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NO reduction by CH_4 over La_2O_3: temperature-programmed reaction and *in situ* DRIFTS studies

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The chemistry between NO_x species adsorbed on La_2O_3 and CH_4 was probed by temperature-programmed reaction (TPR) as well as *in situ* DRIFTS. During NO reduction by CH_4 in the presence of O_2, NO_3^- does not appear to activate CH_4, thus either an adsorbed O species or an NO_2^- species is more likely to activate CH_4. In the absence of O_2, a different reaction pathway occurs and NO^- or $(N_2O_2)^{2-}$ species adsorbed on oxygen vacancy sites seem to be active intermediates, and during NO reduction with CH_4 unidentate NO_3^-, which desorbs at high temperature, behaves as a spectator species and is not directly involved in the catalytic sequence. Because reaction products such as CO_2 or H_2O as well as adsorbed oxygen cannot be effectively removed from the surface at lower temperatures, steady-state catalytic reactions can only be achieved at temperatures above 800 K, even though formation of N_2 and N_2O from NO was observed at much lower temperature during the TPR experiments.

Keywords: NO reduction by CH_4 over La_2O_3, TPR, *in situ* DRIFTS

1. Introduction

During the past few years, rare earth oxides have been found to be good materials for the selective catalytic reduction (SCR) of NO with CH_4 at temperatures above 800 K [1–4]. Although rates are too low for application to mobile sources such as diesel engines, specific activity is high enough around 873 K to offer the possibility of use with stationary sources such as combined-cycle electrical generating plants. At 973 K, the specific activity (mol/s m^2) and turnover frequency on La_2O_3 are significantly higher than comparable values on Co/ZSM-5 [5]. The mechanism and characterization of SCR with CH_4 over metal ion-exchanged zeolites has been widely discussed [6–12], but studies related to metal oxides are limited [13–16]. Reaction mechanisms for NO reduction by CH_4 on La_2O_3 have been proposed, and these models provided rate expressions that have successfully fitted the experimental kinetic data [14,17]. The surface chemistry of NO adsorbed on La_2O_3 has been studied recently by *in situ* FTIR and temperature-programmed desorption [22–24]. In the present study, temperature-programmed reaction (TPR) of adsorbed NO species on La_2O_3 with CH_4 was used to complement these previous studies by probing the reactivity of surface groups. *In situ* DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy) under steady-state reaction conditions was also applied to search for any intermediates that might participate in the reaction sequence. The combination of these two techniques was used to learn more about the surface chemistry involved in this reaction.

2. Experimental

The La_2O_3 sample was prepared by calcining a commercial La_2O_3 powder (99.99%, Rhone-Poulenc Inc.) at 1023 K under 50 sccm O_2/min for 10 h. The sample was stored in a desiccator after calcination. The surface area of this La_2O_3 sample was 2.4 m^2/g, as measured by N_2 adsorption at 77 K.

The temperature-programmed reaction (TPR) experimental procedure was as follows. Prior to the TPR runs, the La_2O_3 sample (ca. 240 mg) was pretreated in He at 973 K for 1 h, cooled, exposed to a stream of 4.01% NO in He at 300 K for 30 min, and then purged with pure He until no NO was detected in the effluent gas. During the TPR runs, the reductant in a carrier gas was flowed through the reactor at 30 cm^3/min and the sample was heated at a linear ramp rate of 50 K/min. The gases evolved during the TPR runs were monitored by a UTI quadrupole mass spectrometer, as described elsewhere [20]. ^{15}NO was used in some experiments in order to distinguish between certain species which have the same mass number, such as N_2 and CO ($m/e = 28$), and N_2O and CO_2 ($m/e = 44$). The reactor system was modified to allow the reactor cell to be either evacuated or operated under steady-state flow and also to allow the gas lines to be purged before introduction of the gas (figure 1). The adsorption of ^{15}NO was conducted by either admitting the isotopic gas into a closed and pre-evacuated (<1 Torr) reactor containing La_2O_3, with $P_{^{15}NO} \approx 25$ Torr at 300 K for 15 min, or by injecting ten 250 μl pulses of ^{15}NO into a He carrier gas stream which was flowing through the catalyst bed at 20 cm^3/min. After the NO exposure at 300 K and a He purge, the catalyst was heated at a rate of 50 K/min from 300 to 973 K inflowing a mixture of either 1.01% CH_4 in He or 0.83% $CH_4 + 1.67\%$

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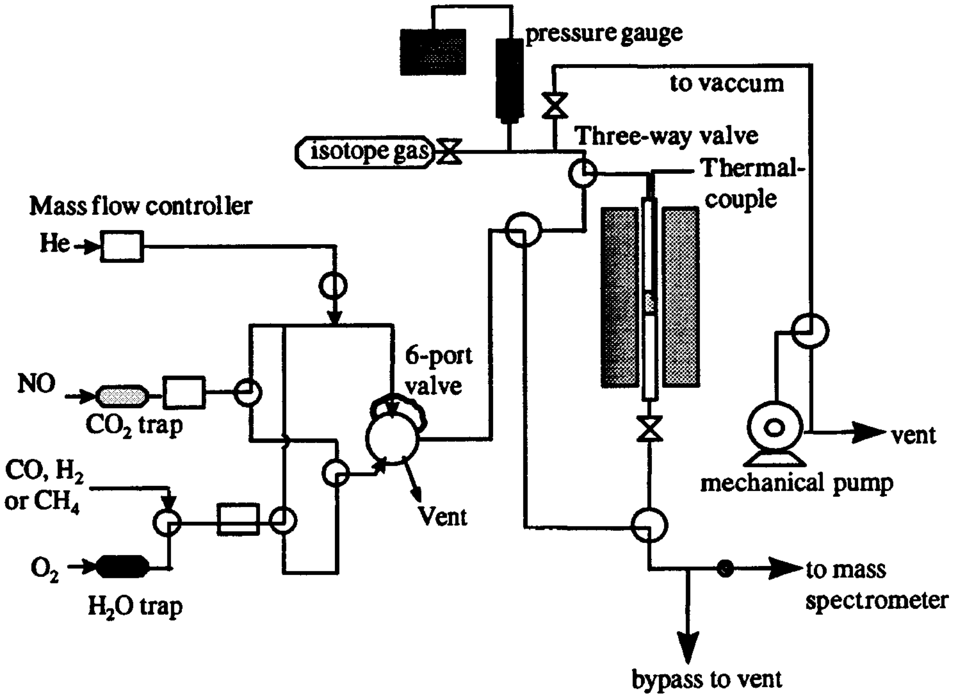

Figure 1. Reactor system for TPD and TPR experiments.

O_2 in He, with $^{15}NO/CH_4$ and $^{15}NO/(CH_4 + O_2)$ designating the former and latter runs, respectively. The notation A/B indicates A as the adsorbate and B as the gas (or gases) in the carrier gas during the TPR runs. In addition, $(NO + O_2)/CH_4$ TPR was carried out by exposing the catalyst to a gas mixture containing 3.2% NO + 2.0% O_2 in He, purging in He, then heating in 0.5% CH_4 in He from 300 to 973 K. The gases used were UHP grade He (99.999%), 4.01% NO in He, 1.01% CH_4 in He and 10% O_2 in He (all from MG Ind.). The desired gas concentration was achieved by further dilution with pure He. NO was passed through both an Ascarite trap and a Drierite trap to strip CO_2 and moisture. He and O_2 were passed through molecular sieve moisture traps. Isotopically labeled ^{15}NO from either Isotec Inc. (99%) or Cambridge Isotope Lab. (98%) was used as received. All experiments were conducted at 1 atm.

In situ DRIFTS was conducted with a Mattson Research Series 10000 FTIR with wavenumbers detected from 700 to 4000 cm^{-1}. A diffuse reflection cell (Harrick Scientific-DRA) with NaCl windows was connected to a gas handling system to allow measurements under controlled gas environments and at temperatures up to 800 K in flowing Ar, as described elsewhere [19]. The gases used were Ar (UHP grade, 99.999%, MG Ind.), 10.0% O_2/90% Ar (MG Ind.) and 4.11% NO in Ar (Matheson). Ar was passed through a UOP model P100 purifier and the 4.11% NO in Ar was passed through an Ascarite trap to remove CO_2. The gases were fed at atmospheric pressure in all pretreatments and experiments. The La_2O_3 samples were pretreated *ex situ* in He at 973 K for 1 h and then stored in a N_2 dry box without air exposure. Transfer of the catalysts to the IR cell was conducted in the N_2 dry box. The sample was then pretreated *in situ* in Ar at 800 K for 1 h before any experiment.

3. Results

Figure 2(a) shows the results from the TPR of ^{15}NO with CH_4 ($^{15}NO/CH_4$), while the TPD spectra after ^{14}NO adsorption on this sample at 300 K are shown in figure 2(b) for comparison. During the TPR experiment, ^{15}NO desorbed at 450 and 730 K, $^{15}N_2$ was formed primarily at 475, 650 and 760 K, $^{15}N_2O$ was formed at 475 K, and CO_2 was detected above 800 K (figure 2(a)). When heating in a mixture of 0.83% CH_4 and 1.67% O_2 in He, three ^{15}NO desorption peaks were observed at 410, 690 and 800 K, with the broad 690 K peak covering a temperature range from 500 to 900 K (figure 3). Two $^{15}N_2$ desorption peaks were detected, i.e., a weak, very broad band from 500 to 900 K with a maximum near 700 K, and a well defined peak at 800 K. A small amount of $^{15}N_2O$ was detected at 800 K concomitant with the ^{15}NO and $^{15}N_2$ bands. The combustion reaction between CH_4 and O_2 did not start until nearly 800 K, at which point CO_2 formation began along with O_2 consumption.

When La_2O_3 was exposed to NO at 300 K in the presence of O_2, the TPD results (heating in He) showed a small NO desorption peak at 360 K, while both NO and O_2 desorbed at 770 K. The latter peaks were greater in intensity and shifted 30 K lower compared to those obtained when only NO was present during adsorption (e.g., compare figure 4(b) with 2(b)). Heating La_2O_3 in a stream of 1.01% CH_4 in He after the same exposure to ^{14}NO and O_2 (($^{14}NO + O_2)/CH_4$ TPR) at 300 K did not affect the

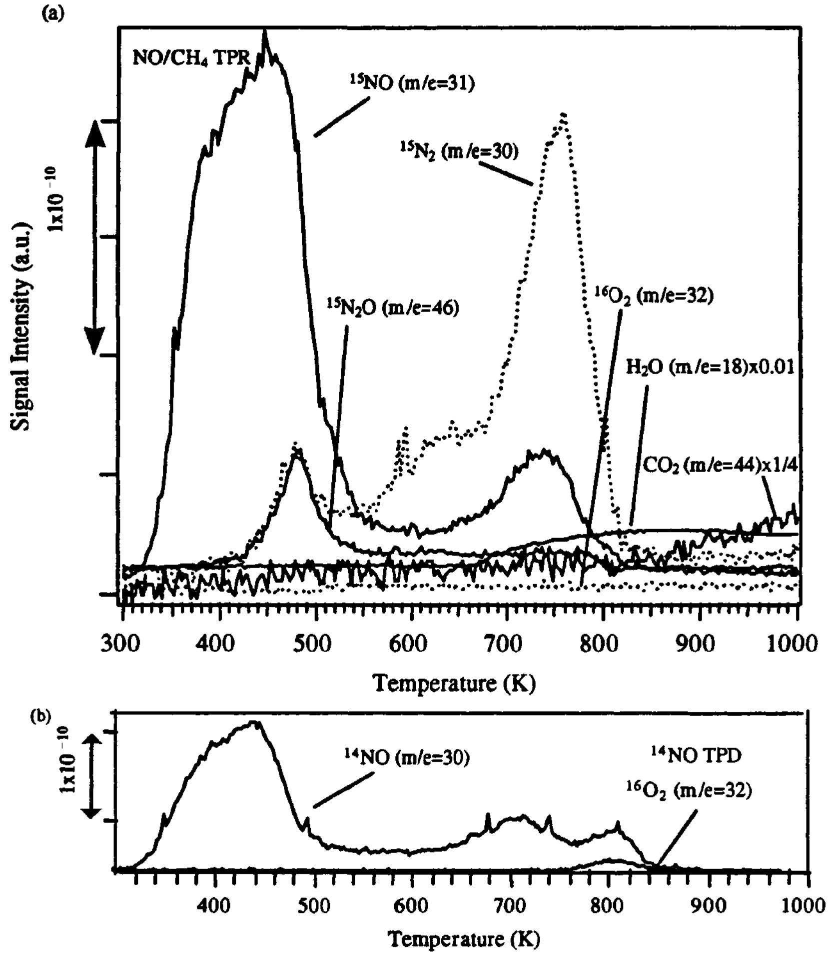

Figure 2. (a) TPR of preadsorbed ^{15}NO on La_2O_3 using 1.01% CH_4 in He mixture ($^{15}NO/CH_4$) and (b) TPD of ^{14}NO adsorbed on La_2O_3 at 300 K.

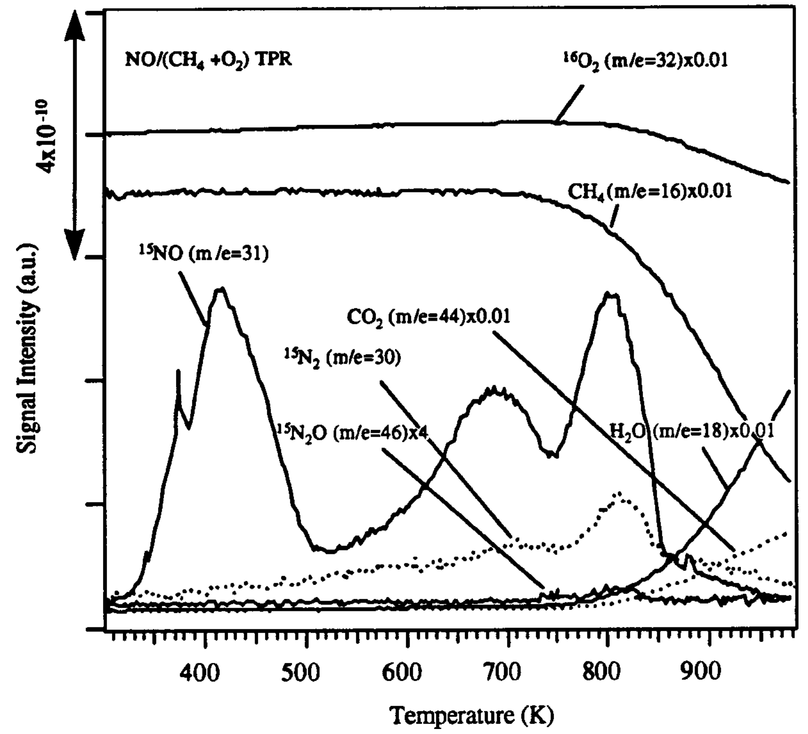

Figure 3. TPR on ^{15}NO preadsorbed on La_2O_3 in a stream containing 0.83% CH_4 and 1.67% O_2 in He ($^{15}NO/(CH_4 + O_2)$).

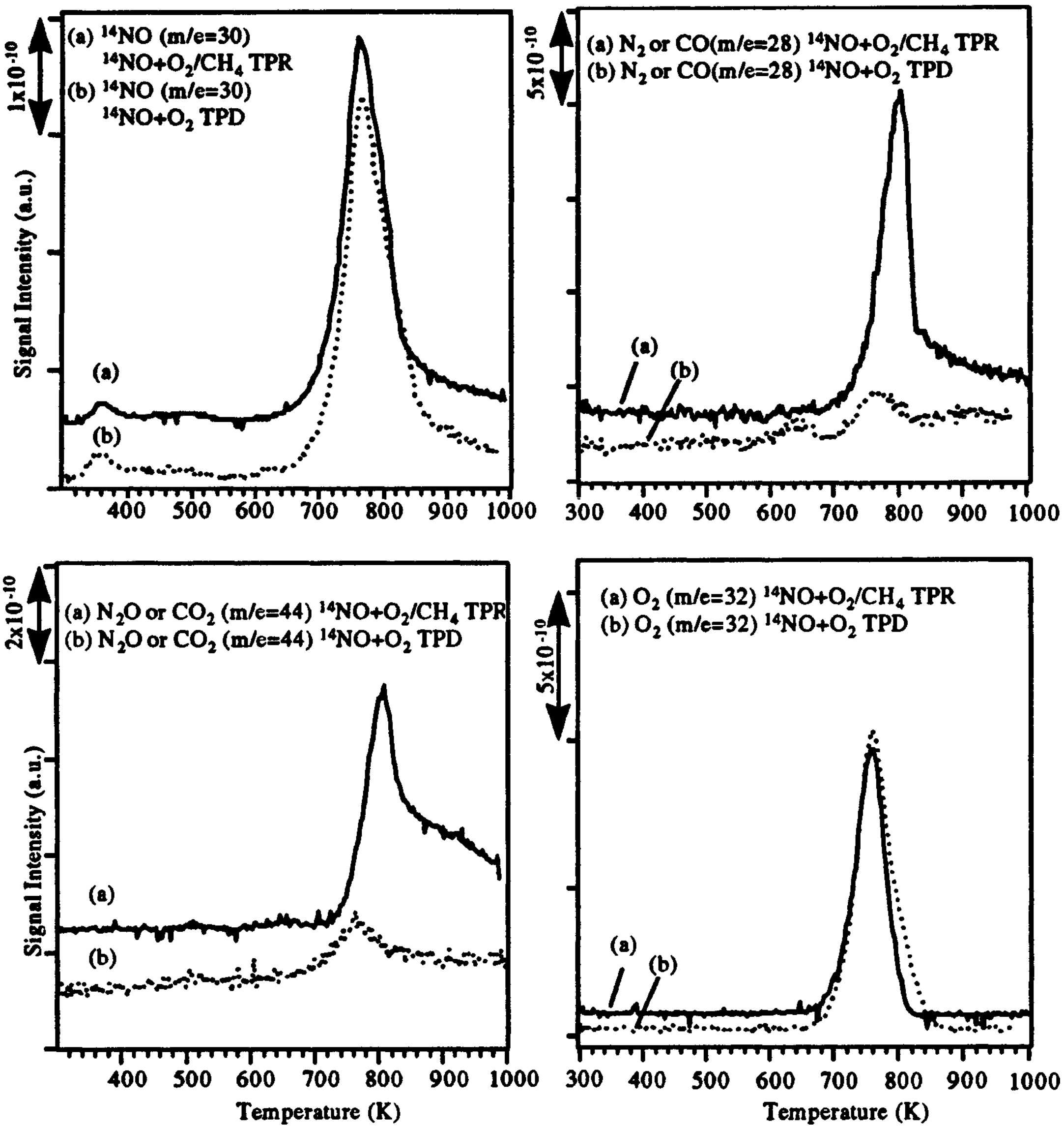

Figure 4. (a) TPR of ^{14}NO preadsorbed on La_2O_3 in the presence of O_2 at 300 K while heating in 1.01% CH_4 in He to 973 K (($NO + O_2$)/CH_4); and (b) TPD of NO preadsorbed in the presence of O_2 at 300 K while heating in He.

low-temperature NO desorption peak (figure 4), and the NO and O_2 desorbed concomitantly at 760 K. The spectra for both $m/e = 44$ and $m/e = 28$ showed a sharp peak at 800 K followed by a broad, tailing band. The spectrum for $m/e = 28$ represents desorption of N_2 and CO as well as CO from CO_2 fragmentation. The spectrum for $m/e = 44$ contains N_2O and CO_2; nevertheless, by examining C^+ and N^+ fragmentation bands [21], one can tell that N_2 or N_2O formed as a sharp peak at 800 K, while CO_2 ($m/e = 44$) or CO ($m/e = 28$), through readily desorbed at 800 K, also contributes to the broad feature above 810 K.

In situ DRIFT spectra taken in the presence of a $NO + CH_4$ or a $NO + CH_4 + O_2$ mixture flowing over La_2O_3 at 800 K are illustrated in figures 5 and 6, respectively. The spectra are referenced to that of a pretreated La_2O_3 surface at 800 K before introducing the reactants. When flowing $NO + CH_4$, unidentate carbonates were formed on the surface as indicated by bands at 1540, 1354, 1080 and 850 cm^{-1} [22], while a very weak band at 2167 cm^{-1} represents a CN stretch (figure 5(a)) [23,24]. The $(N_2O_2)^{2-}$ and NO^- species (broad band at 1123 cm^{-1}), which were observed when flowing NO alone, were not observed. Exposure of La_2O_3 to an $NO + O_2$ mixture at 800 K produced bands at 1540, 1262 and 1006 cm^{-1}, which have previously been assigned to unidentate nitrate species (figure 6(b)) [19]. When CH_4 was added to the $NO + O_2$ gas stream, the band intensities at 1540, 1262 and 1006 cm^{-1} for unidentate nitrate species, through decreased, were still significant (figure 6(a)). Gas-phase CO_2 (2348 cm^{-1}) and unidentate carbonate (1540, 1362, 1080 and 850 cm^{-1}) were formed either from the reaction between CH_4 and NO or from CH_4 combustion.

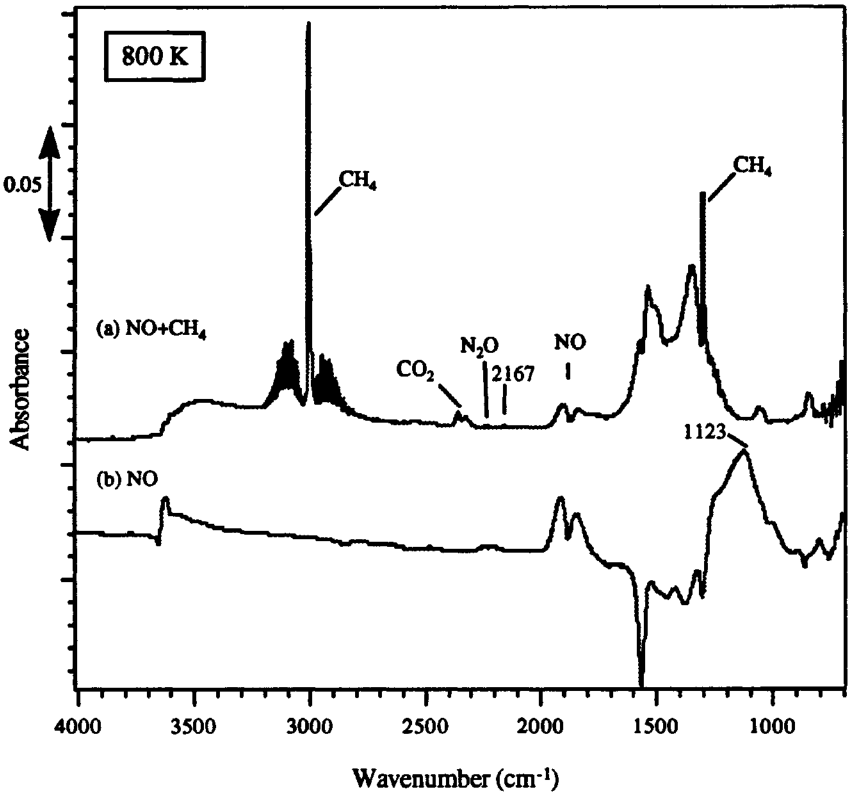

Figure 5. *In situ* DRIFT spectra during the flow of (a) NO + CH_4 or (b) 4% NO/Ar over La_2O_3 at 800 K. Bands for gas-phase molecules are designated.

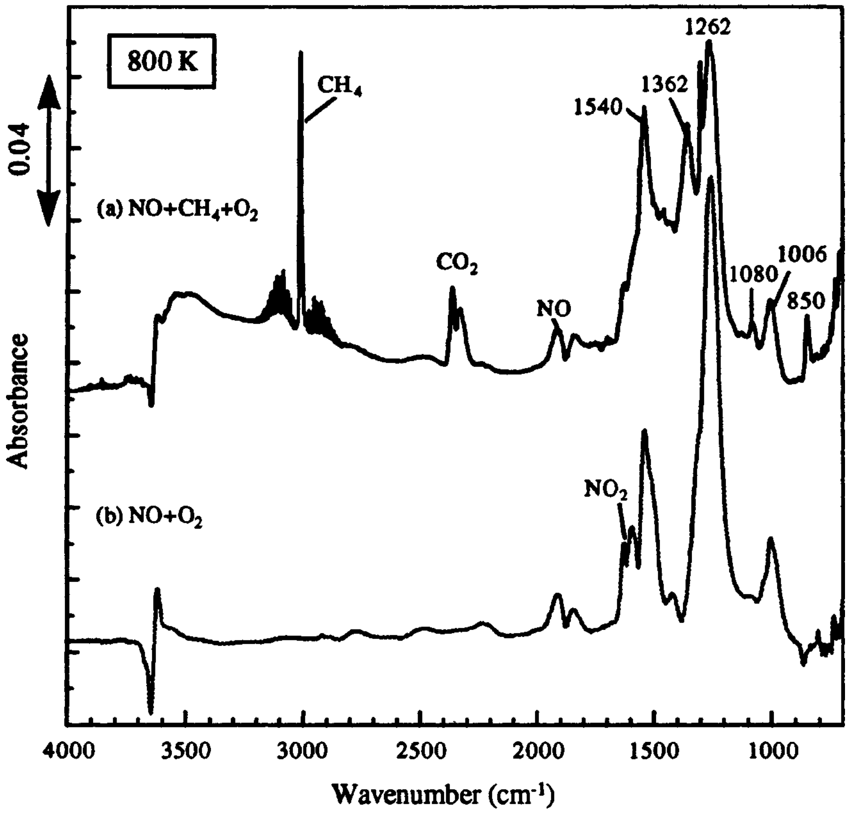

Figure 6. *In situ* DRIFT spectra during the flow of mixtures of: (a) NO + O_2 + CH_4 and (b) NO + O_2 over La_2O_3 at 800 K. Unidentate nitrates have bands at 1540, 1262 and 1006 cm^{-1} and unidentate carbonates have bands at 1540, 1362, 1080 and 850 cm^{-1}. Bands for gas-phase molecules are designated.

4. Discussion

It is of interest to compare the TPR results with the corresponding TPD results and to examine the transient behaviour of each surface species when exposed to CH_4. In previous TPD and DRIFTS studies of NO adsorbed on La_2O_3, it was found that the low-temperature NO desorption peak corresponds to the decomposition of chelated nitrite (NO_2^-), nitrito (ONO^-) and bridging nitrate (NO_3^-) species, while the middle desorption peak near 700 K represents loss of nitric oxide ions (NO^-) and hyponitrite ions ($(N_2O_2)^{2-}$), and the highest temperature NO desorption peak at 800 K represents decomposition of unidentate nitrate (NO_3^-) species [19,20]. In the absence of O_2, the ($^{15}NO/CH_4$) TPR shows that CH_4 can readily react with adsorbed NO_x species at 475 K to produce N_2 and N_2O. More pronounced N_2 production began at 700 K, whereas N_2O production was small and much less than that at 475 K. The highest NO desorption peak at 800 K in the TPD experiment was not present in the NO/CH_4 TPR experiment, indicating that this species had already reacted with CH_4 at lower temperatures. Furthermore, since N_2 production was maximized at 760 K, rather than 800 K, it is possible that NO_3^- species which decomposed near 800 K in the TPD experiment transformed to less stable adsorbed species such as NO_2^- or NO^- and interacted with CH_4 or a CH_x species at 760 K. This could occur on some of the vacant, lower-temperature NO adsorption sites not blocked by products from the reaction during TPR. Although one can argue that NO_3^- species simply interact with CH_4 at 760 K, this seems to be less probable for the following reasons. The $NO/(CH_4 + O_2)$ TPR results for NO reduction in the presence of O_2 (figure 3) show that, although formation of N_2 at 700 K was seen in this experiment, it occurred to a greater extent at 800 K, at which temperature NO_3^- species are decomposed. If NO_3^- species reacted directly with CH_4 at 760 K, the N_2 peak would be expected to be maximized at 760 K and the amount of NO desorbed at 800 K should be diminished or shifted to a lower temperature. In fact, in this $NO/(CH_4 + O_2)$ TPR experiment, the gas-phase O_2 appears to interact with the NO desorbed at lower temperature and allow it to readsorb to form NO_3^- species, as evidenced by the enhancement of the high-temperature NO desorption peak. This could be due to the presence of NO_2. Evidence for this comes from the experiment in which NO was adsorbed at 300 K in the presence of O_2 and then reacted with CH_4, i.e., the $(NO + O_2)/CH_4$ run shown in figure 4. In this case N_2 formation occurs with only one peak at 810 K, but NO_3^- decomposition peaked earlier at about 760 K. Furthermore, O_2 may also competitively adsorb on the lower-temperature NO desorption sites because these sites for NO_2^-, NO^- or $(N_2O_2)^{2-}$ species involve either one or two oxygen vacancies [19,20]; therefore, this would prevent the transformation of NO_3^- species to species more reactive with CH_4. In addition, NO^- and/or $(N_2O_2)^{2-}$ species on La_2O_3 were observed by *in situ* FTIR while flowing an NO/Ar mixture at 800 K, but they disappeared when an $NO/CH_4/Ar$ mixture was passed over the catalyst. During the NO/CH_4 TPR, desorption of water started at ∼680 K and desorption of CO_2 began at ∼800 K although they must be formed when N_2 and N_2O are first produced at 475 K, thus both H_2O and CO_2 react with the La_2O_3 surface to form hydroxide, hydroxycarbonate and carbonate species which may transform the surface and prevent regeneration of the adsorption sites for NO at this low temperature. This is consistent with previous studies of steady-state NO reduction by CH_4 which showed that stable activity was achieved only at temperatures higher than 800 K [1–3].

The mechanism of selective catalytic reduction (SCR) of NO with CH_4 over oxides has been widely discussed [6–16]. Cowan et al. reported a primary kinetic isotope effect of ∼2 for the reaction of CH_4 versus CD_4 with NO in excess O_2 over Co-ZSM5, suggesting that the rate-determining step involves breaking of a carbon–hydrogen bond [22]. A similar isotope effect was seen with a La_2O_3 catalyst [25]. With metal-exchanged zeolite systems, it has been proposed that the activation of CH_4 occurs via adsorbed NO_2 species [6–9,11,12], although NO_3-type species were also suggested to be involved in the reaction over a Cu/mordenite catalyst [10]. Bell and coworkers have found that CN species observed by IR spectroscopy during NO reduction by CH_4 over Co-ZSM5 are likely to be reaction intermediates, based on an analysis of their reactivity with NO or NO_2 [11]. They postulated that CN species can be formed by the interaction of adsorbed NO_2 with CH_4, and the intermediate in this process is envisioned to be CH_3NO. Vannice et al. have proposed a mechanism on La_2O_3 in excess O_2 with a rate-determining step involving a reaction between adsorbed NO_2 and adsorbed CH_4 to generate a methyl species and the formation of CN-containing species [14].

A simplified mechanism for the sequence of elementary steps proposed by Zhang and coworkers is as follows [14]:

$$4\left[NO + * \overset{K_{NO}}{\rightleftharpoons} NO*\right] \tag{1}$$

$$2\left[O_2 + 2* \overset{K_{O_2}}{\rightleftharpoons} 2O*\right] \tag{2}$$

$$2\left[CH_4 + * \overset{K_{CH_4}}{\rightleftharpoons} CH_4*\right] \tag{3}$$

$$3\left[NO* + O* \overset{K_{NO_2}}{\rightleftharpoons} NO_2* + *\right] \tag{4}$$

$$2\left[CH_4* + NO_2* \xrightarrow{k} CH_3* + HNO_2*\right] \quad \text{rds} \tag{5}$$

$$2HNO_2* + 2CH_3* + NO_2* + NO* + O* \overset{K}{\rightleftharpoons} 2N_2 + 2CO_2 + 3H_2O + 7* \tag{6}$$

$$4NO + 2CH_4 + 2O_2 \rightarrow 2N_2 + 2CO_2 + 4H_2O$$

Here $*$ represents an active site, step (5) is assumed to be the rate-determining step (rds), and all other steps are then quasi equilibrated. Step (6) is comprised of eight elementary steps which include the formation and disappearance of CN-containing species such as $CN*$, $NCO*$

and HCN$*$ [14]. The two former species have also been proposed to exist on Co/ZSM-5 during this reaction [11].

When O_2 is co-fed with NO, unidentate NO_3^- species are clearly formed preferentially on La_2O_3 surfaces, even in the presence of CH_4 at 800 K, as observed by both DRIFTS (figure 6) as well as by TPR (see figure 3 and, especially, figure 4). In the presence of O_2, the surface concentration of NO_3^- species is much higher, and N_2 formation seems to occur at a higher temperature via a pathway different from that during NO reduction by CH_4 in the absence of O_2. This is attributed to the requirement that some vacant sites must be made available, and decomposition of the NO_3^- species accomplished this. Lunsford and coworkers have detected gas-phase $CH_3^\bullet$ radicals during the reaction between CH_4 and NO in the presence of O_2 over Sr/La_2O_3 and Ba/MgO, and they suggested that these radicals react with NO, presumably to form CH_3NO, which is believed to be an intermediate in the reaction [15,16]. The enhancement by O_2 was attributed to its role in the generation of gas-phase $CH_3^\bullet$ radicals. They also suggested that the reaction of NO with CH_4 in the absence of O_2 may occur via a nonradical pathway because no $CH_3^\bullet$ radicals were observed during the reaction of NO with CH_4. Unfortunately, the NO/($CH_4 + O_2$) and (NO $+ O_2$)/CH_4 TPR experiments conducted here do not allow us to determine which species is responsible for the activation of CH_4. The nitrate species that are stable at high temperatures are not capable of activating CH_4, as seen from the results from the NO/CH_4 and NO/($CH_4 + O_2$) experiments (figures 2 and 3); however, since the nitrate species decompose at 770 K when the coverage is about half monolayer [20], gas-phase concentrations of NO and O_2 are high during the (NO $+ O_2$)/CH_4 TPR experiment and conditions become more similar to the NO/($CH_4 + O_2$) run. It is suggested that under reaction conditions when both gas-phase NO and O_2 are present, either the adsorbed O or NO_2 species is more likely to activate CH_4.

5. Summary

Combing these new TPR and *in situ* DRIFT spectroscopic results under reaction conditions with previous kinetic, TPD and DRIFTS studies of NO adsorption and reaction on La_2O_3 [14,17–21], the surface chemistry associated with the interaction between NO and CH_4 has been clarified. In the absence of O_2, the reaction pathway for NO reduction by CH_4 appears to occur via NO^- or $(N_2O_2)^{2-}$ species reacting with adsorbed CH_4, whereas the nitrite or nitro species (NO_2^-) are not stable at reaction temperatures. The unidentate NO_3^- species that are stable at high temperatures do not directly interact with CH_4, but they may transform to a reactive adsorbed form such as NO^- or $(N_2O_2)^{2-}$ if adjacent vacant sites are available. The presence of oxygen inhibits the formation of NO^- or $(N_2O_2)^{2-}$ species, and this implies that NO reduction by CH_4 in excess O_2 follows a reaction path different from that in the absence of O_2. It is suggested that either an adsorbed O species or an NO_2^- species is responsible for the activation of CH_4 to form a methyl radical which rapidly reacts on the surface, because NO_3^- species formed preferentially on La_2O_3 when exposed to NO and O_2 do not appear to activate CH_4. High temperatures are required to achieve a catalytic cycle during NO reduction by CH_4 in the presence or absence of O_2 because neither the by-products of CO_2 or H_2O nor adsorbed oxygen can be effectively desorbed from the surface at lower temperatures to regenerate the active sites.

Acknowledgement

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References

[1] X. Zhang, A.B. Walters and M.A. Vannice, Appl. Catal. B 4 (1994) 237.
[2] X. Zhang, A.B. Walters and M.A. Vannice, J. Catal. 155 (1995) 290.
[3] X. Zhang, A.B. Walters and M.A. Vannice, Catal. Today 27 (1996) 41.
[4] X. Zhang, A.B. Walters and M.A. Vannice, Appl. Catal. B 7 (1996) 321.
[5] C. Shi, A.B. Walters and M.A. Vannice, Appl. Catal. B 14 (1997) 175.
[6] Y. Li, T.L. Slager and J.N. Armor, J. Catal 150 (1994) 388.
[7] E. Kikuchi and K. Yogo, Catal. Today 22 (1994) 73.
[8] J.N. Armor, Catal. Today 26 (1995) 147.
[9] D.B. Lukyanov, E.A. Lombardo, G.A. Sill, L.J. d'Itri and W.K. Hall, J. Catal. 163 (1996) 447.
[10] M. Shimokawabe, K. Itoh and N. Takezawa, Catal. Today 36 (1997) 65.
[11] L. Lobree, A.W. Aylor, J.A. Reimer and A.T. Bell, J. Catal. 169 (1997) 188.
[12] E.A. Lombardo, G.A. Sill, L.J. d'Itri and W.K. Hall, J. Catal. 173 (1998) 440.
[13] H. Hamada, Catal. Today 22 (1994) 21.
[14] M.A. Vannice, A.B. Walters and X. Zhang, J. Catal. 159 (1996) 119.
[15] S. Xie, T.H. Ballinger, M.P. Rosynek and J.H. Lunsford, in: *11th Int. Congr. on Catalysis, 40th Anniversary* (Elsevier, Amsterdam, 1996) p. 711.
[16] S. Xie, M.P. Rosynek and J.H. Lunsford, Catal. Lett. 43 (1997) 1.
[17] S.-J. Huang, A.B. Walters and M.A. Vannice, Appl. Catal. B 17 (1998) 183.
[18] B. Klingenberg and M.A. Vannice, Appl. Catal. B 21 (1999) 19.
[19] S.-J. Huang, A.B. Walters and M.A. Vannice, submitted for publication.
[20] S.-J. Huang, A.B. Walters and M.A. Vannice, submitted for publication.
[21] S.-J. Huang, Ph.D. thesis, The Pennsylvania State University (1999).
[22] A.D. Cowan, R. Dumpelmann and N.W. Cant, J. Catal. 151 (1995) 356.
[23] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Part B, 5th Ed. (Wiley, New York, 1997).
[24] G. Socrates, *Infrared Characteristic Group Frequencies: Tables and Charts*, 2nd Ed. (Wiley, New York, 1994).
[25] C. Shi and M.A. Vannice, unpublished data, 1997.