Catalysis Letters, Vol. 115, Nos. 3–4, June 2007 (© 2007)
DOI: 10.1007/s10562-007-9081-1

FT-IR spectroscopic investigation of the surface reaction of CH_4 with NO_x species adsorbed on $Pd/WO_3–ZrO_2$ catalyst

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Received 9 March 2007; accepted 9 March 2007

The interaction of methane at various temperatures with NO_x species formed by room temperature adsorption of $NO + O_2$ mixture on tungstated zirconia (18.6 wt.% WO_3) and palladium(II)-promoted tungstated zirconia (0.1 wt.% Pd) has been investigated using *in situ* FT-IR spectroscopy. A mechanism for the reduction of NO over the Pd-promoted tungstated zirconia is proposed, which involves a step consisting of thermal decomposition of the nitromethane to adsorbed NO and formates through the intermediacy of cis-methyl nitrite. The $HCOO^-$ formed acts as a reductant of the adsorbed NO producing nitrogen.

KEY WORDS: *in situ* FT-IR; WO_3/ZrO_2; $Pd^{2+}/WO_3–ZrO_2$; surface NO_x complexes; reactivity toward CH_4; CH_4-SCR; mechanism; decomposition of nitromethane; cis-methyl nitrite.

1. Introduction

The removal of nitrogen oxides from flue gases of thermal power plants using methane as reductant (CH_4-SCR) has emerged as a cost-effective and safe technology that can replace existing SCR with ammonia. Zeolites containing Co or/and Pd were found to be particularly active in the CH_4-SCR in the presence of oxygen [1–5]. The main drawback of these catalysts is their low hydrothermal stability and deactivation by SO_2. The use of non-zeolitic support with strong acidity such as tungstated zirconia provides an alternative approach for improving the durability of the catalysts for CH_4-SCR of nitrogen oxides. In comparison to the zeolite-based catalysts, Pd-promoted tungstated zirconia is less sensitive to structural damages under moist conditions and displays good resistance toward SO_2 poisoning [6–8]. Tungstated zirconia is able to stabilize highly dispersed Pd^{2+} species (which are believed to be the active sites for catalytic reduction of NO with methane) in a similar manner as the acidic zeolites [6,7].

Many investigations have focused on the fundamental aspects of the reduction of NO catalyzed by Pd-exchanged zeolites. Regarding the reaction mechanism, Misono and co-workers [9,10] proposed reaction steps deduced from activity measurements, in which the oxidation of NO to NO_2 takes place on Pd and/or H^+ sites, followed by the dissociation of methane to CH_x species on Pd and subsequent reaction (assisted by protonic sites) between NO_2 and CH_x fragments to N_2 and CO_x. Moreover, these authors concluded that the C–H dissociation is not a rate-limiting step; reactions involving organic nitro species to N_2 could be slower. According to Adelman and Sachtler [11], adsorbed NO_x complexes associated with protons of the Pd-ZSM5 catalyst are able to activate the methane. The results of the in situ FT-IR investigation of Lobree *et al.* [12] reveal that the reduction of NO begins with the interaction between the methane and the NO adsorbed on the Pd^{2+} site rather than adsorbed NO_2 (nitrite species). It is assumed that in this process CH_2NO is produced, which decomposes to CN species and water. The nitrile reacts with NO or NO_2 to N_2 and CO_x. Recently, Shimizu *et al.* [13] presented spectroscopic evidence that nitrosyl species adsorbed on Pd^{2+} react with the methane producing NH_4^+ ions that are located on the acid sites of the Pd-H-MOR catalyst. The NH_4^+ species reduce the adsorbed NO to dinitrogen. The role of oxygen is to suppress the reduction of Pd^{2+} at high temperatures and to accelerate the rate of interaction between the adsorbed NO and NH_4^+ ions by oxidizing NO to NO_2. However, the reaction pathways from the activated methane and adsorbed NO to ammonia (NH_4^+ ions) have not been elucidated experimentally. It is important to note that ammonia has been proposed as possible intermediate in the reduction of NO with methane on Co-H-ZSM5 [14,15].

Resasco and co-workers [7] suggested from kinetic data that the activation of methane during the selective reduction of NO over $Pd/WO_3–ZrO_2$ catalyst is most probably initiated by adsorbed NO or NO_2 species.

In a recent article Sadykov *et al.* [16] reviewed the main features of the mechanism of the SCR of nitrogen oxides with methane, propane and propene in the presence of oxide systems containing transition

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metal cations. They concluded that inorganic surface nitrate complexes are key reaction intermediates. The mechanistic schemes proposed involve a reaction between the surface nitrates and the hydrocarbons or their activated fragments leading to the formation of organic nitro compounds in a rate-limiting step. The interaction of methane with NO_x complexes strongly adsorbed on catalysts based on anion-modified zirconias has been studied recently by using *in situ* FT-IR spectroscopy [17–19]. It has been concluded that the activation of methane over CoO_x/SO_4^{2-}–ZrO_2 catalysts [17] occurs on cobalt sites and the products of the latter process – formate species – are capable of selectively reducing the surface nitro-nitrato species. Tsyntsarski *et al.* [18] observed that the nitrates coordinated to cobalt ions of an analogous catalytic system react with the methane. Knözinger and coworkers [19] investigated the reactivity of surface nitrates adsorbed on tungstated zirconia toward methane. They found that at 473 K the NO_3^- species can interact with the hydrocarbon that is most probably activated by strong Brønsted acid sites. However, the possible intermediates in this process have been not elucidated. To the best of our knowledge mechanistic studies on the selective reduction of NO with methane on Pd-containing tungstated zirconia using *in situ* FT-IR spectroscopy have been not reported. This paper describes the results of the interaction of methane with surface NO_x complexes obtained by room-temperature adsorption of NO + O_2 mixture on Pd-promoted (0.1 wt.% Pd) and Pd-free tungstated zirconia (18.6 wt.% WO_3). The structural characterization of the materials and the results of identification of the NO_x species upon adsorption of NO and its co-adsorption with oxygen have been reported previously [20].

2. Experimental

2.1. Samples

Tungstated zirconia (notation WZ) was prepared by coprecipitation of aqueous solutions of $ZrOCl_2 \cdot 8H_2O$ (Merck) and ammonium metatungstate (Aldrich) with ammonia using polyvinyl alcohol (Aldrich) as a template according to a procedure described in detail in the literature [21]. The analytical content of WO_3 was 18.6 wt.%. Palladium-promoted tungstated zirconia (denoted Pd/WZ) was prepared by the impregnation of the WZ sample with a solution of $Pd(NO_3)_2 \cdot 2H_2O$ (Merck-Schuchardt) ensuring 0.1 wt.% of nominal palladium content. After drying the samples were calcined at 500 °C for 5 h. According to XRD, the materials obtained have tetragonal structure and contain randomly distributed mesoporous phase [20].

2.2. Infrared spectroscopy

The FT-IR spectra were recorded on a Bomem MB 102 FT-IR spectrometer equipped with a liquid-nitrogen cooled MCT detector at a resolution of 4 cm^{-1} (128 scans). The self-supporting discs were activated *in situ* by heating for 1 h in a vacuum at 500 °C, and in oxygen (100 Torr, passed through a trap cooled in liquid nitrogen) at the same temperature, followed by evacuation for 1 h at 500 °C. A specially designed transmission IR cell (Xenonum Scientific, USA) equipped with BaF_2 windows allowed recording of the spectra at elevated temperatures. The sample holder of the cell can be moved up and down relative to the light beam which allows detection of the gas-phase spectra. The FT-IR spectra of the samples are obtained by subtracting the spectra of the activated samples from the spectra recorded. The sample spectra are also gas-phase corrected.

In order to evaluate the ability of the catalyst containing pre-adsorbed NO_x species for methane activation, the following experiments were performed:

(i) A "Blank NO_x" experiment involving the formation of surface NO_x species by NO + O_2 adsorption, followed by evacuation at room temperature and heating the closed IR cell containing the NO_x-precovered catalyst at various temperatures.
(ii) A "Blank CH_4" experiment consisting of interaction of the activated catalyst with methane at elevated temperatures.
(iii) A "NO_x–CH_4" experiment in which the interaction of methane with the catalyst containing adsorbed NO_x species is studied at various temperatures.
(iv) Investigation of the routes of transformation of nitromethane adsorbed on the catalysts, and
(v) Investigation of the interaction between formaldehyde and NO adsorbed on the Pd/WZ catalyst.

The ability of the NO_x-precovered catalysts to activate the hydrocarbon can be evaluated by measuring the temperature dependence of the consumption of the strongly bound NO_x species in a methane atmosphere. If the catalyst contains NO_x species that can be reduced with methane, their surface concentration detected after the interaction with the hydrocarbon at elevated temperatures, should be lower than that obtained in the "Blank NO_x" experiment. In the absence of an interaction, the spectra detected should be similar to those obtained in the "Blank NO_x" experiments. The last two experiments were performed in order to confirm the identity of the reaction intermediates and to model their transformations on the catalyst surface.

Nitromethane and paraformaldehyde were supplied by Aldrich. The purity of the NO gas was 99.9% (Air Products).

3. Results

3.1. Blank NO_x experiment

Figure 1 shows the spectra of the WZ (panel A) and Pd/WZ samples (panel B) obtained in the "Blank NO_x" experiment. The pre-adsorbed NO_x species are created allowing the samples to stay in contact with NO + O_2 mixture (20 Torr, NO:O_2 = 1:2) for 30 min at room temperature followed by evacuation to 3.0×10^{-3} Torr (spectra RT). According to the results of our previous investigation [20], the absorptions in the 1650–1000 cm^{-1} region detected on both samples at room temperature (spectra RT) are characteristic of various types of surface nitrates. The band at 2134–2140 cm^{-1} corresponds to the ν(NO) stretching mode of NO^+ species [20]. The weak bands at 1867 and 1815 cm^{-1} observed on the Pd/WZ catalyst (figure 1(B)) belong to the ν(NO) stretching vibrations of NO adsorbed on Pd(II) sites in two different environments [20]. The NO_x species adsorbed on both samples disappear at 400 °C. The spectra of the gas phase over the Pd/WZ catalyst (figure 1(C)) indicate that NO_2 forms during the desorption of the surface NO_x compounds. In the case of the WZ sample, no gaseous NO_x species have been found most probably because of detection limits under the conditions of the existing path length of the IR cell. The spectrum of the WZ sample obtained after cooling to room temperature (figure 1(A), spectrum (RT)′) contains bands at 2108 and 1184 cm^{-1}, which correspond to adsorbed NO^+ and bidentate nitrito species, respectively [20]. Similar bands are observed upon room temperature adsorption of 10 Torr of NO (figure 1, spectrum RT(NO)). The band at 1608 cm^{-1} is assigned to the bending mode of adsorbed water molecules. They appear by recombination of the surface hydroxyls in the process of formation of adsorbed NO_x species at room temperature [20]. The higher intensity of the water band at 1608 cm^{-1} in the spectrum (RT)′ relative to that in spectrum (RT(NO)) is attributed to the fact that the high-temperature treatment under the conditions of the "Blank NO_x" experiment causes desorption of the surface hydroxyls, which readsorb as water molecules at room temperature. These results lead to the conclusion that, in contrast to the Pd/WZ catalyst, the main product of the decomposition of the surface nitrates on the WZ sample is NO.

3.2. "Blank CH_4" experiment

The spectra obtained upon heating the activated WZ and Pd/WZ samples under constant pressure of methane (60 Torr) in the closed IR cell (evacuated prior the admission of methane) in the temperature range 250–450 °C are shown in figure 2. Over the WZ sample (figure 2(A)) the oxidation of CH_4 starts at 250 °C, which is evident by the appearance of weak bands in the carboxylate–carbonate region at 1660–1655, 1610–1608 and about 1550–1520 cm^{-1} and absorption in the ν(OH) stretching region. Due to the various surface structures possible, an unequivocal identification of the adsorbed

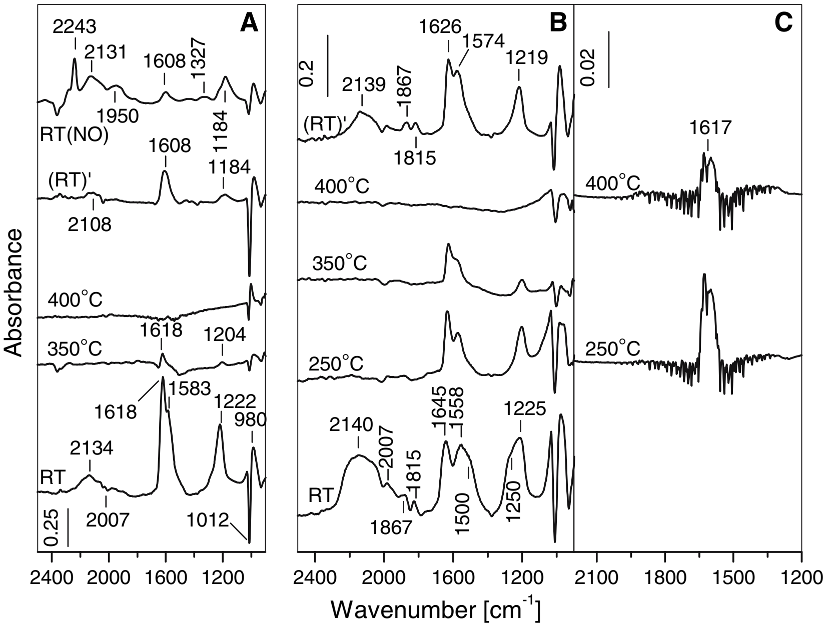


Figure 1. FT-IR spectra of the samples WZ (panel A) and Pd/WZ (panel B) taken after adsorption of NO + O_2 mixture (10 Torr, NO:O_2 = 1:2) for 30 min at room temperature followed by evacuation to 3×10^{-3} Torr, (RT), after heating the closed IR cell for 15 min at the indicated temperatures and after cooling to room temperature (RT)′. Spectrum RT(NO) in panel A is obtained by room-temperature adsorption of NO (10 Torr) on the WZ sample. Panel C: Spectra of the gas phase detected in the presence of the sample Pd/WZ (RT = room temperature, NO = nitrogen oxide).

species is difficult. Absorption bands located between 1680 and 1620 cm^{-1} can be assigned either to the $\nu(C=O)$ stretching vibration of adsorbed carboxylic acid (most probably formic acid [17,22–24]) or bridged carbonate species [25]. The band at 1660 cm^{-1} displays low thermal stability allowing its assignment to adsorbed formic acid. The broad absorption at 1550–1520 cm^{-1} observed in the spectrum taken at 250 °C could be attributed either to bidentate carbonates [the $\nu(C=O)$ mode] or formate species [the $(\nu_{as}(CO_2)$ mode] [17,22–25]. The corresponding concomitant bands should fall in the 1390–1320 cm^{-1} region. These bands are not detected most probably because of the low surface concentrations of the adsorbed species. The band at 1608 cm^{-1} is assigned to the bending mode of adsorbed water molecules. This is supported by the appearance of absorption between 4000 and 2600 cm^{-1} due to H-bonded hydroxyls. At 350 °C the amount of adsorbed water decreases considerably and the adsorbed formic acid and the species at 1550 cm^{-1} disappear from the spectrum. The increase in the temperature to 450 °C leaves the species at 1520 cm^{-1}. The spectrum detected after cooling to room temperature (figure 2(A), spectrum (RT)′) contains strong bands at 1606, 1460, 1430 cm^{-1} (shoulder) and a weak band at 1222 cm^{-1}. These bands are characteristic of bidentate hydrogencarbonates and are attributed to the $\nu_{as}(CO)$, $\nu_s(CO)$ and $\delta(OHO)$ modes [25,26]. Adsorbed water molecules contribute also to the intensity of the band at 1606 cm^{-1}. The sharp band at 2362 cm^{-1} corresponds to weakly adsorbed CO_2. Upon evacuation (figure 2(A), spectrum evacuation (RT)′), the complex band with a maximum at 1450 cm^{-1} decreases in intensity which suggests that the vibrational mode of another species is superimposed on the $\nu_s(CO)$ stretching of the HCO_3^- ion. This species is best assigned to symmetrical carbonate or carboxylate species [25]. The decrease in the intensity of the band at 1450 cm^{-1} causes a simultaneous enhancement of the intensities of the band at 1606 cm^{-1} and the shoulder at 1680 cm^{-1}. This behavior indicates that upon evacuation the species at 1450 cm^{-1} most probably transform to bridged carbonates.

Since the experiment with the WZ sample is performed in the absence of gaseous oxygen, the oxidation of methane is caused by the $W^{6+}=O$ species, which leads to a reduction of the tungsten ion. This is confirmed by the appearance of a positive band at 997 cm^{-1} in the spectrum taken at 250 °C (figure 2(A)) which shifts to 983 cm^{-1} with the increase in the temperature. This absorption could be associated with W-O bonds of reduced tungsten. The weak features at 1994 and 1988 cm^{-1} observed in the spectra at 350 and 450 °C, respectively, most probably are due to combination bands of fundamental W–O stretching vibrations of the reduced WO_x species.

The oxidation of methane on the Pd/WZ sample starts also at 250 °C. The spectra obtained in the 250–450 °C temperature range (figure 2(B)) contain absorptions in the OH stretching and carbonate–carboxylate regions. At 350 °C the envelope of the bands between 1650 and 1400 cm^{-1} is more complex on the Pd/WZ sample than on the tungstated zirconia. However, the spectra of both samples at 450 °C are identical. The sample spectrum (figure 2(B), spectrum (RT)′) and the gas phase spectrum taken in the presence of the Pd/WZ catalyst after cooling to room temperature do not contain bands of adsorbed and gaseous CO_2, respectively. In addition, the intensities of the hydrogencarbonate bands are lower on the Pd/WZ than those on the WZ sample (compare spectra (RT)′ in figure 2(A), (B)). It

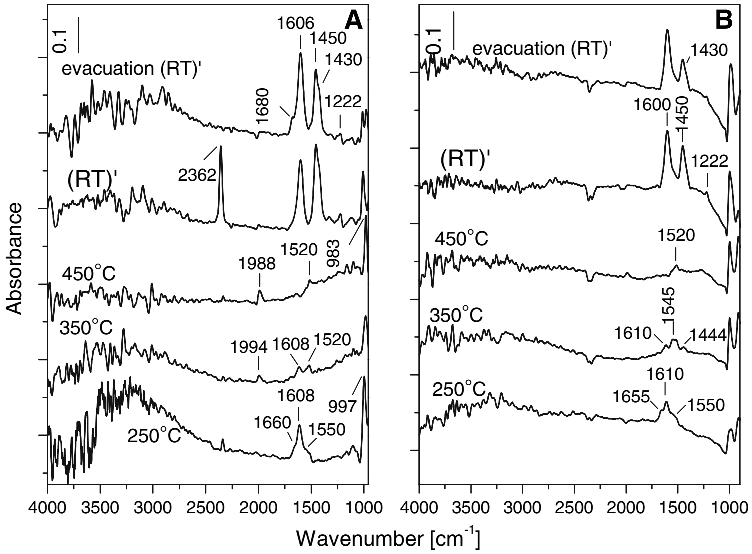


Figure 2. FT-IR spectra of the samples WZ (panel A) and Pd/WZ (panel B) obtained upon heating in CH_4 (60 Torr) for 15 min at the indicated temperatures and after cooling to room temperature (RT)′ followed by evacuation (RT = room temperature).

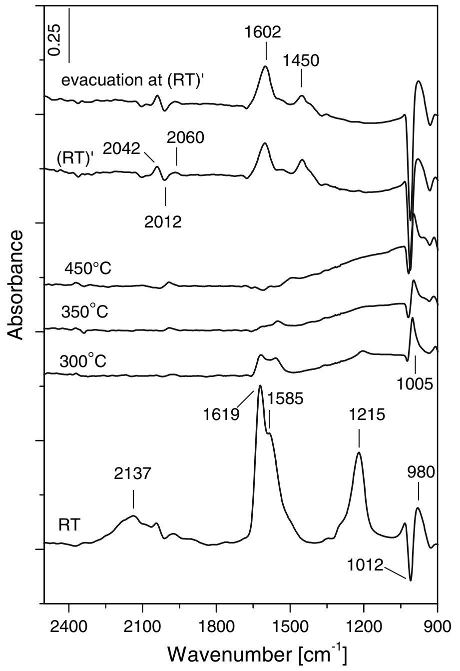


Figure 3. FT-IR spectrum of the sample WZ containing adsorbed NO_x species (spectrum (RT), see the caption figure 1 for the conditions) and spectra taken upon heating in CH_4 (60 Torr) for 20 min at the indicated temperatures and after cooling to room temperature (RT)′ followed by evacuation (RT = room temperature).

seems that the promotion of tungstated zirconia with palladium does not have a positive effect on the oxidation of methane under anaerobic conditions. This leads to the conclusion that the activation of the hydrocarbon on both samples takes place with the participation of the WO_x species.

3.3. "NO_x–CH_4" experiment

Stable NO_x species pre-adsorbed on the WZ sample were formed in the same way as described in the "Blank NO_x" experiment above. Then methane (60 Torr) was added (figure 3, spectrum RT) and the closed IR cell was heated in the 200–450 °C temperature range. The intensities of the nitrate bands decrease significantly at 300 °C. The spectrum taken at 350 °C contains unresolved bands between 1650 and 1500 cm^{-1}. It is difficult to make a conclusion about the origin of these weak absorptions because the frequencies of the bands corresponding to nitrate (residual) and carbonate species (eventually formed) are close. It should be pointed out that the gas-phase spectra detected at high temperatures and after cooling to room temperature do not contain NO_x or CO_x species. The spectrum of the WZ sample in the 1700–1200 cm^{-1} region taken after cooling to room temperature (figure 3, spectrum (RT)′) differs from that of the "Blank-NO_x" experiment (see figure 1(A), spectrum (RT)′) and resembles the spectrum (RT)′ in figure 2 obtained by the interaction of the methane with the activated WZ sample. Therefore, the bands at 1602 and 1450 cm^{-1} in spectrum (RT)′ (figure 3) are assigned also to bidentate hydrogencarbonate. However, the intensities of these bands are weaker than those of the hydrogencarbonates obtained in the "Blank CH_4" experiment. This leads to the conclusion that the NO_x species adsorbed on the WZ sample do not promote the oxidation of CH_4. The weak band at 2042 cm^{-1} (which resist the evacuation) can be attributed to CO adsorbed on reduced tungsten ions. For example, Kohler and Ekerdt [27] assigned a pair of bands at 2112 and 2040 cm^{-1} to the cis-$W^{4+}(CO)_2$ species formed during ultraviolet photoreduction of W^{6+}/SiO_2 in CO. The integrated intensity of the former band was 0.6 times the integrated intensity of the peak at 2040 cm^{-1}. It is possible that $W^{4+}(CO)_2$ species are formed also in our experiment. However, because of the low intensity of the band at 2042 cm^{-1}, the high-frequency component of the dicarbonyl (expected to be positioned at around 2110 cm^{-1}) cannot be detected. The negative band at 2012 cm^{-1} is due to the overtone of the perturbed $W^{6+}{=}O$ groups at 1012 cm^{-1}.

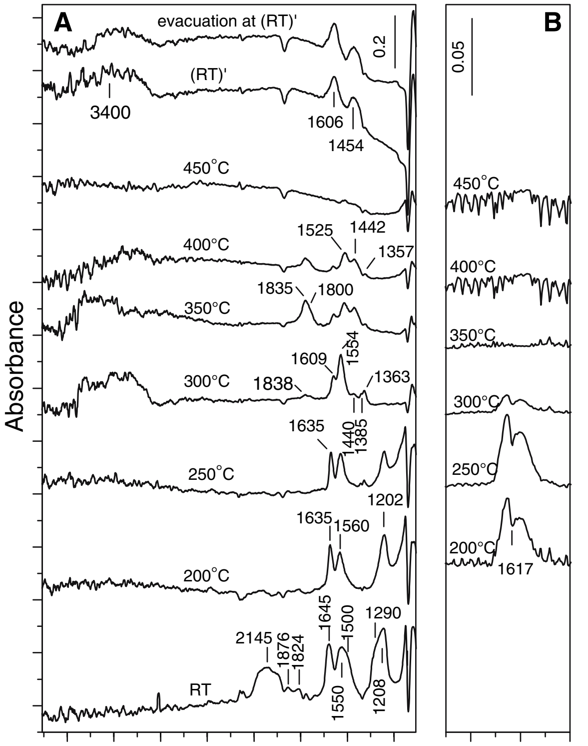


Figure 4. Panel A: FT-IR spectrum of the sample Pd/WZ containing adsorbed NO_x species (spectrum (RT), see the caption of figure 1 for the conditions) and spectra taken upon heating in CH_4 (60 Torr) for 20 min at the indicated temperatures and after cooling to room temperature (RT)′ followed by evacuation. Panel B: Spectra of the gas phase detected at the indicated temperatures (RT = room temperature).

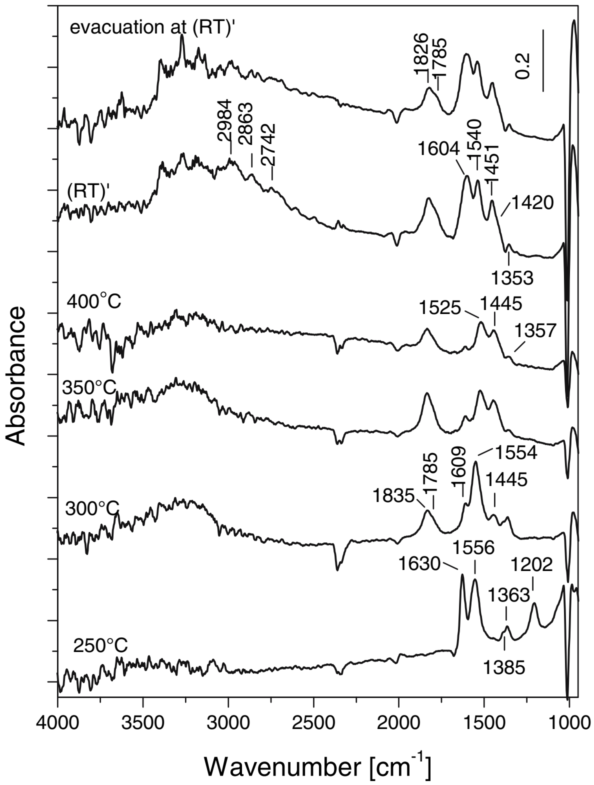


Figure 5. FT-IR spectra of the sample Pd/WZ containing adsorbed NO_x species taken upon heating in CH_4 (60 Torr) for 20 min in the 250 –400 °C temperature range, after cooling to room temperature (RT)′ and after evacuation (RT = room temperature).

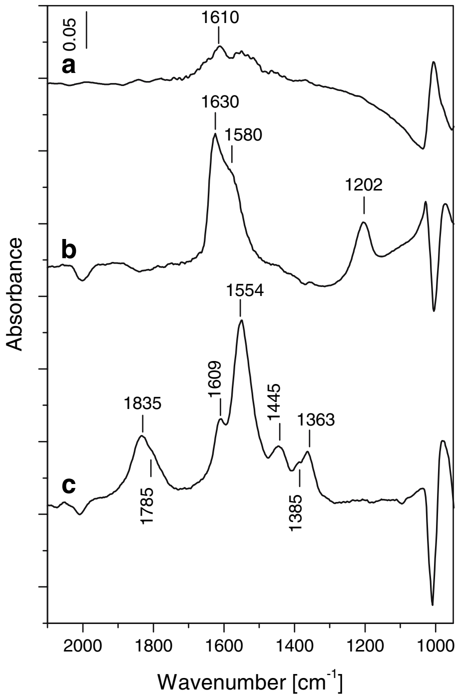


Figure 6. FT-IR spectra of the sample Pd/WZ obtained at 300 °C in the "Blank CH_4" (a), "Blank NO_x" (b) and "CH_4–NO_x" experiments (c). For the experimental conditions, see the captions of figures 1, 2, 4, respectively.

The results of the "NO_x–CH_4" experiment in the presence of the Pd/WZ catalyst are shown in figure 4. The panel B of the figure displays the spectra of the gas phase, whereas figure 5 represents the results of the experiment with a final reaction temperature of 400 °C.

The treatment at 200 °C (figure 4(A)) causes the disappearance of the NO^+ species (broad absorption between 2250 and 2000 cm^{-1}) and Pd(II) nitrosyls (1876 and 1824 cm^{-1}). The monodentate nitrate species giving rise to the unresolved bands at about 1500 and 1290 cm^{-1} [20,28] disappear as well. In the gas phase, formation of NO_2 is detected (figure 4(B), spectrum 200 °C). A further increase in the temperature to 250 °C (figure 4(A), spectrum 250 °C) results in a decrease in the intensities of the bands corresponding to the bridged (1645–1635 and 1202 cm^{-1}) and bidentate (1560–1550 and 1202 cm^{-1}) nitrates [20,28] leading to an additional increase in the amount of gaseous NO_2 (figure 4(B), spectrum 250 °C). At 300 °C all of the surface nitrates have decomposed (figures 4(A), 5), which is evident by the absence of the band at 1202 cm^{-1} corresponding to the $\nu_{as}(NO_2)$ modes. Note that the nitrates on the Pd/WZ sample are still present at 350 °C in the absence of CH_4 (see figure 1(B)). The gas-phase spectra (figure 4(B)) show that at 300 °C the amount of NO_2 has decreased significantly and no gaseous NO_2 is observed at higher temperatures. This result suggests that the NO_2 is consumed interacting with the methane. It is reasonable to propose that the product of this process is nitromethane identified in the spectrum taken at 300 °C (figures 4(A), 5) by the absorption bands at 1554 ($\nu_{as}(NO_2)$), 1385 ($\nu_s(NO_2)$) and 1363 cm^{-1} ($\delta(CH_3)$) [29–39] (see also figure 6, spectrum c). Simultaneously with the nitromethane formation, absorption between 3600 and 3000 cm^{-1} characteristic of H-bonded hydroxyls is detected (figures 4(A), 5). A careful inspection shows that the two bands at 1385 and 1363 cm^{-1} are present as weak features in the spectrum taken at 250 °C (figures 4(A), 5) which indicates that the nitromethane forms already at this temperature. The increase in the temperature to 350 °C results in a vanishing of the nitromethane bands and appearance of bands at 1835, 1800 (shoulder), 1525, 1442 and 1357 cm^{-1}. This is accompanied by a decrease in the intensity of the absorption at 1609 cm^{-1} which was detected at 300 °C simultaneously with the nitromethane bands. The pair of bands at 1835 and 1800 cm^{-1} has been observed during the high-temperature adsorption of NO on the Pd/WZ sample and has been attributed to two types of Pd^+–NO nitrosyls [20]. Note that at 350 °C no Pd(I) nitrosyls are observed in the "Blank NO_x" experiment (figure 1(B)). This indicates that the Pd^+–NO species do not arise as products of the decomposition of the inorganic nitrates or NO_2. It can be proposed that the nitromethane formed *in situ* decomposes through the intermediacy of the surface species at 1609 cm^{-1} giving rise to adsorbed NO and the surface compounds characterized by the absorptions between 1550 and 1300 cm^{-1}. The band at 1609 cm^{-1} is best assigned to the $\nu(N=O)$ stretching vibration of the isomer of nitromethane, cis-methyl nitrite [40,41]. The decomposition of nitromethane starts at 300 °C which is evident by the presence of a band with maximum at 1838 cm^{-1} characteristic of the Pd^+ nitrosyls (figures 4(A), 5, spectra 300 °C and figure 6, spectrum c).

A further increase in the temperature to 400 °C leads to a significant decrease in the intensities of the nitrosyl bands (figures 4(A), 5). The bands at 1609, 1525, 1442 and 1350 cm^{-1} also lose somewhat of their intensities. Increasing the temperature to 450 °C (figure 4(A)), results in the complete disappearance of all of the absorption bands. It should be pointed out that the Pd^+–NO species have high thermal stability and if present, they can be observed at 450 °C in the absence of evacuation [20]. The spectra taken after cooling to room temperature followed by evacuation (figure 4(A)) display bands at 1606, 1454 and 1415 cm^{-1} (shoulder). Similar bands are observed after the interaction of methane with the activated Pd/WZ sample (figure 2(B)) and are attributed to hydrogencarbonate species [25,26]. Under these conditions, no Pd(I) nitrosyls are detected suggesting that the adsorbed NO has been reduced to N_2. This conclusion is supported by the fact that the spectrum obtained in the absence of methane (figure 1(B), spectrum (RT)′) contains absorption bands characteristic of NO^+, Pd^{2+}–NO and NO_3^- species. Most probably, the adsorbed NO formed during the "CH_4–NO_x" experiment is reduced to N_2 by the surface compounds characterized by the bands at 1525 and 1357 cm^{-1} (figure 4(A)). In order to verify this assumption, we performed the same experiment as described above, however, with a final reaction temperature of 400 °C. Figure 5 shows the spectra obtained in the temperature range from 250 to 400 °C followed by cooling to room temperature. The spectrum in the low-frequency region taken after cooling to room temperature (spectrum (RT)′) differs from that shown in figure 4(A) by the presence of bands at 1826, 1785, 1540 and 1354 cm^{-1}. The former two bands are due to Pd^+–NO species. Their intensities are somewhat lower than those detected at 350 °C. The bands at 1540 and 1353 cm^{-1} are attributed to formate species and correspond to the $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$ modes, respectively [17, 22–25]. The bands at 2984, 2863 and 2742 cm^{-1}, characteristic of formate moiety [17, 22–25], support this assignment. The simultaneous existence of adsorbed NO and formate species in the spectrum taken at room temperature, after the termination of the reaction at 400 °C (figure 5), suggests that the reaction between the adsorbed NO and $HCOO^-$ leads to a reduction of NO to nitrogen. This process starts at 400 °C and is completed at 450 °C. The bands at 1525 and 1357 cm^{-1} detected in the spectra at 350 and 400 °C (figures 4(A), 5) are assigned to formate species with perturbed spectral features as compared to those observed at room temperature most probably because of a temperature effect and/or different way of coordination (bidentate versus monodentate). The band at 1445–1442 cm^{-1} detected at 350–400 °C (figures 4(A), 5) is attributed to monodentate carbonate [25]. The latter species could form by direct interaction of the methane with the catalyst surface (see figure 2(B)).

The assignment of the bands observed during the "CH_4–NO_x" experiment on the Pd/WZ catalyst is summarized in table 1. Figure 6 compares the sample spectra in the 2100–900 cm^{-1} region obtained at 300 °C in the "Blank CH_4" (spectrum a), "Blank NO_x" (spectrum b) and "CH_4–NO_x" experiments (spectrum c) over the Pd/WZ catalyst. The band envelop of spectrum c differs from those of spectra a and b. It is obvious that the absorptions in spectrum c do not arise as a result of superimposition of bands due to carbonate–carboxylate (spectrum a) and nitrate species (spectrum b). As proposed above, the bands in spectrum c correspond to NO adsorbed on Pd^+ sites (1835 and 1785 cm^{-1} [20]), cis-methyl nitrite (1609 and 1445 cm^{-1} [40, 41]) and nitromethane (1554, 1385 and 1363 cm^{-1} [29–39]).

3.4. *Adsorption of nitromethane*

In order to confirm the assignment of the absorption bands and the occurrence of the processes described, we studied the adsorption of authentic nitromethane (1.5 Torr) on the WZ support and Pd/WZ catalyst at various temperatures. Figure 7 shows the FT-IR spectra obtained from the adsorption of nitromethane on the WZ sample. The bands at 1566 ($\nu_a(NO_2)$), 1415 ($\nu_s(NO_2)$) and 1377 cm^{-1} ($\delta_s(CH_3)$) observed at room temperature belong to the physisorbed nitromethane [29–39]. The shoulder at approximately 1610 cm^{-1} and the weak band at 1248 cm^{-1} most probably indicate the formation of the aci-anion of nitromethane ($CH_2NO_2^-$) and correspond to the $\nu(C=N)$ and $\nu_{as}(NO_2)$ modes, respectively [32, 34, 36–39]. The heating at 150 °C causes a decrease in the intensities of the nitromethane bands and a strong enhancement of the absorption at 1610 cm^{-1} which shifts to 1620 cm^{-1}. At the same time a new band at 1471 cm^{-1} appears. The intensity of the band at 1248 cm^{-1} does not change significantly, which suggests that the band at 1620 cm^{-1} is not associated with the aci-anion of nitromethane. The bands at 1620 and 1471 cm^{-1}, (which appear simultaneously in the spectrum taken at 150 °C) are best assigned to the cis-methyl nitrite and correspond to the $N=O$ stretching and CH_3 bending modes, respectively [40, 41]. Increasing the temperature to 200 °C causes the appearance of new bands at 1672, 1554 and 1366 cm^{-1} at the expense of the intensities of the cis-CH_3ONO bands. The sharp band at 1248 cm^{-1} detected at 150 °C due to the

Table 1
Assignment of the bands resulting from the "CH_4–NO_x" experiment on the Pd/WZ catalyst (figures 4(A), 5, RT = room temperature)

Temperature (°C)	Wavenumber (cm^{-1})	Surface species	Vibration
RT – 200 °C	2145	NO^+	$\nu(NO)$
	1876, 1824	Pd^{2+}–NO (2 types)	$\nu(NO)$
	1645, 1208	NO_3^- (bridged)	$\nu(N=O)$, $\nu_{as}(NO_2)$
	1550, 1208	NO_3^- (bidentate)	$\nu(N=O)$, $\nu_{as}(NO_2)$
	1500, 1290	NO_3^- (monodentate)	$\nu_{as}(NO_2)$, $\nu_s(NO_2)$
250 °C	1635–1630, 1202	NO_3^- (bridged)	$\nu(N=O)$, $\nu_{as}(NO_2)$
	1560–1556, 1202	NO_3^- (bidentate)	$\nu(N=O)$, $\nu_{as}(NO_2)$
	1385, 1363	CH_3NO_2	$\nu_{as}(NO_2)$, $\delta(CH_3)$
300 °C	3600–3000	H-bonded OH groups	$\nu(OH)$
	1838–1835, 1785	Pd^+–NO (2 types)	$\nu(NO)$
	1609, 1445–1440	cis-CH_3ONO	$\nu(N=O)$, $\delta(CH_3)$
	1554, 1385, 1363	CH_3NO_2	$\nu_{as}(NO_2)$, $\nu_s(NO_2)$, $\delta(CH_3)$
350–400 °C	3600–3000	H-bonded OH groups	$\nu(OH)$
	1835, 1800–1785	Pd^+–NO (2 types)	$\nu(NO)$
	1609	cis-CH_3ONO	$\nu(N=O)$
	1525, 1357	$CHOO^-$	$\nu_{as}(CO_2)$, $\nu_s(CO_2)$
	1445–1442	CO_3^{2-} (monodentate)	$\nu_{as}(CO_2)$
(RT)′ (figure 4(A))	3600–3000	H-bonded OH groups	$\nu(OH)$
	1606, 1415	HCO_3^-	$\nu_{as}(CO)$, $\nu_s(CO)$
	1454	CO_3^{2-} (monodentate)	$\nu_{as}(CO_2)$
(RT)′ (figure 5)	3600–3000	H-bonded OH groups	$\nu(OH)$
	2984, 2863, 2742	$HCOO^-$	$\nu_{as}(CO_2) + \delta(CH)$, $\nu(CH)$
		$HCOO^-$	$\nu_s(CO_2) + \delta(CH)$
	1826, 1785	Pd^+–NO (2 types)	$\nu(NO)$
	1604, 1420	HCO_3^-	$\nu_{as}(CO)$, $\nu_s(CO)$
	1540, 1353, 1451	$HCOO^-$	$\nu_{as}(CO)$, $\nu_s(CO)$
		CO_3^{2-} (monodentate)	$\nu_{as}(CO_2)$

$\nu_{as}(NO_2)$ mode of the adsorbed aci-anion loses somewhat of its intensity and converts into a broad unresolved absorption with maxima at 1250 and 1220 cm^{-1}. The intensities of these bands do not change synchronously with the increase in the temperature. Therefore, they are assigned to the $\nu_{as}(NO_2)$ modes of two types of inorganic bidentate nitrito species [20, 42]. It should be pointed out that no adsorbed NO_x compounds have been detected during the high-temperature adsorption of NO on the WZ sample [20] which confirms that the species associated with the bands at 1250 and 1220 cm^{-1} originate from the thermal transformation of the cis-methyl nitrite. Formation of NO_2^- species as a decomposition product of alkyl nitrites has been proposed by Zuzaniuk *et al.* [36]. The bands at 1550 and 1367 cm^{-1} are typical of formate species and correspond to the $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$ modes, respectively [17, 22–25]. The unresolved band at 1672 cm^{-1} is attributed to the $\nu(C=O)$ mode of adsorbed formic acid [17, 22–24]. The appearance of formates during the decomposition of nitromethane on oxide surfaces has been reported also by others [32, 36, 37, 39]. Increasing the temperature to 250 °C leads to dissociation of the formic acid and decomposition of the cis-methyl nitrite resulting in further increase in the amount of the formate and nitrite species. At 300 °C the methyl nitrite decomposes completely. The heating at 350 and 400 °C causes progres-

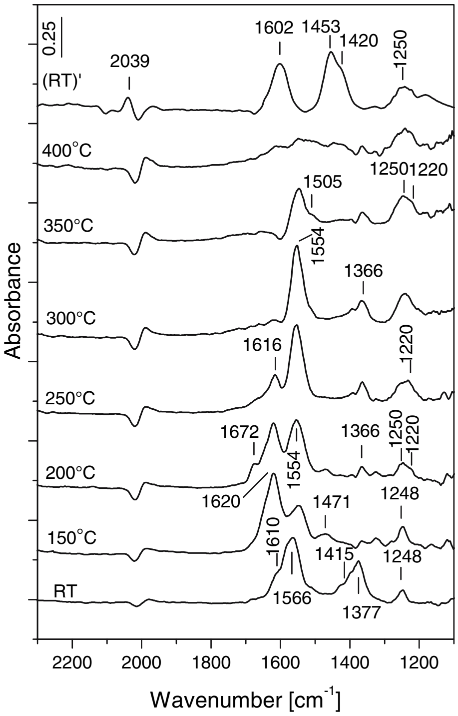


Figure 7. FT-IR spectra of the sample WZ obtained by adsorption of nitromethane (1.5 Torr) at room temperature (RT) followed by heating of the closed IR cell at various temperatures and after cooling to room temperature (RT)′.

Table 2
Assignment of the bands resulting from the adsorption of nitromethane (NM) on the WZ and Pd/WZ catalysts (figures 7, 8, RT = room temperature)

Temperature (°C)	Wavenumber (cm^{-1})	Surface species	Vibration
RT	1610, 1248	$CH_2NO_2^-$	$\nu(C=N)$, $\nu_{as}(NO_2)$
	1566, 1402, 1377	Physisorbed NM	$\nu_{as}(NO_2)$, $\nu_s(NO_2)$, $\delta(CH_3)$
150 °C	1837, 1800	Pd^+–NO (2 types)	$\nu(NO)$
	1620, 1471–1465	cis-CH_3ONO	$\nu(N=O)$, $\delta(CH_3)$
	1554	CH_3NO_2	$\nu_{as}(NO_2)$
	1248	$CH_2NO_2^-$	$\nu_{as}(NO_2)$
200–250 °C	1837, 1800	Pd^+–NO (2 types)	$\nu(NO)$
	1672–1670, 1640	HCOOH	$\nu(C=O)$
	1620–1616	cis-CH_3ONO	$\nu(N=O)$
	1554–1550, 1367–1366	$HCOO^-$	$\nu_{as}(CO_2)$,$\nu_s(CO_2)$ superimposed $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ modes
	1255–1250 1227–1220	NO_2^- (bidentate nitrito, 2 types)	Superimposed $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ modes
300–400 °C	1554–1550, 1367–1366	$HCOO^-$	$\nu_{as}(CO_2)$,$\nu_s(CO_2)$
	1505–1504	CO_3^{2-} (bidentate)	$\nu(C=O)$
	1436	CO_3^{2-} (monodentate)	$\nu_{as}(CO_2)$
	1255–1250 1227–1220	NO_2^- (bidentate nitrito, 2 types)	Superimposed $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ modes
(RT)′	2039	W^{4+}–CO	$\nu(CO)$
	1602, 1420, 1250	HCO_3^-	$\nu_{as}(CO)$, $\nu_s(CO)$, $\delta(OHO)$
	1453	CO_3^{2-} (monodentate)	$\nu_{as}(CO_2)$
	~1250	NO_2^- (bidentate nitrito, 2 types)	Superimposed $\nu_{as}(NO_2)$ and ν_s (NO_2) modes

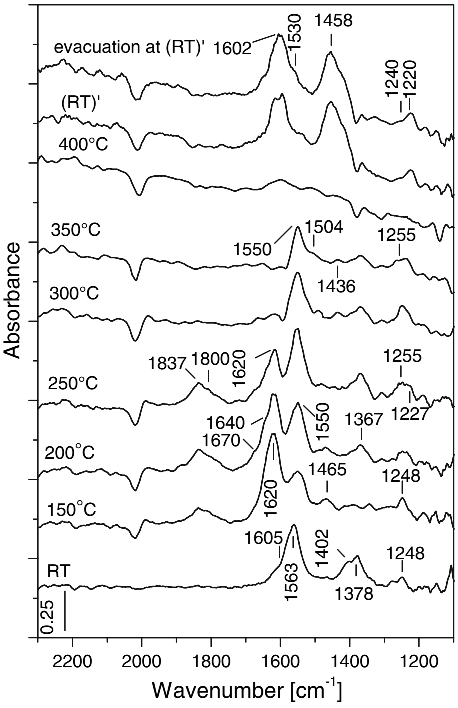


Figure 8. FT-IR spectra of the sample Pd/WZ obtained by adsorption of nitromethane (1.5 Torr) at room temperature (RT) followed by heating of the closed IR cell at various temperatures and after cooling to room temperature (RT)′.

sive degradation of the formate species. The intensities of the nitrite bands increase up to 300–350 °C. The spectrum taken after cooling to room temperature (figure 7, spectrum (RT)′) contains bands at 1602 and 1453 cm^{-1}, which can be assigned to hydrogen carbonates [25, 26]. The broad absorption at 1245 cm^{-1} reveals the presence of superimposed bands of the inorganic nitrite and δ(OHO) mode of the hydrogen carbonates. The band with maximum at 2039 cm^{-1} has been observed in the "CH_4–NO_x" experiment with the WZ sample after cooling to room temperature (see figure 3, spectrum (RT)′) and has been attributed to CO adsorbed on reduced tungsten sites [27].

Table 2 summarizes the assignment of the bands observed during the adsorption of nitromethane on the WZ sample.

Figure 8 shows the FT-IR spectra obtained from the adsorption of nitromethane on the Pd/WZ sample (see also table 2). The spectra detected between room temperature and 350 °C are similar to those obtained over the WZ sample with the exception that there is absorption in the nitrosyl region. The bands at 1837 and 1800 cm^{-1} (observed also during the "NO_x–CH_4" experiment (figures 4(A)–6) are ascribed to the NO adsorbed on Pd^+ sites. The Pd^+–NO species are detected at 150 °C. This indicates that the decomposition of methyl nitrite begins already at this temperature simultaneously with the isomerization of nitromethane. The formation of NO as a decomposition product of the cis-CH_3ONO implies that a cleavage of the CH_3O–NO bond takes place. This suggests that carbon-containing oxygenates should be formed as well. The bands at 1550 and 1367 cm^{-1} observed between 200 and 350 °C are typical of formate species and correspond to the $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$ modes, respectively [17, 22–25]. Most probably the unresolved bands at 1670 and

1640 cm^{-1} in the spectrum taken at 200 °C are due to the $\nu(C=O)$ modes of formic acid adsorbed on two different sites [17, 22–24].

The treatment at 250 °C causes a further decrease in the intensity of the cis-CH_3ONO band at 1620 cm^{-1} with a simultaneous increase in the amount of adsorbed formate species. However, the intensities of the nitrosyl bands are not affected. This can be explained assuming that during the decomposition of cis-methyl nitrite on the Pd/WZ catalyst, not only NO but also NO_2^- species are formed as in the case of the WZ sample. Indeed, the sharp band at 1248 cm^{-1} detected at 150 °C due to the $\nu_{as}(NO)$ mode of the adsorbed aci-anion disappears at 200 °C. A broad, unresolved absorption develops, which appears with maxima at 1255 and 1227 cm^{-1} at 250 °C. In analogy with the WZ sample, these two bands are assigned to the $\nu_{as}(NO)_2$ modes of two types of inorganic bidentate nitrito species [20, 42]. At 300 °C the adsorbed NO and cis-CH_3ONO disappear from the spectrum which is accompanied by decrease in the intensities of the formate bands. The intensities of the nitrito bands change somewhat as well. Heating to 400 °C causes the disappearance of the remaining formate and nitrito species. The spectrum detected after cooling to room temperature does not contain bands of adsorbed NO implying that NO has been reduced by the formate species to nitrogen. The bands at 1602, 1458 and 1220 cm^{-1} correspond to hydrogencarbonates, whereas the pair of bands at 1530 and 1240 cm^{-1} is assigned to bidentate carbonates [25, 26]. The shapes of the bands in the carbonate–carboxylate region are very similar to those in spectrum (RT)′ obtained in the "CH_4–NO_x" experiment after cooling to room temperature (figure 4(A)).

It can be concluded that the nitromethane adsorbed on the WZ and Pd/WZ samples follows similar decomposition paths. However, in the temperature range 150–250 °C, no NO adsorbed on the WZ sample is observed. In addition, the inorganic nitrito species at 1240–1230 cm^{-1} are more abundant and have a higher thermal stability on the WZ than on the Pd/WZ sample.

It has been shown in prior studies [32–39] that $CH_2NO_2^-$ species formed on oxide surfaces undergo dehydration into isocyanic acid (HNCO) upon heating at 200–400 °C. Isocyanic acid adsorbed onto metal oxide or metal surfaces give rise to absorptions in the 2300–2140 cm^{-1} region [12, 16, 30–39, 43–45]. During the thermal decomposition of nitromethane adsorbed on the WZ and Pd/WZ samples no bands in this region have been observed most likely because of the low surface concentration of the $CH_2NO_2^-$ species formed. Another possibility is that the dehydration of aci-nitromethane does not occur on the WZ and Pd/WZ samples and it decomposes to NO/NO_2^- and oxygenates in a similar way as that of the cis-CH_3ONO.

3.5. Interaction of formaldehyde with NO adsorbed on the Pd/WZ sample

Otsuka *et al.* [46] observed formation of $H_2C=O$ and NO during the homogeneous thermal decomposition of methyl nitrite vapor at 215 °C. It can be proposed that formaldehyde is also the primary product formed during the decomposition of the cis-methyl nitrite in our experiments. Therefore, it is of interest to study the interaction of formaldehyde with the Pd/WZ catalyst containing pre-adsorbed Pd^+–NO species. Palladium(I) nitrosyls were created by heating of the Pd/WZ catalyst in atmosphere of NO (10 Torr) at 350 °C for 15 min followed by evacuation for 15 min at the same temperature [20]. The spectrum obtained after cooling to room temperature (figure 9, spectrum RT(NO)) contains a band at 1837 cm^{-1} with a shoulder at about 1800 cm^{-1} corresponding to Pd^+–NO species in two different environments [20]. The weak bands at 1606, 1554 and 1213 cm^{-1} indicate that small amounts of adsorbed nitrate species are present as well. To the sample treated in this way, 2 Torr of formaldehyde (obtained by heating of paraformaldehyde at 80 °C) were added (figure 9, spectrum RT(NO + FA)). The complexity of the spectrum below 1700 cm^{-1} clearly indicates the presence of several types of adsorbed species. The band at 1698 cm^{-1} corresponds to the $\nu(C=O)$ mode of adsorbed formaldehyde [22, 23] whereas the absorption at 1650 cm^{-1} is attributed to the $\nu(C=O)$ stretching mode of adsorbed formic acid [17, 22–24]. The bands at 1562 and 1365 cm^{-1} are typical of formate ions and correspond to the $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$ stretching vibrations, respectively [17, 22–25]. The high-frequency components of the latter band (1420 and 1392 cm^{-1}) are attributed to overlapping bands arising from $\delta(CH_2)$ modes of the adsorbed formaldehyde and formate species. The weak band at 1252 cm^{-1} corresponds to the w(CH_2) mode of formaldehyde [22, 23]. The presence of formic acid and formate species indicate that the formaldehyde is oxidized already at room temperature. The intensities of the nitrosyl bands do not change considerably, which suggests that the oxidation of formaldehyde at room temperature takes place without the involvement of adsorbed NO. It is well-known [22, 23] that formaldehyde is unstable on oxide surfaces and can readily undergo oxidation to formic acid/formate species. At 200 °C the adsorbed formaldehyde disappears which is accompanied by increase in the amounts of adsorbed formic acid and formate species. This indicates that further oxidation of the formaldehyde takes place, which also leads to the formation of Pd^+–CO species (ν(CO) at 2126 cm^{-1} [20]) and adsorbed water or another carboxylic species (strong band at 1620 cm^{-1}). The intensities of the Pd(I) nitrosyl bands decrease, most likely as result of displacement of the adsorbed NO by the products of formaldehyde oxidation. The increase in

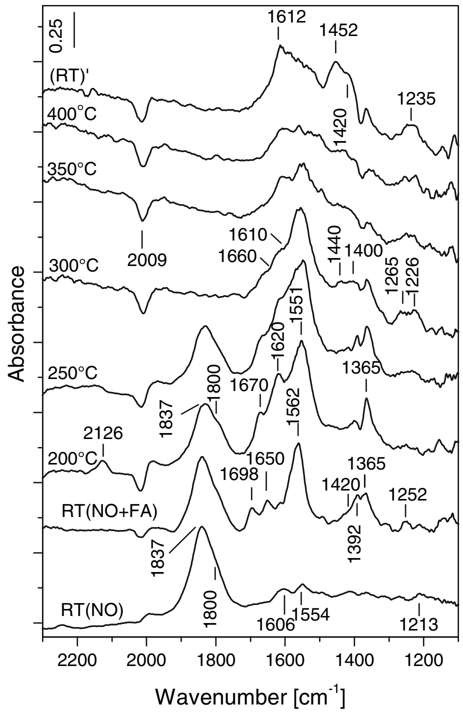


Figure 9. FT-IR spectra of the sample Pd/WZ obtained by adsorption of NO (10 Torr) at 350 °C followed by evacuation for 15 min at the same temperature and after cooling to room temperature (RT(NO)), after adsorption of formaldehyde (2 Torr) at room temperature (RT(NO + FA)) and subsequent heating the closed IR cell at the indicated temperatures and after cooling to room temperature (RT)′ (RT = room temperature, NO = nitrogen oxide, FA = formaldehyde).

Table 3
Assignment of the bands resulting from the adsorption of formaldehyde on the Pd/WZ catalyst containing Pd^+–NO species (figure 9, RT = room temperature)

Temperature (°C)	Wavenumber (cm^{-1})	Surface species	Vibration
RT	1837, 1800	Pd^+–NO (2 types)	ν(NO)
	1606, 1554, 1213	NO_3^- (bidentate, 2 types)	$\nu(N=O)$, $\nu_{as}(NO_2)$, $\nu_s(NO_2)$
	1698, 1420, 1252	HCHO	$\nu(C=O)$, $\delta(CH_2)$, w(CH_2)
	1650	HCOOH	$\nu(C=O)$
	1562, 1392, 1365	$HCOO^-$	$\nu_{as}(CO_2)$, δ(CH), $\nu_s(CO_2)$
200–250 °C	2126	Pd^+–CO	ν(CO)
	1837, 1800	Pd^+–NO (2 types)	ν(NO)
	1670	HCOOH	$\nu(C=O)$
	1620	H_2O?	$\delta(H_2O)$?
	1551, 1392, 1365	$HCOO^-$	$\nu_{as}(CO_2)$, δ(CH), $\nu_s(CO_2)$
300–400 °C	1660	HCOOH	$\nu(C=O)$
	1610	H_2O	$\delta(H_2O)$
	1551, 1365	$HCOO^-$	$\nu_{as}(CO_2)$, $\nu_s(CO_2)$
	1440, 1400	CO_3^{2-} (bidentate, 2 types)	$\nu_{as}(CO_2)$
	1265, 1226		$\nu_s(CO_2)$
(RT)′	1612, 1420, 1235	HCO_3^-	ν_{as}(CO), ν_s(CO), δ(OHO)
	1420	CO_3^{2-} (monodentate)	$\nu_{as}(CO_2)$

the temperature to 250 °C causes the disappearance of the adsorbed CO. The Pd^+–NO bands appear with slightly lower intensities as compared with those in the spectrum taken at 200 °C. It is possible that the adsorbed NO and CO interact under these conditions. The intensities of the bands below 1700 cm^{-1} do not change significantly. At 300 °C the amounts of adsorbed formic acid and formate species decreases and the Pd^+–NO species are no longer present. This indicates that a reduction of the adsorbed NO by the hydrocarbon oxygenates takes place. The appearance of bands at 1440, 1400, 1265 and 1226 cm^{-1} points to formation of bidentate carbonates or hydrogencarbonates with the $\nu_{as}(CO_2)$ mode at 1610 cm^{-1}. The increase in temperature to 400 °C causes decomposition of the formate and carbonate species. The spectrum taken after cooling to room temperature does not contain bands corresponding to adsorbed NO and displays features that are similar to the analogous spectra in figure 4(A). Note that the temperature of NO reduction is the same (300 °C) as that observed during the decomposition of nitromethane.

Table 3 shows the assignment of the bands observed during the adsorption of formaldehyde on the Pd/WZ sample containing Pd^+–NO species.

4. Discussion

The experimental results show that the NO_x species formed at room temperature on the WZ sample do not promote the oxidation of methane, whereas in the case of the Pd/WZ catalyst the surface nitrates decompose to NO_2 initiating the formation of nitromethane. This process takes place already at 250 °C (see figures 4(A), 5). According to the results of the "Blank CH_4" experiment, at the same temperature the WZ and Pd/WZ samples are able to activate the hydrocarbon (figure 2(B)). In this process the WO_x species are involved. It has been proposed [20] that the Pd/WZ sample contains dispersed Pd^{2+} ions in two different environments: Pd^{2+} ions, which have only Zr^{4+} ions in their second coordination sphere and Pd^{2+} ions, which are linked to both zirconium and tungsten ions via oxygen bridges. Resasco and co-workers [7] concluded that highly dispersed Pd^{2+} ions stabilized by tungstated zirconia are inactive for direct interaction with CH_4.

The activation of methane on oxide catalysts can occur through heterolytic C–H bond cleavage on a strong Lewis acid–base pair as the active site [47, 48]. In this process an OH group and CH_3^- ion coordinated to a metal cation should be formed. Moro-oka [49] concluded that most of the metal oxide catalysts do not contain such strong acid–base pairs. Furthermore, there is no direct experimental evidence for the heterolytic splitting in the rate determining dissociation of C–H bond of saturated hydrocarbons [49]. The kinetic and thermochemical analyses of the catalytic oxidation of light alkanes revealed that the overall process includes heterogeneous and homogeneous elementary reactions of free radicals [50]. The EPR investigation of Kuba *et al.* [51] presented direct support for a homolytic C–H bond cleavage of *n*-pantane in the presence of tungstated zirconia. This process involves single electron transfer producing free alkyl radical, surface W^{5+} ions and OH^- groups [51]:

$$RH + W^{6+} + O^{2-} \rightarrow \bullet R + W^{5+} + OH^- \qquad (1)$$

The theoretical calculations of Fu *et al.* [52] on the mechanism of methane activation on molybdenum oxide based catalysts support the described one-electron process. Based on these considerations, it is assumed that in the process of methane activation on the Pd/WZ catalyst, CH_3 radicals are formed. The FT-IR spectra of the "CH_4–NO_x" experiment taken at 300 °C (figures 4(A), 5) support indirectly this assumption by the appearance of absorption in the ν(OH) stretching region (due to H-bonded hydroxyls) simultaneously with the nitromethane formation. The $\bullet CH_3$ radicals formed according to reaction (1) are captured by the NO_2 evolved during the thermal decomposition of the nitrate species producing nitromethane:

$$\bullet CH_3 + NO_2 \rightarrow CH_3NO_2. \qquad (2)$$

The nitromethane formed *in situ*, following adsorption, rearranges unimolecularly to cis-methyl nitrate:

$$CH_3NO_2 \rightarrow \text{cis-}CH_3ONO. \qquad (3)$$

The results on the decomposition of authentic nitromethane adsorbed on both Pd-free and Pd-promoted tungstated zirconia (figures 7, 8) confirm the occurrence of this process. The physisorbed nitromethane is the predominant adsorption form at room temperature, while the heating at 150 °C causes its rearrangement to cis-methyl nitrite. At 150–200 °C the decomposition of the latter compound begins, giving rise to hydrocarbon oxygenates (formic acid/formate species), inorganic nitrite species and adsorbed NO (observed on the Pd/WZ catalyst in the 150–250 °C temperature range).

Methyl nitrite is a labile molecule and decomposes upon heating in the 177 –220 °C temperature range following reactions 4 and 5 as predominant steps [53]:

$$CH_3ONO \rightarrow CH_3O + NO \qquad (4)$$

$$CH_3O + NO \rightarrow CH_2O + HNO. \qquad (5)$$

Otsuka *et al.* [46] suggested similar process for the homogeneous decomposition of methyl nitrite yielding CH_2O and NO + H instead of the nitroxyl. It can be proposed that the decomposition of methyl nitrite formed on the surface of the WZ and Pd/WZ samples occurs by an overall process leading to formation of CH_2O and HNO as primary products.

During the decomposition of methyl nitrite on the WZ and Pd/WZ samples formation of adsorbed formates and inorganic nitrites is observed. This suggests that identical active sites on both samples, i.e., the $W^{6+}=O$ species, are involved in the decomposition route of the methyl nitrite leading to the same products:

$$CH_2O + W^{6+} = O^{2-} \rightarrow W^{4+} + HCOOH \qquad (6)$$

$$HNO + W^{6+} = O^{2-} \rightarrow W^{4+} + HNO_2. \qquad (7)$$

The formic (bands at 1670 and 1640 cm^{-1} in figures 7, 8) and nitrous acids dissociate to formate (1550 cm^{-1}) and nitrito species (1260–1220 cm^{-1}). The appearance of Pd^+–NO nitrosyls in the 150–250 °C temperature range during the decomposition of authentic nitromethane adsorbed on the Pd-promoted catalyst can be explained by assuming the following redox step in which the Pd^{2+} ions are involved:

$$HNO + Pd^{2+} - O^{2-} \rightarrow Pd^{+} - NO + OH^{-}. \quad (8)$$

In the case of tungstated zirconia, a similar process with the participation of the $W^{6+}=O$ species can be proposed:

$$HNO + W^{6+} = O^{2-} \rightarrow W^{5+} - OH^{-} + NO. \quad (9)$$

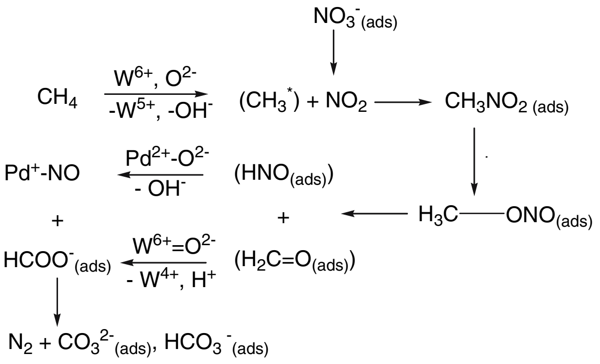
Based on the fact that the nitrito species are more abundant on the tungstated zirconia than on the Pd-promoted catalyst, it can be proposed that reaction 7 predominates on the former sample. The formate ions formed on the Pd/WZ catalyst (reaction 6) reduce the adsorbed NO at 300 °C to molecular nitrogen according to the reaction:

$$HCOO^{-} + NO \rightarrow HCO_3^{-} + 0.5N_2. \quad (10)$$

The surface concentration of the NO_2^- species on the WZ sample does not change considerably between 250 and 400 °C (figure 7). In contrast, the nitrito species on the Pd/WZ sample disappear completely at 400 °C (figure 8). Most probably the palladium ions promote their decomposition to NO_2. The latter compound can react further with the methane to N_2 following the steps described above.

The proposed primary products of cis-methyl nitrite decomposition, formaldehyde and nitroxyl species, are not detected on both WZ and Pd/WZ samples. Lack of direct observation of CH_2O is associated with its fast oxidation to formic acid. On the Pd/WZ sample, this process is observed to take place at room temperature. The formate species produced by the dissociation of formic acid reduce the NO adsorbed on the Pd^+ sites at the same temperature (300 °C) as that observed during the decomposition of nitromethane. This indicates that identical elementary steps to dinitrogen are involved in both processes, the thermal transformation of nitromethane and the reaction between the formaldehyde and NO adsorbed on the Pd^+ sites. It can be concluded that the precursor of the reductant of adsorbed NO is the formaldehyde produced by decomposition of the nitromethane.

The ν(NO) and δ(HNO) modes of free HNO are at 1570 and 1110 cm^{-1}, respectively [54]. This molecule, when adsorbed, can display stretching and bending vibrations in the 1560–1400 cm^{-1} region [55]. This region is covered by the bands of nitromethane, methyl nitrite and formate species. In order to confirm the formation of the nitroxyl species, additional experiments should be carried out by using labeled nitromethane. However, the fact that during the thermal transformation of nitromethane, the Pd^+–NO nitrosyls are observed already at 150 °C suggests that the thermal stability of HNO, if formed on the Pd/WZ sample, should be low.



Scheme 1. Mechanism for the interaction of methane with NO_x species adsorbed on the Pd/WZ catalyst.

The decomposition of CH_3NO_2 produced *in situ* on the Pd/WZ catalyst follows the same reaction steps as proposed for the authentic nitromethane. However, because in the "CH_4–NO_x" experiment the nitromethane appears at 250 °C, the temperature at which the reduction of NO by the formate species begins, is shifted to 400 °C. At this temperature, the byproducts of nitromethane decomposition, the inorganic nitrites, are unstable and they are not detected. The thermal stability of the adsorbed nitromethane formed *in situ* is higher than that of the authentic compound. This can be related to differences in the way of coordination and state of the catalyst surface. The adsorption of authentic nitromethane is preformed on the oxidized Pd/WZ sample, whereas the catalyst surface is partially reduced during the "CH_4–NO_x" experiment (see reaction 1). Similar difference in the stability is observed for formate species formed by adsorption of formic acid and formates produced upon adsorption of CO on hydrated Cr_2O_3 surface [56]. The former being less stable, decompose at 50 °C while the latter species undergo degradation at 200 °C.

Scheme 1 summarizes the proposed mechanism for the interaction of methane with the NO_x complexes pre-adsorbed on the Pd/WZ catalyst. The species shown in parentheses have not been detected in the "CH_4–NO_x" experiment. In the reaction scheme proposed, the role of palladium is (i) to promote the thermal decomposition of the nitrate species formed by room-temperature adsorption of NO + O_2 to NO_2 and (ii) to provide sites at high temperatures for the adsorption of NO released by the decomposition of cis-methyl nitrite. The results show that both tungstated zirconia and Pd-promoted tungstated zirconia are able to interact with the methane at 250 °C. Therefore, we believe that the role of the $W^{6+}=O$ species is to activate the methane and to oxidize the formaldehyde (proposed as one of the primary products of the decomposition of CH_3NO_2) to surface formates.

In recent years, the decomposition of nitromethane on various oxide systems containing simple oxides such as Al_2O_3 [14, 32, 34], SiO_2 [14], MgO [34, 57], alumina-based catalysts [33, 34, 36, 39], zeolites such as H-ZSM5 [14, 35], Na-ZSM5 [14], BaNa-Y [38], transition metal-exchanged H-ZSM5 [14, 16, 30, 58, 59], X and Y zeolites [60] have been extensively studied. For the most part, these investigations were promoted by the assumption that nitromethane could be an intermediate in the SCR of nitrogen oxides with CH_4 [58, 61, 62]. Nitromethane in the presence of the majority of the oxide materials investigated, decomposes upon heating at 200–400 °C producing ammonia and CO_2 [14, 32, 36, 38, 57, 60]. Transformation of nitromethane to its enol tautomer, aci-nitromethane, with a subsequent step of dehydration to HNCO followed by hydrolysis of the latter compound to NH_3 was proposed as a possible route from nitromethane to ammonia [14, 32, 36, 60]. Based on these results, the produced HNCO is considered to be an intermediate species in the CH_4-SCR on Co-ZSM5. The final step in this mechanism involves the formation of N_2 by ammonia oxidation and/or NH_3-SCR [14].

The anion of aci-nitromethane is detected by IR [32, 34, 36, 37, 39] and NMR spectroscopy [32, 57] on basic and amphoteric oxides. However, this compound is not observed on acidic oxides such as H-ZSM5 [57]. The theoretical calculations on the homogeneous isomerization and dissociation of nitromethane show that both reaction pathways passing through an initial nitromethane – methyl nitrite and nitromethane – aci-nitromethane rearrangements have very close activation barriers differing by 0.6 [63] or 3 kcal/mol [64]. This leads to the conclusion that both channels are possible and competitive [64]. The presence of a catalyst can make one reaction pathway more favorable than the other. Levoguer and Nix [31] reported that the major decomposition products of nitromethane at 300 K on polycrystalline Pt foil are adsorbed NO and CO. They proposed also as a possible step in the reaction mechanism the isomerization of nitromethane to methyl nitrite.

In this study we found that the authentic nitromethane and nitromethane formed *in situ* decompose over Pd-promoted tungstated zirconia through the intermediacy of cis-methyl nitrite yielding adsorbed NO and formates as the major products. The $HCOO^-$ ions reduce the adsorbed NO producing nitrogen. This is evident from the simultaneous disappearance of the Pd^+ nitrosyls and formate species at 450 °C (see figures 4, 5). The nitrosyls formed on the Pd^+ sites are stable at 450 °C in the absence of a reducer [20] and they would stay intact if the surface formates underwent decomposition to H_2O and CO_x at this temperature without interaction with the adsorbed NO. Possible reactive intermediates, which could not be detected under the conditions of the "NO_x–CH_4" experiment, could be the isocyanate ions, NCO^-. The precursor for these species is the aci-nitromethane [32–39]. NCO^- ions could form simultaneously with the appearance of nitromethane at 250–300 °C. These species are able to react rapidly with NO_2 [16, 33, 38] (which is available in the gas phase at these temperatures) and could escape from detection. The isocyanate ions are stable in vacuum [33] or inert atmosphere [16, 36] and under NO below 350 °C [12]. If formed, they should appear during the decomposition of authentic nitromethane. However, despite of the presence of some amount of aci-nitromethane at 150 °C, no adsorbed NCO^- ions (see figures 7, 8) or gaseous HNCO are observed. As proposed above, the surface concentration of the isocyanates is either too low to be detected or the dehydration of aci-nitromethane to isocyanic acid, respectively, NCO^- ions, does not take place to a significant extent on the WZ and Pd/WZ samples.

We believe that the results of this study can offer insights into the reaction mechanism of the reduction of nitric oxide with methane in excess oxygen catalyzed by a non-zeolite solid acid.

5. Conclusions

The interaction of methane at various temperatures with NO_x species formed by room temperature adsorption of NO + O_2 mixture on tungstated zirconia (18.6 wt.% WO_3) and palladium(II)-promoted tungstated zirconia (0.1 wt.% Pd) has been investigated using *in situ* FT-IR spectroscopy. The experimental results show that the methane interacts in a different way with the NO_x-precovered tungstated zirconia and Pd-promoted tungstated zirconia, although both materials in absence of adsorbed NO_x species are able to activate the hydrocarbon at the same temperature (250 °C). The surface nitrates adsorbed on tungstated zirconia do not promote the oxidation of the hydrocarbon whereas the nitrate species on the Pd-containing sample decompose to NO_2 initiating the formation of nitromethane at 250–300 °C. The latter compound decomposes at 300–350 °C through the intermediacy of cis-methyl nitrite to formates and NO adsorbed on Pd^+ sites. The $HCOO^-$ formed acts as a reductant of the adsorbed NO producing nitrogen.

The results on the thermal transformation of authentic nitromethane at various temperatures show that both tungstated zirconia and Pd-promoted tungstated zirconia catalyze the isomerization of nitromethane to cis-methyl nitrite at 150 °C. It is concluded that the role of palladium is to promote the thermal decomposition of the nitrate species formed by room-temperature adsorption of $NO+O_2$ to NO_2 and to provide sites at high temperatures for the adsorption of NO released as a decomposition product of the cis-methyl nitrite. The $W^{6+}=O$ species are responsible for the activation of the methane and for the oxidation of the formaldehyde (proposed as one of the primary products of the thermal transformation of nitromethane) to surface formates. The results of the reaction between the formaldehyde and NO adsorbed on Pd^+ sites of the Pd-promoted tungstated zirconia confirm the suggestion that the precursor of the reductant of the adsorbed NO is the formaldehyde produced by decomposition of the isomer of nitromethane, cis-methyl nitrite.

Acknowledgements

This work was financially supported by Bilkent University and the Scientific and Technical Research Council of Turkey (TÜBITAK), Project TBAG-2140.

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