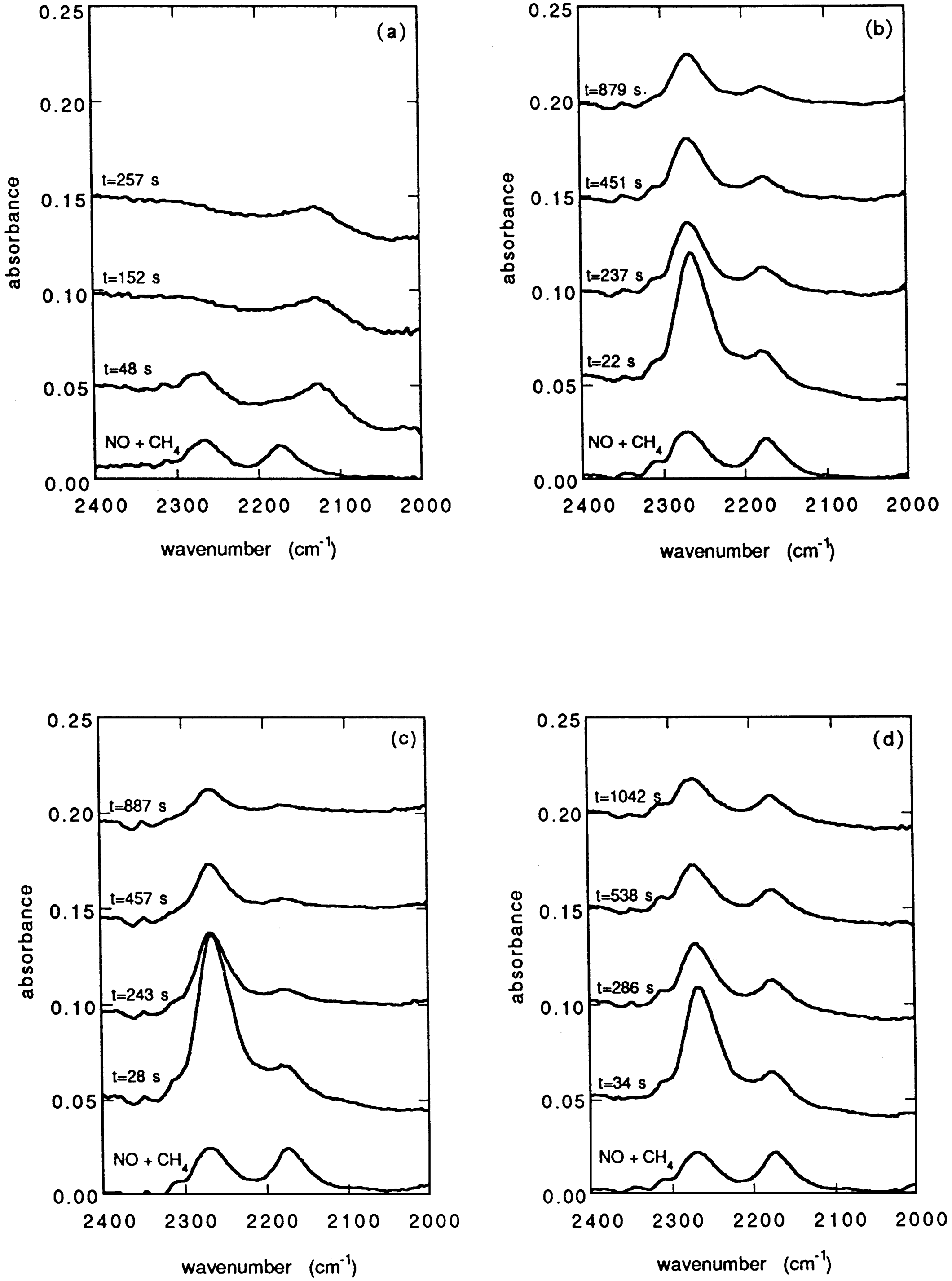

**FIG. 2.** Infrared spectra showing the decay of bands at 2270 and 2173 cm$^{-1}$ in (a) 1% $NO_2$, (b) 1% NO, (c) 1% $O_2$, and (d) He.

an additional band at 2128 cm$^{-1}$ when $NO_2$ is present that can be assigned to $H^+–NO_2$ (14). Rate coefficients were determined from an analysis of the decay in the isocyanate and cyanide bands. The slope of the line generated by plotting the natural logarithm of the integrated band intensity versus time yields the apparent first-order rate coefficient for each species. The true rate coefficient, *k*, is then obtained by dividing the apparent first-order rate coefficient by the gas-phase concentration of $O_2$, NO, or $NO_2$. The results are shown in Table 2.

Figure 3 shows the formation of $^{13}CO_2$ and $N_2$ as a function of time after the catalyst has been pretreated in a

**TABLE 2**

**Rate Coefficients for the Reaction of CN and NCO Species in $NO_2$, $O_2$, and NO**

| | MS $k$ ($s^{-1}$ $ppm^{-1}$) | | IR $k$ ($s^{-1}$ $ppm^{-1}$) | |
|---|---|---|---|---|
| Reactant gas | $^{13}CO_2$ | $N_2$ | CN | NCO |
| $NO_2$ | $8.4 \times 10^{-5}$ | $9.3 \times 10^{-5}$ | $>10^{-5}$ | $2.9 \times 10^{-6}$ |
| $O_2$ | $1.9 \times 10^{-6}$ | $1.7 \times 10^{-6}$ | $3.5 \times 10^{-7}$ | $3.9 \times 10^{-7}$ |
| NO | $3.3 \times 10^{-7}$ | $2.1 \times 10^{-7}$ | $3.7 \times 10^{-7}$ | $3.8 \times 10^{-7}$ |

mixture of 6300 ppm NO and 1.8% $^{13}CH_4$ and then exposed to a stream of He containing 1% $NO_2$, $O_2$, or NO. Products are not observed for the first 10 s, which corresponds to the transit time between the reactor and the mass spectrometer. In $NO_2$, the production of both $^{13}CO_2$ and $N_2$ occurs very rapidly, and any detectable production ceases after 60 s. In NO, the production of $N_2$ is more rapid than the production of $^{13}CO_2$, but still much slower than is observed during the reaction in $NO_2$. A quick burst of $N_2$ production followed by a sharp decrease in the rate of $N_2$ production is observed, as well, during the reaction with NO. Both $^{13}CO_2$ and $N_2$ are detectable as products up to 30 min. In $O_2$, the production of $^{13}CO_2$ is more rapid than the production of $N_2$, but still much slower than in $NO_2$; however, the formation of both $^{13}CO_2$ and $N_2$ is faster in $O_2$ than in NO. The production of both $^{13}CO_2$ and $N_2$ is barely detectable in a flow of pure He.

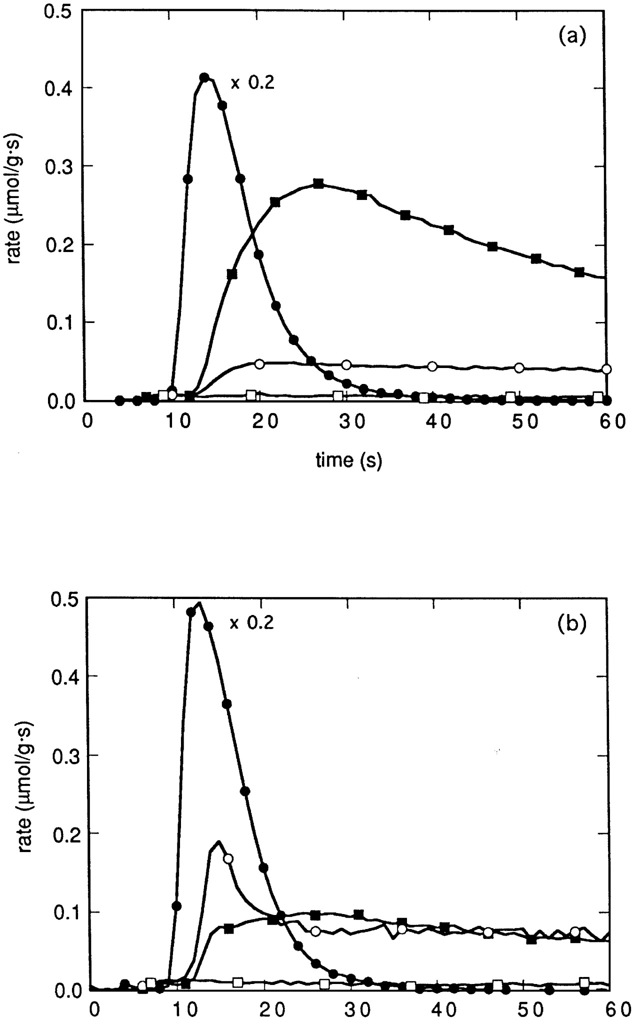

**FIG. 3.** Formation of (a) $^{13}CO_2$ and (b) $N_2$ as a function of time in (●) 1% $NO_2$, (○) 1% NO, (■) 1% $O_2$, and (□) He.

The stoichiometry of the adsorbed species contributing to the formation of $CO_2$ and $N_2$ during the transient experiments can be determined from analysis of the ratio of $^{13}CO_2$ to $N_2$ produced. The amounts of $CO_2$ and $N_2$ were determined by integrating the rate of formation of each product versus time over the duration of the experiment, 10 min. In the case of reaction in $NO_2$ and $O_2$, neither $CO_2$ nor $N_2$ was observed for times longer than 10 min, but in the case of reaction in NO, product formation was observed for as long as 30 min. As indicated in Table 3, the observed values of $^{13}CO_2 : N_2$ are 0.92, 2.06, and 0.49, for reaction in $NO_2$, $O_2$, and NO, respectively. Also listed in Table 3 are the anticipated ratios of $CO_2 : N_2$ assuming that CN or NCO species are the dominant source of $CO_2$ and $N_2$. The best agreement between the observed ratio and the expected ratio is achieved when it is assumed that CN species are the dominant source of $CO_2$ and $N_2$. The excess amount of $N_2$ formed during the reaction carried out in NO may be due to $N_2$ formed via decomposition of some NO to $N_2$ and $O_2$ during the early stage of the experiment. Such a process might account for the burst of $N_2$ at 55 s seen in Fig. 3b.

Rate coefficients were determined by analysis of the rate of formation of $^{13}CO_2$ and $N_2$. In the case of the experiments carried out with $O_2$ and NO, the gas-phase concentration of the reactant was virtually constant throughout the experiment, so that the rate coefficient, $k$, could be determined from the slope of a plot of the natural logarithm of product concentration versus time. In the case where $NO_2$ is the

**TABLE 3**

**Observed Yields of $^{13}CO_2$ and $N_2$ during Transient Response Experiments and the Observed and Predicted Ratios of $CO_2/N_2$**

| Reactant gas | $^{13}CO_2$ ($\mu$mol) | $N_2$ ($\mu$mol) | $^{13}CO_2/N_2$[a] | $CO_2/N_2$[b] | $CO_2/N_2$[c] |
|---|---|---|---|---|---|
| NO | 1.96 | 2.13 | 0.92 | 1.00 | 1.33 |
| $O_2$ | 2.18 | 1.06 | 2.06 | 2.00 | 2.00 |
| NO | 1.84 | 3.77 | 0.49 | 0.66 | 1.00 |

[a] Observed.

[b] Anticipated ratio for CN assuming the stoichiometry $CN + a(NO, O_2, \text{or } NO_2) \rightarrow bN_2 + cCO_2$.

[c] Anticipated ratio for NCO assuming the stoichiometry $NCO + a(NO, O_2, \text{or } NO_2) \rightarrow bN_2 + cCO_2$.

reactant, correction must be made for the partial decomposition of $NO_2$ to NO and $O_2$ and for the consumption of gas-phase $NO_2$. In all cases, the reaction of CN species was assumed to occur via an Eley–Rideal process. This assumption was confirmed for reaction in $NO_2$, where it was observed that the rate was first order in $NO_2$. Values of the rate coefficients are listed in Table 2. The magnitudes of the rate coefficients determined from the measurements of $^{13}CO_2$ and $N_2$ formation are very similar, confirming that both products arise from a common precursor. With the exception of the experiment carried out in $O_2$, the rate coefficients determined from an analysis of the decay in the infrared band intensity for adsorbed CN species are virtually identical to those determined from an analysis of $^{13}CO_2$ and $N_2$ formation. This also supports the conclusion that the dominant source of $CO_2$ and $N_2$ is adsorbed CN.

To assess the possible role of adsorbed CN as a reaction intermediate in the reduction of NO by $CH_4$, it is useful to recall how this species might be formed and consumed. Figure 4 presents a simplified form of the reaction scheme we have proposed previously (6). It is assumed that in the presence of $O_2$, equilibrium is rapidly achieved between NO, $O_2$, and $NO_2$; this has been confirmed experimentally (3). It is proposed that adsorbed $NO_2$ reacts with gas-phase $CH_4$ to produce $H_2O$ and adsorbed CN. The intermediate in this process is envisioned to be $CH_3NO$. While this species was not observed in the present studies, Bergman and coworkers demonstrated its existence as a ligand in Co and Ru complexes (15) and, in a related study, showed that on heating, ligated $CH_2NO$ decomposes to CN and $H_2O$ (16). The last step in the sequence is the reaction of gas-phase $NO_2$ with adsorbed CN species to produce $N_2$ and $CO_2$, the occurrence of which is observed in the present study.

If CN species are the reaction intermediates, the rate of their consumption in reaction 7 should be equivalent to the overall rate of $N_2$ formation derived from the reduction of NO. At 450°C and for a feed containing 3600 ppm NO, 6.0% $O_2$, and 1.1% $CH_4$ flowing at 100 $cm^3$/min, the turnover frequency (TOF) for $N_2$ formation is $8.4 \times 10^{-4}$ $s^{-1}$ and the concentration of $NO_2$ is 910 ppm (6). The value of $\theta_{CN}$ required to achieve the observed TOF can be calculated from the relationship

$$\mathrm{TOF} = kC_{\mathrm{NO_2}}\theta_{\mathrm{CN}}.$$

Taking the value of $k$ from Table 2 and the observed concentration of $NO_2$, we determine the value of $\theta_{CN}$ to be 0.01. Consistent with these calculations, our previously reported *in situ* infrared observations (6) have shown that the surface concentration of CN species is below the detectable level when NO is reduced by $CH_4$ in the presence of $O_2$. These results suggest that CN species are sufficiently reactive in the presence of $NO_2$ to be considered as intermediates in the formation of $N_2$ and $CO_2$ via reaction 7 in Fig. 4.

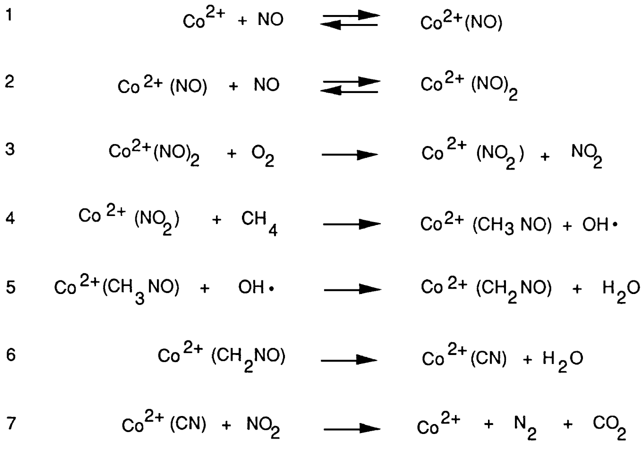

**FIG. 4.** Proposed mechanism for NO reduction by $CH_4$ in the presence of $O_2$.

## CONCLUSIONS

$Co^{2+}$–CN and $Al^{3+}$–NCO are observed by *in situ* infrared spectroscopy during the reduction of NO by $CH_4$. From an estimation of the relative surface concentrations of CN and NCO surface species, and analysis of the stoichiometry of product formation when these species react with $NO_2$, $O_2$, and NO, it is concluded that the species in greatest concentration is CN. The rate of reaction of CN species with $NO_2$ is an order of magnitude higher than the rate of reaction with $O_2$ or NO. At 450°C, the rate coefficients (based on $CO_2$) for the reaction of CN species with $NO_2$, $O_2$, and NO are $8.5 \times 10^{-5}$, $1.9 \times 10^{-6}$, and $3.3 \times 10^{-7}$ $s^{-1}$ $ppm^{-1}$, respectively. Calculations show that the reactivity of CN groups is high enough for these species to be considered as reaction intermediates for the formation of $N_2$ and $CO_2$ during the reduction of NO by $CH_4$ in the presence of $O_2$. NCO species associated with $Al^{3+}$ cations of the zeolite are much less reactive than $Co^{2+}$–CN species and are likely formed by the oxidation of the latter species and subsequent migration to $Al^{3+}$ cations.

## ACKNOWLEDGMENTS

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