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Nature and Reactivity of the Surface Species Formed after NO Adsorption and NO + O_2 Coadsorption on a WO_3–ZrO_2 Catalyst

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Adsorption of NO and its coadsorption with oxygen on WO_3–ZrO_2 as well as the reactivity of the surface NO_x species toward propene have been studied by FTIR spectroscopy and temperature-programmed desorption. NO adsorption on WO_3–ZrO_2 results in the formation of N_2O (2282, 2243, and 1224 cm^{-1}), NO^+ (2140 and 2119 cm^{-1}), surface nitrates (1614, 1570, and 1230 cm^{-1}), and nitrosyls (1936 cm^{-1}) created on cationic sites, which are affected by nitrates. Except for N_2O, the other species are developed with time. Addition of oxygen to the NO–WO_3–ZrO_2 system results mainly in an increase in the concentration of the surface nitrates. The latter are stable up to ca. 673 K and are thermally decomposed, yielding NO and NO_2, at higher temperatures. The nitrates interact with propene at ca. 473 K, giving an organic deposit which is decomposed to isocyanates (2296, 2278, and 2250 cm^{-1}). These species easily react with a NO + O_2 mixture, producing dinitrogen. The assignments of the IR bands are supported by ^{15}N-labeling experiments and analysis of the spectral region where the overtones and combination modes of surface nitrites and nitrates appear. Finally, some new aspects of the mechanism of selective catalytic reduction of NO_x by hydrocarbons are discussed.

Key Words: **adsorption; coadsorption; FTIR spectroscopy; nitrates; nitrites; nitrogen monoxide; ^{15}NO; nitrosyls; NO^+; propene; selective catalytic reduction; WO_3–ZrO_2.**

1. INTRODUCTION

During the past decade a large number of IR studies concerning different aspects of the mechanism of the selective catalytic reduction of NO_x by hydrocarbons have appeared (1–25). This is due to the fact that IR spectroscopy seems to be the most convenient and informative technique for this purpose (26). Although different hypotheses have been proposed, analysis of the literature data (1–25) suggests the following general scenario: Surface nitrates or nitrites are produced on the catalyst surface and react with hydrocarbons to form organic nitro compounds. The latter decompose to isocyanates, which react with NO_x from the gas phase, thus producing nitrogen. However, many details and peculiarities of certain catalysts are not yet clear and some reaction steps are still not generally accepted. To establish the process mechanism in detail, several additional precise studies are necessary.

In this work we report the results obtained mainly by IR spectroscopy on the mechanism of interaction of the SCR reactants (NO, O_2, and propene) over a WO_3–ZrO_2 catalyst. For better assignment of some IR bands ^{15}NO was also used in the experiments. Valuable information was obtained by analyzing the 2700- to 2400-cm^{-1} spectral region in which the overtones and combination modes of nitrates and nitro–nitrito compounds appear (27). Some additional information on the nature, properties, and reactivity of the surface species was obtained by temperature-programmed desorption.

2. EXPERIMENTAL

2.1. *Samples and Reagents*

The WO_3–ZrO_2 sample was prepared by suspending amorphous $Zr(OH)_4 \times nH_2O$ (MEL Chemicals, Manchester) in an appropriate amount of aqueous solution of ammonium metatungstate. The suspension was refluxed for 16 h at 383 K followed by evaporation of the water at 383 K. The precipitate was dried for 12 h at 383 K and finally calcined at 923 K. The nominal concentration of WO_3 in the sample was 19 wt%. This corresponded to a theoretical monolayer of tungsta on the zirconia surface. The sample thus obtained had a B.E.T. specific surface area of 120 $m^2\ g^{-1}$.

Nitrogen monoxide (>99.5%), propene (99.95%), and oxygen (99.996%) were supplied by Messer Griesheim. Labeled NO (^{15}NO) was supplied by Isotec, Inc., and was diluted in He (molar ratio of NO : He = 1 : 10).

2.2. *Methods*

FTIR spectroscopy studies were carried out with a Bruker IFS-66 apparatus at a spectral resolution of 2.0 cm^{-1} accumulating 128 scans. Self-supporting wafers (ca. 10 mg cm^{-2}) were prepared from the sample powders and heated directly in the IR cell. The latter was connected

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with a vacuum/sorption apparatus with a residual pressure of less than 10^{-3} Pa. Before the measurements all samples were activated for 1 h in a flow of oxygen at 673 K followed by a 1-h evacuation at the same temperature.

For the temperature-programed-desorption experiments, the sample was pretreated for 1 h at 673 K in a mixture of O_2 (5 ml min^{-1}) and He (20 ml min^{-1}) to remove adsorbed water and then cooled to room temperature in a stream of He (20 ml min^{-1}) within 1 h. A mixture of He (15.8 ml min^{-1}), O_2 (2.8 ml min^{-1}), and NO (1.4 ml min^{-1}) was fed over the sample for 1 h, followed by flushing with He (30 ml min^{-1}) for 1 h to remove the NO and O_2 in the gas phase. The thermal desorption was carried out by increasing the temperature with a ramp of 10 K min^{-1} from room temperature to 673 K. The desorbed gases were detected online by an SX200 quadrupole mass spectrometer (Vacuum Generators).

The gases were fed into a quartz reactor 8 mm in diameter, which could be heated by an oven to 673 K. The temperature was recorded by a thermocouple located close to the center of the catalyst bed. After passing through a jet separator, the gases were directly fed into the mass spectrometer. The sample amount was 800 mg, with particle sizes of 0.2–0.4 mm.

The specific surface area of the catalyst was determined by low-temperature nitrogen adsorption according to the B.E.T. method.

3. RESULTS AND DISCUSSION

3.1. Sample Characterization

The IR spectrum of the sample activated at 723 K contains two bands in the ν(OH) stretching region, at 3740 and 3620 cm^{-1}, assigned to Zr–OH and W–OH hydroxyls, respectively. In addition, an intense band at 1018 cm^{-1}, due to ν(W=O), and the respective overtone at 2025 cm^{-1} (28) are observed. Another weak band is observed at 1388 cm^{-1}. Usually, bands at this frequency are assigned to surface sulfates (30, 31). However our experiments (not reported here) suggest that this band is rather a combination mode involving W=O stretches, since its intensity changes in concert with the W=O stretching band. Also sulfate species that have been present in the catalyst as impurities would be decomposed after calcinations at 923 K.

3.2. Adsorption of NO

Introduction of NO (600-Pa equilibrium pressure) to the activated WO_3–ZrO_2 sample leads to the immediate appearance of two bands, at 2288 and 2243 cm^{-1}, in the IR spectrum (Fig. 1, spectrum a). These bands have been observed after N_2O adsorption on pure zirconia and assigned to the N–N stretching modes of N_2O located on Zr^{4+} sites (27). In addition, a weak band at 2140 cm^{-1}, characterizing NO^+ species (32), and a band at 1936 cm^{-1}, assigned to nitrosyl species (26), are also visible. Two bands of very weak intensity, at 1605 and 1220 cm^{-1}, are observed in the lower frequency region and assigned to ν_3' and ν_3'' modes, respectively, of surface bidentate nitrates (26). The free nitrate ion is characterized by one active ν_3 vibration which is split in the adsorbed state as a result of the reduction of the NO_3^- symmetry (33). Part of the absorbance at ca. 1220 cm^{-1} arises also from the N–O modes of adsorbed NO. A weak overtone of this mode (not shown) is detected at 2436 cm^{-1}. The bands at 2025 and 1388 cm^{-1} decrease simultaneously in intensity, showing interaction of NO with W-containing species. Since a great number of bands were observed in this study, their assignments are summarized in Table 1.

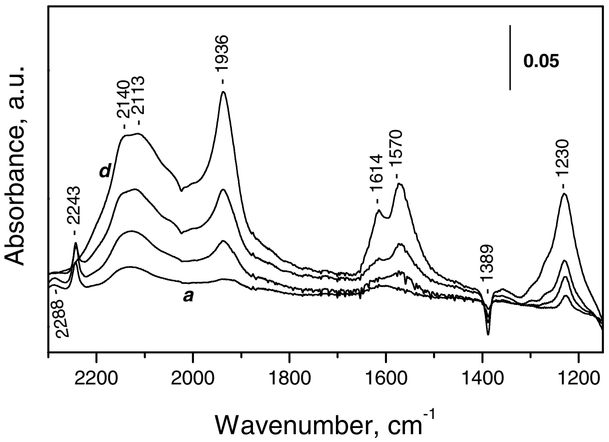

FIG. 1. FTIR spectra of NO (equilibrium pressure of 600 Pa) adsorbed on WO_3–ZrO_2. Spectrum taken immediately after NO admission (a) and development of the spectra with time (b–d). The spectra are background corrected.

Allowing the sample to stay in the NO atmosphere (Fig. 1, spectra b–d) results in a strong increase in intensity of all bands except those caused by N_2O. The higher frequency component of the nitrate band is split into two bands, at 1614 and 1570 cm^{-1}, and a shoulder at 1280 cm^{-1} is visible for the lower frequency component. The synchronous change in the intensity of all bands suggests that the corresponding species are produced via one surface reaction,

$$2NO_2 \rightarrow NO^+ + NO_3^-, \quad [1]$$

where NO_2 is produced by NO oxidation from the surface or NO disproportionation,

$$3NO \rightarrow N_2O + NO_2. \quad [2]$$

N_2O might also be formed in a redox process (29).

The development of the nitrosyl band at 1936 cm^{-1} can be explained by the assumption that bare zirconium (IV) ions do not form nitrosyls, but their electrophilicity increases when nitrate ions are coordinated to them. Indeed, an increase in the electrophilicity of cations has been observed after formation of nearby sulfates (30, 31), carbonates (34, 35), and nitrates (36).

TABLE 1

IR Bands Observed in This Study and Assigned to N-Containing Species

Band (cm^{-1})	After ^{15}N substitution	Isotopic shift factor	Assignment	Mode
Adsorption of NO				
2436	2396	0.9836	N_2O	2ν(N–O)
2243	2173	0.9688	N_2O	ν(N–N)
2140	2100	0.9813	NO^+	ν(N–O)
2113	2072	0.9806	NO^+	ν(N–O)
1936	1903	0.9829	$Zr^{4+}(NO_3^-)$–NO	ν(N–O)
1614	1581	0.9796	Bridging nitrates	ν_3'
1570	1538	0.9796	Bridging nitrates	ν_3'
1280	1250?	0.9765	Bridging nitrates	ν_3''
1230	1212	0.9853	Bridging nitrates	ν_3''
Coadsorption of NO and O_2				
2620	2580	0.9847	Nitrates	$\nu_3' + \nu_1$
2531	2490	0.9851	Nitrates or nitrites	Overtones or comb. modes
2496	2459	0.9853	Nitrites or nitrates	”
2464	2428	0.9856	Nitrites or nitrates	”
2433	2398	0.9838	Nitrites or nitrates	”
2143	2102	0.9807	NO^+	ν(N–O)
1930	1896	0.9824	$Zr^{4+}(NO_3^-)$–NO	ν(N–O)
1748	1704	0.9748	N_2O_4	ν_{as}(N–O)
1617	1579	0.9765	Bridging nitrates	ν_3'
1578	1540	0.9759	Bridging nitrates	ν_3'
1535	1511	0.9843	Nitrates and/or N_2O_3	ν_3' or $\nu_{as}(NO_2)$
1280	1260	0.9843	Bridging nitrates	ν_3''
1258	1243	0.9880	Nitrates and/or N_2O_3	ν_3'' or $\nu_s(NO_2)$
1235	1215	0.9938	Bridging nitrates	ν_3''
Interaction of surface NO_x species with propene				
2296	2272	0.9895	Isocyanates or nitriles	ν(C–N)
2278	2249	0.9873	Isocyanates or nitriles	ν(C–N)
2250	2219	0.9862	Isocyanates or nitriles	ν(C–N)

3.3. Coadsorption of NO with O_2

Addition of increasing amounts of oxygen to the sample exposed to a NO atmosphere (Fig. 2, spectra b–e) leads mainly to an increase in intensity of the nitrate bands, i.e., NO is oxidized to NO_3^-. The nitrosyl band at 1930 cm^{-1} initially increases in intensity and then almost disappears from the spectrum due to oxidation of NO. In addition, a weak band at 1744 cm^{-1} (in-phase antisymmetric NO stretches) suggests formation of a small amount of adsorbed N_2O_4 (26). Evacuation at ambient temperature (Fig. 3,

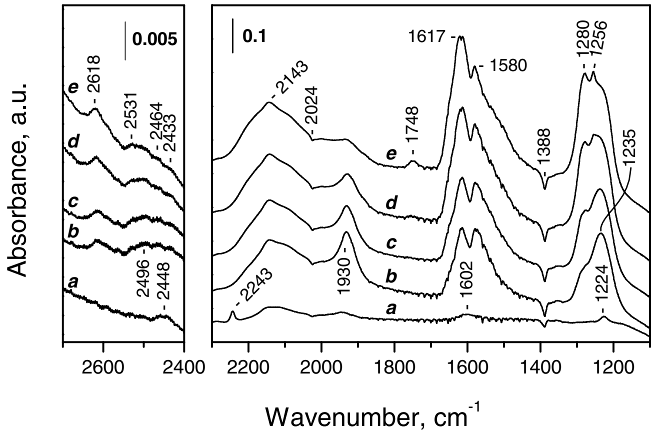

FIG. 2. FTIR spectra of NO and O_2 coadsorbed on WO_3–ZrO_2. Equilibrium NO pressure of 600 Pa (a); at 300 Pa (b) and 900 Pa (c) initial pressure after addition of O_2; after 5 min (d); and at 2.5 kPa initial pressure (e). The spectra are background corrected.

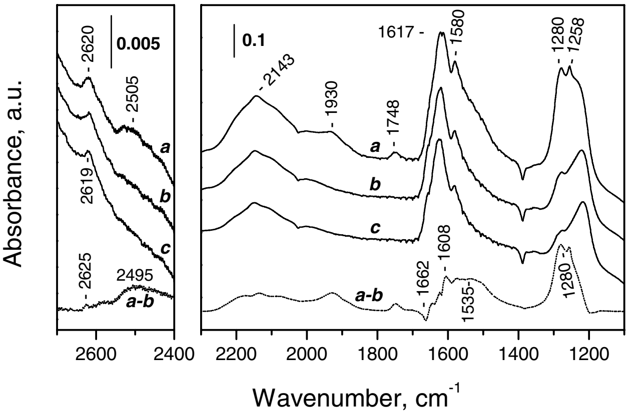

FIG. 3. FTIR spectra of NO (600-Pa initial pressure) and O_2 (2.5 kPa initial pressure) coadsorbed on WO_3–ZrO_2 (a), after a short evacuation (b), and under dynamic vacuum (c). The spectra are background corrected.

spectra b and c) leads to the disappearance of the bands due to adsorbed NO and N_2O_4 and to a slight decrease in the amounts of NO^+ and nitrates. Difference spectra indicate the disappearance of bands at 1608, 1535, 1280, and 1258 cm^{-1} and development of bands at 1662 and 1205 cm^{-1}. These bands are assigned to bridging nitrate species (33), suggesting that the symmetry of part of the nitrates changes as the coverage decreases. When the sample is evacuated at 423 K (spectrum not shown), NO^+ disappears and the nitrate bands decrease in intensity. After consumption of all NO^+, however, further evacuation leads to no substantial changes in the spectra. This suggests recombination of NO^+ with surface nitrates according to the reverse of reaction [1]. The nitrates are thermally stable up to 673 K and start to decompose during evacuation at higher temperatures.

Special analysis of the spectra was made in the 2700- to 2400-cm^{-1} region (see the left panels in Figs. 2 and 3). Coadsorption of NO and O_2 results in the appearance of several bands with very low intensity in this region. A band at 2620–2618 cm^{-1} develops with time and is stable toward evacuation. According to literature data (27) this band is assigned to a combination mode of the ν_3' nitrate band at 1617 cm^{-1} with the ν_1 band at ca. 1005 cm^{-1} (not observed here because of the sample cutoff). Indeed, the band at 2620 cm^{-1} follows the changes in the nitrate bands. Another broad band is observed at lower frequencies. It consists of three components, located at 2496, 2464, and 2433 cm^{-1}. A band at 2531 cm^{-1} appears in a strongly oxidizing atmosphere, whereas the three bands at lower frequencies decrease in intensity. This band is most probably also due to a combination mode of monodentate nitrates (27). The bands below 2500 cm^{-1} disappear after evacuation, whereas the bands at higher frequencies are quite stable.

The positions of the bands below 2500 cm^{-1} are too low to arise from nitrate combination modes. Analysis of the spectra indicates that these bands could be due to overtones of bands at around 1230 cm^{-1}. Indeed, the difference spectra (see Fig. 3) show an enhanced intensity of the bands around 1300–1200 cm^{-1} with respect to the intensity of the bands at 1600–1500 cm^{-1} (compare, for instance, with Fig. 3 spectrum a). These results can be rationalized by the assumption that nitrito species absorb around 1300–1200 cm^{-1} but are masked by the strong nitrate bands. This assumption is also supported by the fact that the respective overtones at 2500–2400 cm^{-1} decline in the presence of excess oxygen. The disappearance of these bands after evacuation could be due to disproportionation of the nitrites or their interaction with NO^+ with formation of NO and nitrates.

The products of the decomposition of the surface species were followed by temperature-programmed desorption (Fig. 4). The TD signal of NO ($m/e = 30$) shows a broad peak with a maximum at about 380 K. As NO is fragmented in the mass spectrometer, the signals of $m/e = 16$ and 14 show a similar pattern. It can also be seen that NO_2 ($m/e = 46$) desorbs from the sample. Other gases, e.g., H_2O, N_2, N_2O, and O_2, are not produced in detectable amounts during the interaction of NO and O_2 with this catalyst. The results are consistent with the infrared data if we infer the desorption of NO and the reverse of reaction [1] as being responsible for the desorption trace between 320 and 550 K. The surface nitrates decompose at temperatures >670 K, a temperature region which was not accessible in the TD system used.

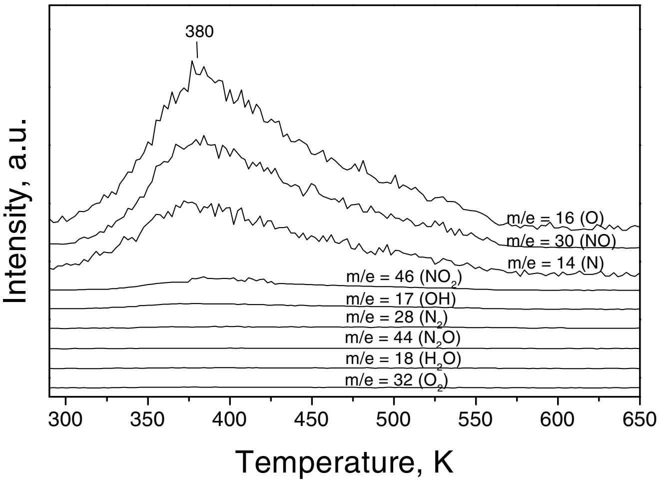

FIG. 4. Temperature-programmed-desorption patterns of NO and O_2 coadsorbed on WO_3–ZrO_2. Signals of different fragments recorded in the mass spectrometer are shown.

3.4. *Adsorption of ^{15}NO and Its Coadsorption with O_2*

The isotopic shift factor for the ^{14}N–$^{14}N \rightarrow {}^{15}N$–$^{15}N$ modes is 0.9661, while it is 0.9821 for the ^{14}N–$^{16}O \rightarrow {}^{15}N$–$^{16}O$ substitution (26). The isolated stretching modes between two atoms follow well these theoretical values, whereas some deviations are observed when the vibrations involve more than two atoms (37). For instance, the antisymmetric NO_2 stretches of $^{14}N_2O_3$ are shifted, in $^{15}N_2O_3$, by a factor of 0.9785, whereas the factor is 0.9877 for the corresponding symmetric modes (38).

Adsorption of ^{15}NO and its coadsorption with O_2 generally leads to the formation of the same type of species as those observed after NO adsorption but involving ^{15}N atoms (Figs. 5–7). The band observed at 2243 cm^{-1} is assigned to $^{14}N_2O$ and suggests the presence of small amounts of this compound in our adsorbate. The respective band of $^{15}N_2O$ is detected at 2173 cm^{-1}. This mode undergoes the largest shift (factor of 0.9688; see Table 1), which is consistent with the nature of this vibration, namely N–N stretching modes. A very good coincidence with the expected shift was established for the bands assigned to NO^+ and nitrosyls. As expected, some deviations were observed with the nitrate bands (see Table 1).

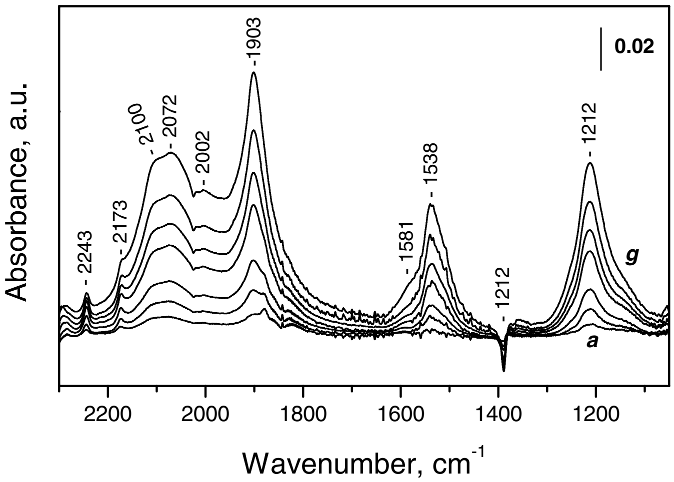

FIG. 5. FTIR spectra of ^{15}NO in He (partial ^{15}NO equilibrium pressure of 600 Pa) adsorbed on WO_3–ZrO_2. Spectrum taken immediately after ^{15}NO admission (a) and development of the spectra with time (b–g). The spectra are background corrected.

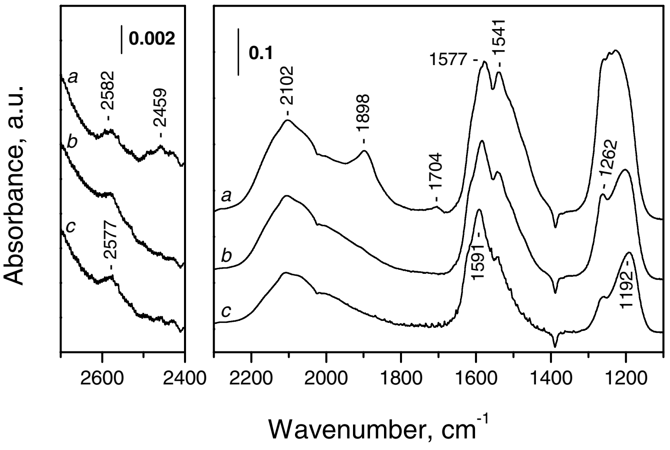

FIG. 7. FTIR spectra of ^{15}NO (600-Pa initial partial pressure) and O_2 (2.5 kPa initial pressure) coadsorbed on WO_3–ZrO_2 (a), after short evacuation (b), and under dynamic vacuum (c). The spectra are background corrected.

3.5. Adsorption of Propene

Introduction of propene (1.2-kPa equilibrium pressure) to the activated WO_3–ZrO_2 sample results in an immediate appearance of bands located at 2985, 2950, 2880, 1668, 1610, 1580, 1466, 1455, 1390, 1375, 1183, and 1138 cm^{-1} (Fig. 8, spectrum a). Simultaneously, the W=O overtone band at 2023 cm^{-1} is shifted to 1993 cm^{-1}, which indicates that propene is also adsorbed on the tungsta-containing part of the surface. Heating in the propene atmosphere at 373 K results mainly in an increase in intensity of the bands in the 1500- to 1300-cm^{-1} region (Fig. 8, spectrum b). Interaction of the sample with propene at 473 K leads to a strong increase in intensity of the 1668-cm^{-1} band and appearance of a new band at 1540 cm^{-1}. Simultaneously, a new band at 1596 cm^{-1} masks the 1616-cm^{-1} band (Fig. 8, spectrum c). Difference spectra also indicate the appearance of bands at 1593 and 1419 cm^{-1} and the disappearance of bands at 1470 and 1380 cm^{-1}. The surface species thus produced are relatively stable. Evacuation at 473 K hardly affects the spectrum: Only the 1596-cm^{-1} band slightly decreases in intensity and the band at 1540 cm^{-1} slightly increases (Fig. 8, spectrum d).

Adsorption of propene, depending on the sample nature, may result in the appearance of various species (39). One possibility is the formation of π-bonded complexes. However, they are weakly bonded and characterized by a C–H stretching mode at 3090 cm^{-1}, which is hardly observed in our spectra. In agreement with data from the literature

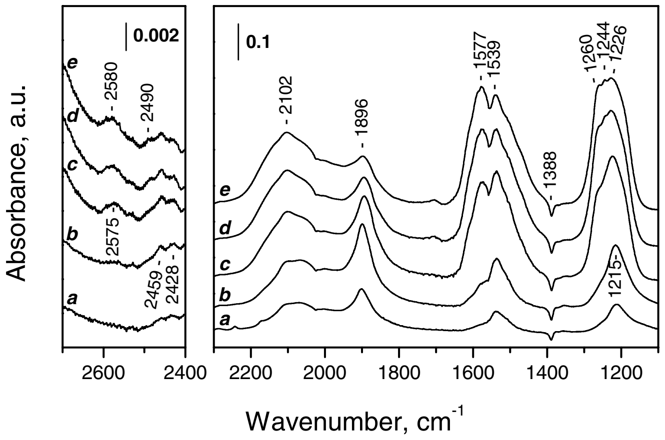

FIG. 6. FTIR spectra of ^{15}NO and O_2 coadsorbed on WO_3–ZrO_2. Partial ^{15}NO equilibrium pressure of 600 Pa (a); at 400 Pa initial pressure after addition of O_2 (b); after 5 min (c); and at 900 Pa (d) and 2.5 kPa (e) initial pressure. The spectra are background corrected.

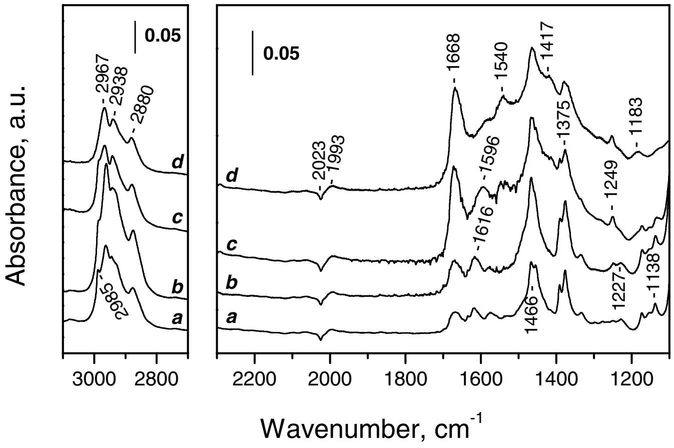

FIG. 8. FTIR spectra of C_3H_6 (equilibrium pressure of 1.2 kPa) adsorbed on WO_3–ZrO_2 (a), after 30 min of heating in propene at 373 (b) and 473 K (c), and after a 30-min evacuation at 473 K (d). The spectra are background corrected.

(18), we assign the bands at 1466–1455 and 1390–1375 cm^{-1} to the $\delta_{as}(CH_x)$ and $\delta_s(CH_x)$ modes, respectively, of allylic species. The bands produced at higher temperatures of interaction are assigned to O-containing species. Namely, the pair of bands at 1596 and 1420 cm^{-1} characterizes carboxylates (5, 18). Indeed, they are developed at the expense of the allylic complexes. The strong band at 1668 cm^{-1} is indicative of the presence of acrolein and is assigned to the C=O stretching mode (16, 18).

3.6. Interaction of Propene with Surface NO$_x$ Species

It is established that the reaction order of HC-SCR is ca. 1 toward hydrocarbons and ca. 0 toward NO (40). This suggests that the hydrocarbons react with a catalyst surface modified by NO$_x$. To be intermediates in SCR, the surface NO$_x$ species have to be thermally stable at temperatures at which SCR proceeds, but they have to react easily with hydrocarbons. The only stable surface NO$_x$ species on our sample were nitrates and NO$^+$ (less stable), being thus potential candidates for SCR intermediates. For this reason we studied their interaction with propene.

Surface NO$_x$ species were produced by coadsorption of NO and O$_2$, followed by evacuation (Fig. 9, spectrum a). Introduction of propene to this sample leads to the appearance of weak bands at 1455, 1378, and 1173 cm^{-1} (Fig. 9, spectrum b). These bands have a lower intensity compared to those created by propene adsorption on the pure sample, which is consistent with the blocking of part of the surface with NO$_x$ species. The nitrate band at 1623 cm^{-1} is slightly redshifted and the intensities of the nitrate bands at 1278 and 1217 cm^{-1} slightly decrease. The overtone band at 2617 cm^{-1} also appears with a slightly reduced intensity. Simultaneously, the band due to NO$^+$ disappears completely, which indicates either replacement of NO$^+$ by propene or their interaction. However, we suggest the former possibility, since no interaction products were evident in the spectra. It is possible that propene-induced recombination of part of NO$^+$ with nitrates, according to the reverse of reaction [1], has occurred.

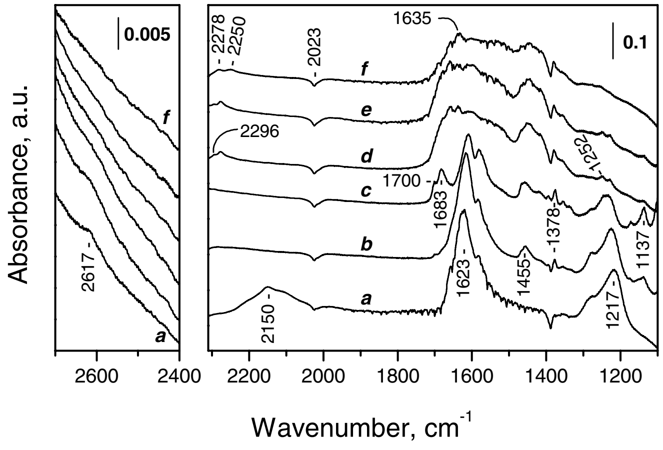

FIG. 9. FTIR spectra of NO (600-Pa initial pressure) and O$_2$ (2.5-kPa initial pressure) coadsorbed on WO$_3$–ZrO$_2$, followed by evacuation (a); after introduction of C$_3$H$_6$ (1.2-kPa pressure) (b); after 30 min of heating in propene at 373 (c) and 473 K (d); and after a 30-min evacuation at ambient temperature (e) and at 473 K (f). The spectra are background corrected.

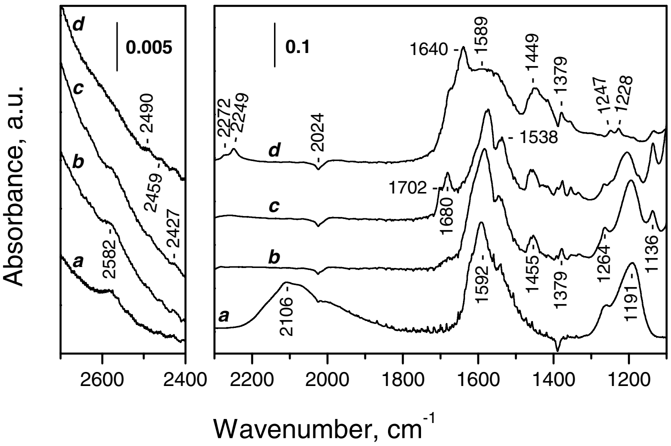

FIG. 10. FTIR spectra of ^{15}NO (600-Pa partial pressure) and O$_2$ (2.5-kPa initial pressure) coadsorbed on WO$_3$–ZrO$_2$, followed by evacuation (a), after introduction of C$_3$H$_6$ (1.2-kPa pressure) (b), and after 30 min of heating in propene at 373 (c) and 473 K (d). The spectra are background corrected.

Heating the sample in propene at 373 K results in a strong decrease in the nitrate concentration, the band at 1623 cm^{-1} being shifted to 1610 cm^{-1}. Due to the superposition of the different bands it is difficult to estimate this decrease by analysis of the region of the fundamental vibrations. However, this information can be obtained from the combination modes: It is seen that the nitrate band at ca. 2620 cm^{-1} has very low intensity (Fig. 9, spectrum c). In addition, two new bands, at 1700 and 1683 cm^{-1}, appeared in the spectrum.

Interaction with propene at 473 K results in complete disappearance of the nitrates and development of a broad absorption below 1700 cm^{-1}, where two maxima, at 1635 and 1450 cm^{-1}, can be distinguished (Fig. 9, spectrum d). In addition, two very weak bands, at 2296 and 2278 cm^{-1}, appear. After this treatment the sample color turns black, which suggests the formation of organic deposits. This deposit is quite stable. Its characteristic IR bands are not affected by evacuation at ambient temperature (Fig. 9, spectrum e) and evacuation at 473 K produces only a small change in the broad band below 1700 cm^{-1} (Fig. 9, spectrum f). In this case the band at 2296 cm^{-1} disappears and a new band at 2250 cm^{-1} appears instead.

The spectra recorded under the same conditions, but using ^{15}NO in the experiments, allow the distinguishing of N-containing from N-free surface species (Fig. 10). It is evident that the bands at 2300–2200 cm^{-1} spectral region are due to

N-containing species. The isotopic shift coincides very well with the theoretical shift for C–N vibrations (0.9845) (26). On this basis, and in agreement with data from the literature, we assign these bands to the C–N modes of different isocyanate species. However, the possibility is not excluded that some of the bands characterize C–N vibrations of nitriles (26).

The bands at 1700 and 1680 cm^{-1} were not observed after propene adsorption and are not affected by ^{15}N isotope labeling. Therefore, they correspond to N-free compounds and we assign these bands to C=O stretching modes. These results suggest the direct oxidation of the hydrocarbon by the surface NO_x species. The bands at 1700 and 1680 cm^{-1} decrease in intensity when heating at 473 K and bands assigned to isocyanates appear instead. This suggests a conversion of –C=O-containing species into –NCO-containing species, presumably with the participation of the surface nitrates.

Many reported data suggest that surface isocyanates are important SCR intermediates (2, 3, 5, 8, 10–12, 21–25). It had been found that they easily interact with $NO + O_2$ mixtures (2, 3, 11, 12). It is of interest to test their reactivity toward NO and O_2 also on the present samples. Surface isocyanate species (bands at 2282 and 2251 cm^{-1}) were produced after evacuation of the sample containing the organic deposit at 533 K (Fig. 11, spectrum a). Exposure to NO alone does not change the IR spectrum (Fig. 11, spectrum b). Addition of oxygen also hardly affects the spectrum (Fig. 11, spectra c and d). Development of a weak band at 2620 cm^{-1} in the overtones/combination region indicates that only a small amount of nitrates are produced and some nitrosyls are monitored by a band at 1930 cm^{-1}. However, allowing the sample to stay for 30 min in the $NO + O_2$ atmosphere at ambient temperature (see Fig. 11, spectrum e) results in (i) formation of a significant amount of nitrates (bands at 2620, 1617, 1580, 1280, and 1236 cm^{-1}) and (ii) appearance of some NO^+ (a band at 2142 cm^{-1}) and almost complete disappearance of the isocyanate bands. Brief heating in this atmosphere at 573 K results in an enhancement of the NO^+ and nitrate bands and appearance of bands assigned to nitrites (2500–2400 cm^{-1}) and a new band at 1792 cm^{-1} (Fig. 11, spectrum f). This band is assigned to C=O stretching of partially oxidized hydrocarbons (16), i.e., an intermediate of the oxidation of the organic deposit. Indeed, after the described procedure the sample color turns yellow, which suggests removal of the organic deposit. The 1792-cm^{-1} band disappears after heating the sample in the NO_x atmosphere at 673 K (Fig. 11, spectrum g). The ratio between the intensities of the bands around 1600 and 1250 cm^{-1} indicates that after this procedure the organic deposit has been (almost) fully oxidized.

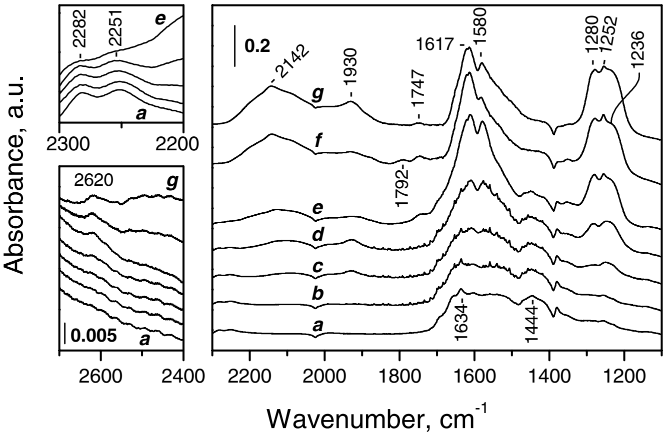

FIG. 11. (Continuation of Fig. 8.) A 30-min evacuation at 523 K (a); addition of NO (500-Pa pressure) (b); addition of O_2 at pressures of 160 Pa (c) and 1 kPa (d); after 30 min (e); and after heating for 10 min in the gas mixture at 573 K (f) and at 673 K (g). The spectra are background corrected.

In conclusion, our results demonstrate that intermediate species between NO_x and propene on WO_3–ZrO_2 are –C=O-containing compounds, which are thermally decomposed into C–N containing species. The latter easily react with a $NO + O_2$ mixtures even at ambient temperature. This results from the higher oxidation ability of $NO + O_2$ mixtures compared to that of pure NO and O_2. These observations are in agreement with the results reported by Chen *et al.* (2). Using ^{15}NO, these authors demonstrated that N_2 is produced by coupling one nitrogen atom from the deposit with one nitrogen atom from gaseous NO_x. It should be emphasized that preliminary catalytic tests in a fixed-bed flow reactor at 670 K clearly showed that the tungstated zirconia is an active catalyst for the $NO + O_2 +$ propene reaction, although quantitative rate data cannot be given as yet.

4. CONCLUSIONS

- The stable surface species produced after coadsorption of NO and O_2 on WO_3–ZrO_2 are surface nitrates and NO^+ (less stable).
- Propene adsorption on WO_3–ZrO_2 results in formation of allylic species and, at 473 K, of carboxylates and acrolein.
- Nitrates interact with propene even at 473 K, giving an organic deposit which is decomposed to isocyanates. The latter easily react with a $NO + O_2$ mixture, giving N_2 and H_2O.
- Analysis of the spectra in the region of overtones and combination modes is very helpful in distinguishing between surface NO_x and C-containing species, since their bands in the region of the fundamental vibrations overlap.

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