

Identification, Stability, and Reactivity of NO_x Species Adsorbed on Titania-Supported Manganese Catalysts

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The nature of the NO_x species obtained on NO adsorption and its coadsorption with O₂ at room temperature on TiO₂ and MnO_x/TiO₂ catalysts with two different manganese loadings has been studied by means of *in situ* Fourier transform infrared spectroscopy. In order to obtain information about the potentials of titania-supported manganese materials as catalysts for selective catalytic reduction (SCR) of NO by hydrocarbons, the stability and reactivity of the adsorbed NO_x species toward decane has been investigated. The adsorption of NO on the support and the catalysts leads to disproportionation of NO to anionic nitrosyl, NO⁻, its protonated form, NOH, and NO₂. On coadsorption of NO and O₂ at room temperature, various kinds of surface nitrates are observed differing in the mode of their coordination. The nitrates on the manganese-containing samples are characterized by significantly lower thermal stability than the NO₃⁻ species on the pure support, titania. The difference in the thermal stability of the nitrates parallels their reactivity toward the reducer (decane). The monodentate and bridged nitrates formed on the manganese catalysts studied are able to oxidize the adsorbed hydrocarbon at temperatures as low as 373 K. A mechanism for the interaction between the surface nitrates and the adsorbed decane is proposed in which the NO₃⁻ and NCO⁻ species are considered as important intermediates leading to dinitrogen formation. The concentration of the reactive surface nitrates on the MnO_x/TiO₂ catalyst with manganese content corresponding to a monolayer is considerably greater than that on the sample with higher manganese loading. The former catalyst is promising for the SCR of NO by longer chain saturated hydrocarbons. © 2001 Elsevier Science

Key Words: adsorption of NO and NO/O₂; *in situ* FTIR; TiO₂; MnO_x/TiO₂; NO_x selective reduction by decane; mechanism.

INTRODUCTION

It is believed that selective catalytic reduction (SCR) by hydrocarbons is the most promising way for elimination of nitrogen oxide emissions from diesel and lean-burn engines. However, most DeNO_x catalysts do not possess sufficient activity for commercial application due to the poisoning effect of sulfur compounds contained in the fuel. It has been reported (1, 2) that sulfation of TiO₂ in a SO₂ atmosphere is difficult, and sulfur-resistant TiO₂ monolithic

supports have been used in lean-DeNO_x catalysts (3). On the other hand, MnO_x species supported on alumina (4, 5), titania (5, 6), and active carbon (7) exhibited a good performance in the removal of NO_x by SCR with ammonia at low temperatures. Recent investigations have shown that ammonia can be replaced by methane as the reducing agent and manganese(II)-exchanged zeolites (8) are among the most promising catalysts. It thus appeared interesting to investigate the potentials of MnO_x/TiO₂ catalytic systems for application to SCR of NO_x by higher hydrocarbons.

There are few papers dealing with *in situ* IR characterization of the species produced during adsorption of NO and NO/O₂ coadsorption on manganese–alumina catalysts (9–11) and Mn–ZSM5 (12), and no data have been published on MnO_x/TiO₂ systems (13).

The aim of this paper is to identify the species formed during NO adsorption and NO/O₂ coadsorption on titania-supported manganese catalysts by application of *in situ* Fourier transform infrared (FTIR) spectroscopy and to study their stability and reactivity toward decane. The catalysts were prepared using ion exchange and impregnation techniques, ensuring two different manganese loadings. Their physicochemical characteristics, nature, and localization of the active phase have been reported (14). On the surface of the ion-exchanged sample two kinds of manganese(III) cations, differing in their coordinative saturation and localization, are stabilized. The impregnated catalyst contains a mixture of manganese(III) and manganese(II) species.

EXPERIMENTAL

The support TiO₂ used was a commercial product (Degussa P25, surface area 52 m²/g) containing 90% anatase and 10% rutile.

Two different catalysts which were obtained by ion exchange and incipient wetness techniques (14) were studied. The sample prepared by ion exchange (denoted by MnT-IE) contained 1.9 wt% manganese, which corresponded to monolayer coverage. For the impregnated catalyst (4 wt%

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of nominal manganese content) the notation MnT-I is used.

The FTIR spectra were obtained on a Bomem-MB102 (Hartman & Braun) FTIR spectrometer at a spectral resolution of 4 cm^{-1} (256 scans). A specially designed IR cell allowed recording of the spectra at ambient temperature and catalyst activation at higher temperatures. The cell was connected to a vacuum/adsorption apparatus. Self-supporting discs were used for the FTIR studies.

The samples were activated in the IR cell by evacuation at 673 K for 1 h, heating at 100 Torr (1 Torr = 133.3 N m^{-2}) of oxygen for 1 h at 673 K, and evacuation for 1 h at the same temperature. The spectra of the catalysts thus activated were taken at ambient temperature and used as a background reference.

The nitrogen monoxide (99.9%) was supplied by Air Products. The decane used was of analytical (gas chromatography) grade.

RESULTS AND DISCUSSION

Adsorption of NO and NO/O₂ Coadsorption

TiO₂

Adsorption of NO at room temperature. The adsorption of NO (10 Torr) on titania at room temperature is a time-dependent process (Fig. 1A). Immediately after introduction of NO into the IR cell (spectrum 0'), a band at 1160 cm^{-1} and weak bands at 1913, 1843, 1710, 1610,

and 1550 cm^{-1} are detected. In the OH stretching region a negative band at 3690 cm^{-1} and weak absorption with maximum at 3565 cm^{-1} are observed. All these bands grow with time except for the bands at 3565, 1160, and 1843 cm^{-1} : they reach saturation in 15 min (compare spectra 15' and 30' and see below). The spectrum taken after 30 min of NO adsorption is characterized by bands at 1913, 1843, 1715, 1625, 1610, and 1580 cm^{-1} and a weak absorption at about 1500 cm^{-1} . The bands at approximately 1270 and 1220 cm^{-1} appear as high-frequency shoulders to the band at 1160 cm^{-1} . In the OH stretching region a negative band at 3718 cm^{-1} , a positive one at 3565 cm^{-1} , and broad absorption between 3500 and 3000 cm^{-1} are observed. Evacuation for 10 min at room temperature causes a decrease in the intensity of the bands at 1913, 1843, 1715, and 1160 cm^{-1} and enhancement of the absorption in the 1625–1200 cm^{-1} region. The negative band at 3718 cm^{-1} and the positive absorption at 3565 cm^{-1} appear less intense.

In order to assign the absorption bands observed, the subtraction spectra are considered (Fig. 1B). The spectrum 15'–0' shows that the intensities of the bands at 1913 and 1843 cm^{-1} and below 1800 cm^{-1} increase in the first period of 15 min. In the next 15 min (spectrum 30'–15') the bands at 3565, 1843, and 1160 cm^{-1} stop growing whereas the bands at 1625, 1610 (shoulder), 1580, 1550, and 1505 cm^{-1} (shoulder) rise in intensity simultaneously with the complex absorption with a maximum at 1220 cm^{-1} . These changes are accompanied by a considerable growth of the band at 1913 cm^{-1} and additional alteration of the isolated

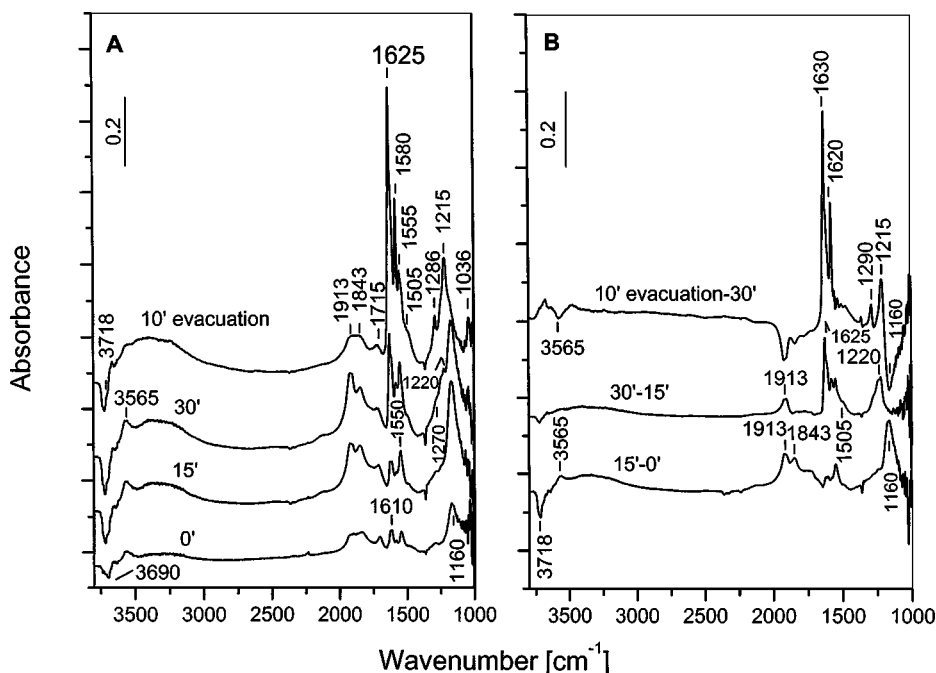


FIG. 1. (A) FTIR spectra of adsorbed NO (10 Torr) at room temperature on the activated TiO₂ sample for various times and after evacuation at room temperature for 10 min. (B) FTIR subtraction spectra obtained from the spectra in part (A) of the figure.

surface OH groups at 3718 cm⁻¹ (negative band). A slight increase in the absorption due to H-bonded hydroxyls (3600–3000 cm⁻¹) is observed.

The region between 1625 and 1200 cm⁻¹ is typical of NO₃⁻ species coordinated to the titania surface (15), and the absorption bands observed can be attributed to bridged (1625 and 1215 cm⁻¹), bidentate (1615, 1580, 1550, and 1215 cm⁻¹), and monodentate (1505 and 1280 cm⁻¹) nitrates. The formation of surface nitrates suggests disproportionation of NO on the surface of TiO₂ and the following reaction can be proposed:

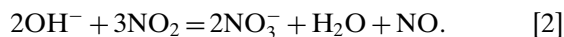


The molecule of NO₂ is characterized by an IR band at 1612 cm⁻¹ due to ν_{as}(NO₂) vibrations (16, 17). The corresponding symmetric mode at 1325 cm⁻¹ is Raman active. When adsorbed on oxide surfaces, NO₂ gives rise to an absorption band in the 1642–1605 cm⁻¹ region (13). This region is typical of surface nitrate species as well. For this reason, the weak band at 1610 cm⁻¹ (Fig. 1A, spectrum 0') can be tentatively assigned to adsorbed NO₂.

The band at 1160 cm⁻¹ can be attributed to the ν(NO) stretching mode of NO⁻ species (18). The involvement of surface OH groups in the interaction with NO is supported by the appearance of a negative absorption at 3690 cm⁻¹ and a positive band at 3565 cm⁻¹ (Fig. 1, spectrum 0'). The latter absorption is characteristic of O–H stretchings in N–OH groups (15–17). The experimental fact that the intensity of the band at 3565 cm⁻¹ changes in parallel with that of the band at 1160 cm⁻¹ (see Fig. 1B, spectra (30'–15') and (10' evacuation–30')) leads to the assumption that protonated anionic nitrosyl (i.e., NOH) species can form. The N–O–H bending mode is expected to fall in the 1300–1200 cm⁻¹ region but could be covered by the absorption due to low-frequency components of the ν₃ split modes of the nitrate species. Anionic nitrosyl NO⁻ species have been observed when NO is adsorbed on alkaline earth metal oxides such as MgO (19) and CaO (20) and on lanthanide metal oxides such as CeO₂ (21) and La₂O₃ (22, 23), giving rise to absorption in the 1195–1100 cm⁻¹ region. Hadjiivanov and Knözinger (18) reported also formation of NO⁻ species (band at 1170 cm⁻¹) during contact of NO with the titania surface, assuming disproportionation of NO to NO⁻, nitrates, and hyponitrite ion, N₂O₂²⁻ (absorption band at 1335 cm⁻¹). Under the conditions of our experiments, the latter species (which can arise by dimerization of NO⁻) is not observed.

The NO₂ produced by reaction [1] can interact with the surface OH groups, giving nitrate species (15, 24). Indeed, the growth of nitrate bands with time is accompanied by development of a negative band at 3718 cm⁻¹ in the OH stretching region and appearance of H-bonded hydroxyls (Fig. 1). The following disproportionation reaction has been proposed (15) as possible for the formation of nitrate

species on the titania surface during adsorption of NO₂:



This is a relatively slow process (15, 24). It can be proposed that the production of NO₂ according to reaction [1] is faster than its consumption (reaction [2]). This can explain the growth of the nitrate bands after establishing the equilibrium of reaction [1]. The occurrence of the process described by reaction [2] has been confirmed by adsorption of NO₂ on deuteroylated TiO₂ (24). This means that part of the absorption at 1625 cm⁻¹ is due to bending modes of adsorbed water molecules.

The bands at 1913 and 1843 cm⁻¹ fall in the nitrosyl region. However, interpretation of them as linear nitrosyls coordinated to two types of coordinatively unsaturated (cus) would be incorrect because the concentration of the more energetic (cus) titanium(IV) cations (α-titanium(IV) sites) is lower than that of β-titanium(IV) cations (25). The intensities of the bands at 1913 and 1843 cm⁻¹ shown in Fig. 1 are reversed (assuming similar absorptivities).

The subtraction spectra in Fig. 1B show that the bands at 1913 and 1843 cm⁻¹ increase in intensity within the period of 0–15 min. However, in the next period of 15 min (spectrum 30'–15') only the former band grows further in parallel with the bands due to nitrate species. For this reason, the band at 1913 cm⁻¹ is attributed to NO adsorbed on the titanium(IV) site to which a nitrate (bridged or monodentate) ion is coordinated (i.e., to the complex ON–Ti⁴⁺–ONO₂⁻). The development of the band at 1843 cm⁻¹ with time follows the behavior of the band at 1160 cm⁻¹ due to NO⁻/NOH species (Fig. 1B). Accordingly, the absorption at 1843 cm⁻¹ is assigned to the complex ON–Ti⁴⁺–NO⁻ and/or ON–Ti⁴⁺–NOH. The NO₃⁻ and NO⁻/NOH species differ in their electronegativity, the nitrate ion possessing electron-accepting ability. As a result the electrophilicity of the titanium(IV) cations increases. This leads to enhancement of the σ component of the bond between the NO and the titanium cation and a stronger N–O bond in the ON–Ti⁴⁺–ONO₂ nitrosyl complex (i.e., the ν(NO) stretching mode is at higher wavenumber). The nitrosyl band at 1843 cm⁻¹ falls below the ν(NO) mode of gaseous nitrogen oxide (1876 cm⁻¹), which suggests a π contribution to the bond of adsorbed NO. It can be assumed that NO⁻/NOH species can act as π-donor ligands. This leads to an increase in the electron density on the titanium ion. Consequently, the ν(NO) stretching mode is shifted to a lower frequency. The higher stability of the nitrosyls at 1843 cm⁻¹ than those at 1913 cm⁻¹, which is observed on evacuation at room temperature (Fig. 1), is consistent with this assumption and indicates stabilization of the adsorbed NO through π-back donation. The proposed interpretation is in agreement with the conclusion made by Hadjiivanov and Knözinger (18) that the titanium(IV) cations alone do not form nitrosyls. However, it contradicts the assignment of this pair of bands

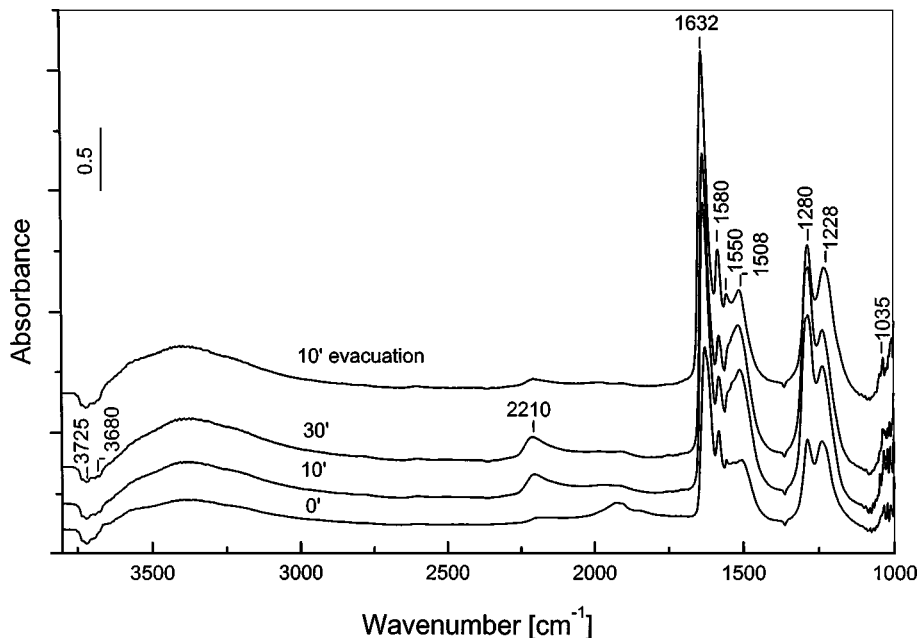
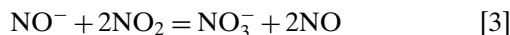


FIG. 2. FTIR spectra of adsorbed NO/O₂ mixture (28 Torr, NO : O₂ = 1 : 4) at room temperature on the activated TiO₂ sample for various times and after evacuation at room temperature for 10 min.

proposed by them. According to Ref. (18), the bands at 1913 and 1848 cm⁻¹ are attributed to Fermi resonance of N–O stretching vibration (in nitrosyl formed on the titanium(IV) site having nitrate species in close proximity) with the Ti⁴⁺–N mode at approximately 900 cm⁻¹. The argument for this interpretation is that the bands at 1913 and 1848 cm⁻¹ grow in parallel. However, this is not the case reported here. In addition, the M–N stretching vibrations in nitrosyl complexes appear at lower frequencies (below 650 cm⁻¹ (17)).

Evacuation for 10 min at room temperature causes a strong decrease in the intensity of the band for the NO⁻ species and an increase in the intensities of the bands corresponding to the nitrates, especially of those due to bridged and bidentate species. This indicates that under these conditions, the population of the respective adsorption forms has increased. This experimental fact can be explained assuming transformation of some monodentate nitrates to bidentate and bridged ones. Another possibility is the occurrence of the process



(i.e., under static experimental conditions, the NO⁻ species are stabilized on the titanium(IV) cations, but NO₂ can oxidize them during dynamic evacuation). It is difficult to decide between these two possibilities from the spectra presented in Fig. 1.

The weak band at 1715 cm⁻¹, which resists evacuation, can be associated with Ti³⁺–NO species (18). Reduced titanium ions can arise from thermovacuum activation.

Finally the weak negative band at 1360 cm⁻¹ (Fig. 1) is due to nitrate ions adsorbed on the NaCl windows of the IR cell.

Co-adsorption of NO and O₂. Development of the FTIR spectra with time of adsorption of an NO/O₂ mixture (28 Torr, NO : O₂ = 1 : 4) is shown in Fig. 2. The weak bands in the 2000–1800 cm⁻¹ region due to nitrosyl species and detected immediately after the introduction of the adsorbates disappear during the contact time, indicating that the adsorbed NO is oxidized by oxygen. At the same time, massive absorption develops in the nitrate region. The assignment of bands is the same as described for NO adsorption (see Table 1). The following differences should be noted: (i) development of a band at 2210 cm⁻¹ due to NO⁺ ion (15, 24), and (ii) absence of the bands at 3565 and 1160 cm⁻¹ due to NO⁻/NOH species.

The disappearance of NO⁻ species when NO and O₂ are coadsorbed has been reported also in Ref. (18) and confirms the low oxidation state of nitrogen.

The thermal stability of the NO_x surface species has been studied under evacuation for 10 min at 373–673 K temperature range (the spectra are not shown). The surface nitrates completely disappear from the spectrum after evacuation at 673 K. It should be pointed out that the spectra obtained on NO/O₂ coadsorption on TiO₂ are practically identical to those obtained during the adsorption of NO₂ (15, 24). However, the thermal stability of the surface NO_x species formed by NO₂ adsorption is higher: a band at 1550 cm⁻¹ has been detected after heating at 673 K and has been interpreted as a bridged nitro–nitrito compound (15).

TABLE 1

Assignment of FTIR Bands Observed on Adsorption of NO and NO/O₂ Coadsorption at Room Temperature on the Catalysts Studied

Catalyst	Frequency (cm ⁻¹) and mode	Possible assignment	
TiO ₂ (NO and NO/O ₂ adsorption)	1913 (ν(NO))	ON-Ti ⁴⁺ -ONO ₂ ⁻	
	1843 (ν(NO))	ON-Ti ⁴⁺ -NO ⁻ /NOH	
	1715 (ν(NO))	Ti ³⁺ -NO	
	1630-25, 1215 (split ν ₃)	NO ₃ ⁻ (bridged)	
	1615, 1215 (split ν ₃)	NO ₃ ⁻ (bidentate)	
	1580, 1215 (split ν ₃)	NO ₃ ⁻ (bidentate)	
	1555, 1215 (split ν ₃)	NO ₃ ⁻ (bidentate)	
	1505, 1286 (split ν ₃)	NO ₃ ⁻ (monodentate)	
	1160 (ν(NO))	Ti ⁴⁺ -NO ⁻ /NOH	
	3565 (ν(OH))	Ti ⁴⁺ -NOH	
	2210 (ν(NO))	NO ⁺	
	MnT-IE (NO adsorption)	1880 (ν(NO))	Mn ³⁺ -NO
		1865 (ν(NO))	Mn ³⁺ -NO
1645 (high-frequency)		NO ₃ ⁻ (bridged)	
1612 components of split ν ₃ mode)		NO ₃ ⁻ (bidentate)	
1555 (ν _{as} (NO ₂ ⁻)),		NO ₃ ⁻ (monodentate)	
1130 (ν _s (NO ₂ ⁻))		NO ₂ ⁻ (bridging nitro-nitrito)	
1200 (ν(NO))		Mn ³⁺ -NO ⁻ /NOH	
~3550 (ν(OH))		Mn ³⁺ -NOH	
MnT-IE (NO/O ₂ adsorption)		2155 (ν(NO))	NO ⁺
	2033 (ν(NO))	ON-Mn ³⁺ -ONO ₂ ⁻	
	1957 (ν(NO))	ON-Mn ³⁺ -ONO ₂ ⁻	
	1905 (ν(NO))	Mn ³⁺ -NO	
	1870 (ν(NO))	Mn ³⁺ -NO	
	1619, 1248 (split ν ₃)	NO ₃ ⁻ (bridged)	
	1610, 1248 (split ν ₃)	NO ₃ ⁻ (bridged)	
	1552, 1276 (split ν ₃)	NO ₃ ⁻ (bidentate)	
	1514, 1320 (split ν ₃)	NO ₃ ⁻ (monodentate)	
	MnT-I (NO adsorption)	1875 (ν(NO))	Mn ³⁺ -NO
1798 (ν(NO))		Mn ²⁺ -NO	
~1850		ON-Ti ⁴⁺ -NO ⁻ /NOH	
1645, 1220 (split ν ₃)		NO ₃ ⁻ (bridged)	
1610, 1220 (split ν ₃)		NO ₃ ⁻ (bridged)	
1540-23, 1220		NO ₃ ⁻ (bidentate)	
1470, 1423, 1300 (ν _{as} (NO ₂ ⁻))		NO ₂ ⁻ (nitro-nitrito)	
1190 (ν(NO))		Mn ⁿ⁺ -NO ⁻ /NOH	
3565 (ν(OH))		Mn ⁿ⁺ -NOH (n = 2 or 3)	
1150 (ν(NO))		Ti ⁴⁺ -NO ⁻ /NOH	
3565 (ν(OH))	Ti ⁴⁺ -NOH		
MnT-IE (NO/O ₂ adsorption)	2210 (ν(ON))	NO ⁺	
	1925-1896 (ν(NO))	ON-Ti ⁴⁺ -ONO ₂ ⁻	
	1620-10, 1275 (split ν ₃)	NO ₃ ⁻ (bridged)	
	1570, 1240 (split ν ₃)	NO ₃ ⁻ (bidentate)	
	1550, 1240 (split ν ₃)	NO ₃ ⁻ (bidentate)	
	1505, 1320 (split ν ₃)	NO ₃ ⁻ (monodentate)	

MnT-IE Catalyst

Adsorption of NO at room temperature. Introduction of NO (10 Torr, room temperature) into the IR cell (Fig. 3) causes the appearance of two bands at 1880 and

1865 cm⁻¹ in the nitrosyl region, corresponding to two types of Mn³⁺-NO species in accordance with the existence of two types of manganese(III) cations in the catalyst studied (14) and in agreement with the literature data on MnO_x/Al₂O₃ (9, 10). No bands which can be assigned to adsorbed NO on titanium(IV) sites are observed.

In the low-frequency region, weak bands at 1645, 1612, 1555, and 1487 cm⁻¹ and a complex absorption with maximum at 1200 cm⁻¹ and shoulder at approximately 1130 cm⁻¹ are detected. The intensities of the nitrosyl bands decrease slightly after 50 min whereas those of the bands in the 1700-1100 cm⁻¹ region increase. With the extent of contact time, a relatively strong absorption develops in the OH stretching region, with a simultaneous increase in the intensities of the negative bands at 3725 and about 3700 cm⁻¹.

Evacuation for 10 min at room temperature (Fig. 3, spectrum 10' evacuation) leads to almost complete disappearance of the Mn³⁺-NO nitrosyls (very weak band at 1860 cm⁻¹). The spectrum contains strong absorption in the ν(OH) stretching region, with a maximum at 3290 cm⁻¹, two bands of moderate intensity at 1612 and 1200 cm⁻¹ and a shoulder at 1645 cm⁻¹, a weaker band at 1478 cm⁻¹, and a poorly resolved absorption at about 1130 cm⁻¹. The species characterized by the band at 1555 cm⁻¹ are not observed.

The interpretation of the spectra observed (Fig. 3) is made on the assumption that the same NO disproportionation reaction [1] involving surface OH groups can occur also in the presence of supported manganese. This means that in the case of the MnT-IE catalyst, NO⁻/NOH species are formed as well. The surface OH groups participating in this process are probably of the type Mn³⁺-OH, and the NO⁻/NOH species (to which the band at 1200 cm⁻¹ due to ν(NO) stretching mode is assigned) are coordinated to manganese(III) cations. This suggestion is supported by the fact that the band at 1200 cm⁻¹ disappears in the presence of the NO/O₂ mixture (see below, Fig. 4A (spectrum 0')). The NO₂ produced *in situ*, following reaction [2], transforms into surface nitrates. Based on the sequence of appearance/disappearance of the surface species and using literature data (10), the bands at 1645 and 1612 cm⁻¹ are tentatively assigned to bridged and bidentate nitrates, respectively. The band at 1555 cm⁻¹, which does not resist the evacuation, is attributed to monodentate nitrates. Compared to the pure support, the intensities of the absorption bands detected in the whole region are much lower for the MnT-IE catalyst, and probably the low-frequency components of the split ν₃ modes of the surface nitrates are superimposed on the band at 1200 cm⁻¹ or are too weak to be detected. The bands at 1487 (shifted to 1478 cm⁻¹ after evacuation) and 1130 cm⁻¹ are assigned to nitro (bridging NO₂⁻) species (13, 15, 17, 23). Since the decrease in the intensity of the Mn³⁺-NO nitrosyl bands is negligible after prolonged NO adsorption, the oxidation of NO to NO₂, respectively NO₃⁻ species, by manganese(III) cations should be excluded.

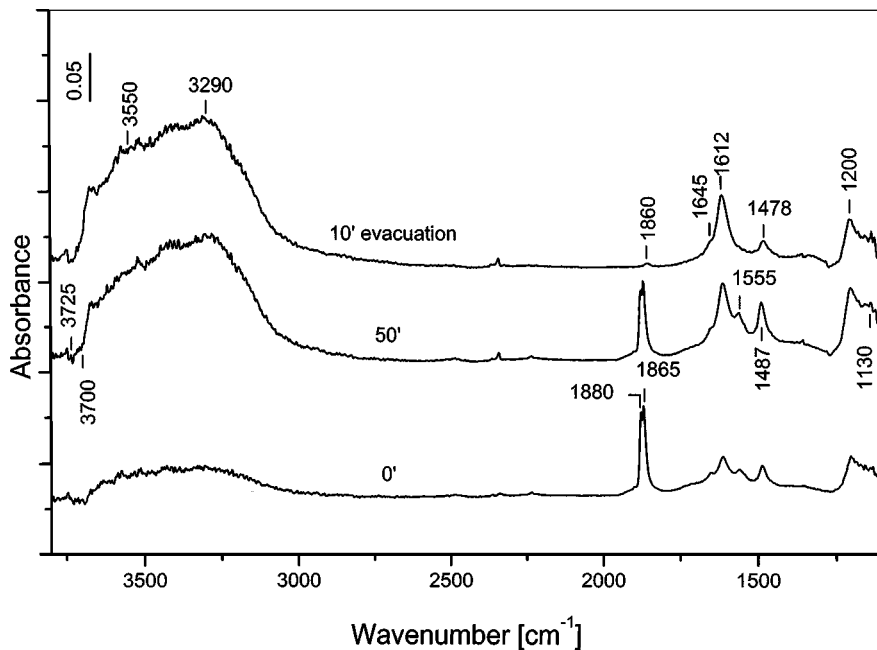


FIG. 3. FTIR spectra of adsorbed NO (10 Torr) at room temperature on the activated MnT-IE catalyst for various times and after evacuation at room temperature for 10 min.

The absorption in the OH stretching region with maximum at 3290 cm⁻¹ and a part of the band at 1612 cm⁻¹ are due to $\nu(\text{OH})$ and $\delta(\text{H}_2\text{O})$ modes, respectively, of adsorbed water molecules produced according to reaction [2].

Coadsorption of NO and O₂ at room temperature. The time evolution of the spectra obtained during the contact of the catalyst MnT-IE with a mixture of NO and oxygen (28 Torr, NO : O₂ = 1 : 4) is shown in Fig. 4A. Immediately

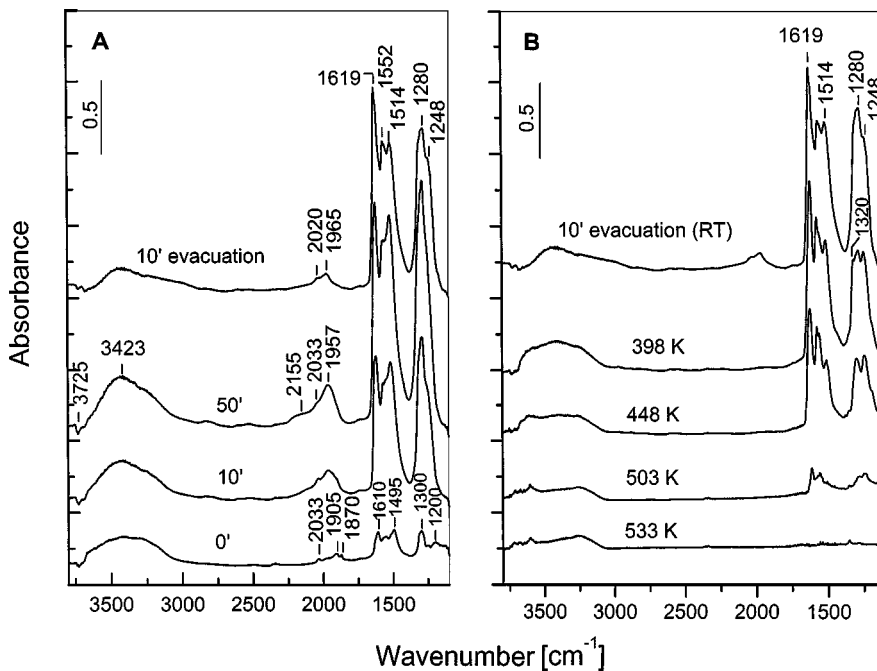


FIG. 4. (A) FTIR spectra of adsorbed NO/O₂ mixture (28 Torr, NO : O₂ = 1 : 4) at room temperature on the activated MnT-IE catalyst for various times and after evacuation at room temperature for 10 min. (B) FTIR spectra obtained after heating for 10 min in vacuum of the catalyst MnT-IE containing adsorbed NO_x species.

after the introduction of the adsorbates into the IR cell, weak bands in the nitrate region (1650–1200 cm⁻¹) are detected. These bands correspond to various nitrate species and grow fast with increasing contact time. The band at 1200 cm⁻¹ attributed to NO⁻/NOH species is not present in the spectrum taken after 10 min. Based on the sequence of appearance and thermal stability (see Fig. 4B), the absorption bands in the nitrate region are assigned as follows: 1619 and 1248 cm⁻¹ (bridged nitrates), 1552 and 1280 cm⁻¹ (bidentate nitrates), and 1514 and 1320 cm⁻¹ (monodentate nitrates).

The bands in the nitrosyl region require special attention. Immediately after introduction of the reaction mixture into the IR cell, weak absorption in the 2100–1850 cm⁻¹ region is observed. The bands at 1905 and 1870 cm⁻¹ are due to Mn³⁺–NO species (two types). In the spectrum taken 10 min later (spectrum 10'), these bands are masked by the broad absorption, with a maximum at 1957 cm⁻¹ and a shoulder at approximately 2030 cm⁻¹. Since the latter bands develop together with the nitrate bands, they are assigned to two types of Mn³⁺–NO nitrosyls, which contain NO₃⁻ ions in their coordination spheres (i.e. (ON)–Mn³⁺–(ONO₂) complexes). The weak and broad absorption at approximately 2155 cm⁻¹ (which disappears after evacuation at room temperature for 10 min) is interpreted as adsorbed NO⁺ ion (13, 15, 18, 24). The intensities of the nitrate bands display a slight decrease after evacuation at room temperature for 10 min (Fig. 4A, spectrum 10' evacuation).

The thermal stability of the adsorbed forms is followed by heating the catalyst containing preadsorbed NO_x species (spectrum 10' evacuation in Fig. 4A) under vacuum for

10 min in the 398–533 K temperature range (Fig. 4B). The least stable species are the nitrosyls (absorption bands at 2020 and 1965 cm⁻¹), which are not observed after evacuation at 398 K. The nitrate species disappear after heating at 533 K.

It should be pointed out that the adsorption of NO₂ (at 2 Torr) at room temperature on the catalyst MnT-IE leads to identical surface species observed during the NO/O₂ coadsorption (the spectra are not shown). No differences in their behavior on desorption at room and higher temperatures are observed.

MnT-I Catalyst

Adsorption of NO at room temperature. The spectra of adsorbed NO (10 Torr) at room temperature on the catalyst MnT-I taken at increasing adsorption times and after evacuation are shown in Fig. 5. The interpretation of the absorption bands is analogous to that proposed above for the MnT-IE catalyst (Table 1).

The following features are noticeable for the impregnated MnT-I catalyst, which are not observed in the case of the ion-exchanged sample, MnT-IE.

1. The MnT-I sample contains a mixture of manganese (II) and manganese(III) cations (14), and Mn²⁺–NO species (weak band at 1798 cm⁻¹) are detected in addition to the Mn³⁺–NO (strong absorption at 1880 cm⁻¹).
2. There is formation of NO⁻/NOH species coordinated to titanium(IV) cations (shoulder at approximately 1150 cm⁻¹ to the band at 1190 cm⁻¹ due to NO⁻/NOH species adsorbed on the manganese sites) and appearance

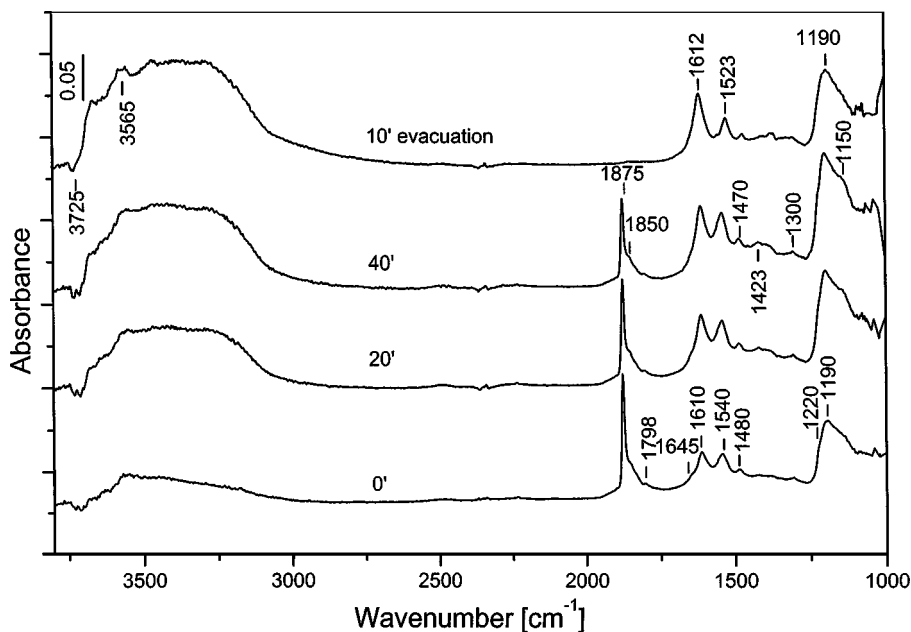


FIG. 5. FTIR spectra of adsorbed NO (10 Torr) at room temperature on the activated MnT-I catalyst for various times and after evacuation at room temperature for 10 min.

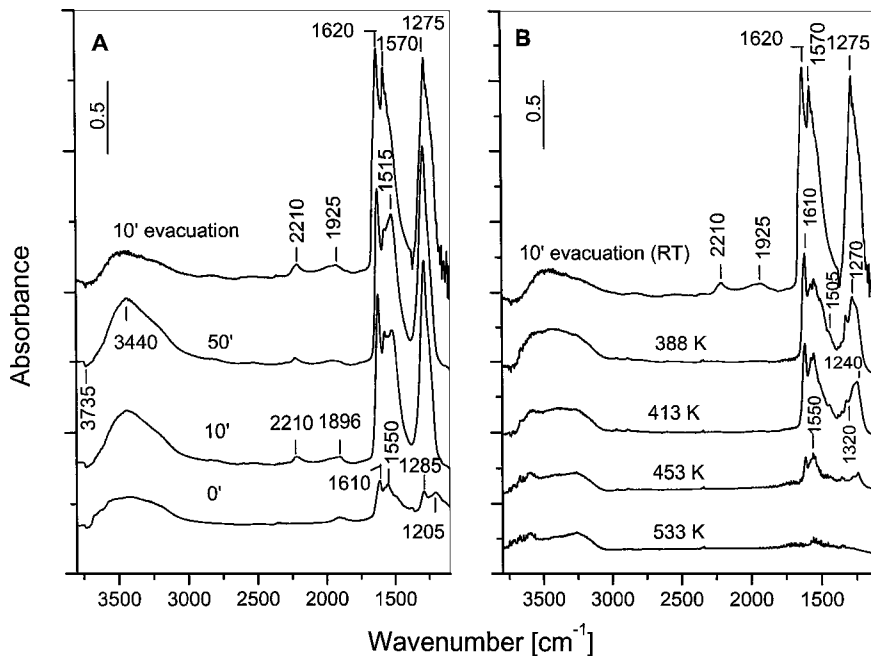


FIG. 6. (A) FTIR spectra of adsorbed NO/O₂ mixture (28 Torr, NO:O₂ = 1:4) at room temperature on the activated MnT-I catalyst for various times and after evacuation at room temperature for 10 min. (B) FTIR spectra obtained after heating for 10 min in vacuum of the catalyst MnT-I containing adsorbed NO_x species.

of ON–Ti⁴⁺–NO[–]/NOH species (poorly resolved absorption at about 1850 cm^{–1}). This shows that there are coordinatively unsaturated titanium(IV) cations ions exposed on the surface of the MnT-I catalyst, which is in agreement with the lower dispersion of the active phase established earlier (14).

Coadsorption of NO and O₂ at room temperature. The time evolution of the FTIR spectra during the NO/O₂ adsorption (28 Torr, NO:O₂ = 1:4) at room temperature is shown in Fig. 6A. The spectra in the OH and nitrate regions are very similar to those observed on the ion-exchanged catalyst (Fig. 4A). The absorption bands in the nitrosyl region (about 1900 cm^{–1}) are associated with the surface complex of the type NO–Mⁿ⁺–NO₃[–] (M = manganese(II/III) or titanium(IV) cations). The band at 2210 cm^{–1} is attributed to Ti⁴⁺–NO⁺ species (see Fig. 2).

The thermal stability of the nitrate species obtained during the NO/O₂ coadsorption seems to be comparable to that of the MnT-IE catalyst (compare Figs. 4B and 6B). Based on the sequence of their formation and thermal stability, the nitrates are identified as bridged (1620 and 1275 cm^{–1}), bidentate (1570 and 1240 cm^{–1} and 1550 and 1240 cm^{–1}), and monodentate species (1505 and 1320 cm^{–1}).

Summary of the Results on NO Adsorption and NO/O₂ Coadsorption on the Catalysts Studied

The proposed assignments of the NO_x species formed during the adsorption of NO and its coadsorption with O₂ are summarized in Table 1.

The common feature observed during the adsorption of NO on the support and manganese-containing catalysts is the appearance of relatively strong bands at 1160 cm^{–1} (TiO₂) and 1200–1190 cm^{–1} (MnT-IE, MnT-I) immediately after introduction of the adsorbate into the IR cell (Figs. 1, 3, and 5). These bands are attributed to the ν(NO) stretching vibration of anionic nitrosyl, NO[–], and its protonated form, NOH. The distinct absorption at 3560–3565 cm^{–1}, which develops in parallel with the bands in the 1200–1150 cm^{–1} region is interpreted as ν(OH) stretching vibration of the NOH species. The NO[–]/NOH species are not stable when NO and O₂ are coadsorbed (Figs. 2, 4, and 6) and are not observed (TiO₂) or disappear fast from the spectrum (manganese-containing catalysts). This behavior confirms the formation of reduced adsorption forms. It should be pointed out that Kapteijn *et al.* (9) reported also formation of reduced species during the adsorption of NO on the MnO_x/Al₂O₃ catalyst: the absorption at 1208 cm^{–1} has been attributed to the hyponitrite ion, N₂O₂^{2–}. For the formation of these species, a disproportionation reaction of NO has been proposed which involves surface O^{2–} ion. In addition, the rapid disappearance of the Mn³⁺–NO species at 1843 cm^{–1} during contact with NO led the authors to the conclusion that nitrosyls (probably dinitrosyls) are related to the appearance of the N₂O₂^{2–} ion. In the case of the MnT-IE and MnT-I catalysts studied, only a slight decrease in the intensities of the Mn³⁺–NO species after prolonged NO adsorption is observed. This indicates that the nitrosyls are not associated with the formation of NO[–] species, and the disproportionation of NO occurs through a reaction, which

is common to both pure TiO₂ and titania-supported manganese catalysts (i.e., with the participation of the surface OH groups).

The second product of the disproportionation of NO is NO₂, which gives rise to surface nitrates. The concentration of the nitrate species is much higher on the pure titania than on the manganese-containing samples. This difference is probably due to different amounts of NO₂ produced *in situ* and leads to the conclusion that the titania surface favors the disproportionation of NO more than the manganese-containing samples.

On coadsorption of NO and O₂ at room temperature on the samples studied, various kinds of surface nitrates are observed differing in the modes of their coordination. The nitrates on the manganese-containing samples are characterized by a significantly lower thermal stability than that of the nitrates on the pure support, TiO₂.

Reactivity of the Surface Nitrates toward Decane

In order to understand the role of the adsorbed NO_x species in the SCR of NO by longer chain hydrocarbons, the interaction of decane with NO_x precovered catalyst surfaces has been studied.

MnT-IE Catalyst

The interaction of decane (0.6 Torr, followed by a 15-min evacuation at room temperature) at various temperatures (Fig. 7) with the stable NO_x species obtained on the surface

of the MnT-IE catalyst by coadsorption of NO and O₂ (40 Torr, NO : O₂ = 1 : 4, followed by evacuation for 10 min at room temperature) has been studied. The introduction of the hydrocarbon to the catalyst at room temperature does not lead to changes in the NO_x bands. Absorption typical for decane is observed in the $\nu(\text{CH})$ stretching region: bands at 2961 ($\nu_{\text{as}}(\text{CH}_3)$), 2926 ($\nu_{\text{as}}(\text{CH}_2)$), and 2852 cm⁻¹ ($\nu_{\text{s}}(\text{CH}_3)$). The bands at 1467 and 1380 cm⁻¹ (weak) are due to CH₂ scissoring vibration ($\beta_{\text{s}}(\text{CH}_2)$) and symmetric CH₃ deformation vibration ($\delta_{\text{s}}(\text{CH}_3)$), respectively (26). The rise in the temperature of the closed IR cell from 373 to 573 K leads to a gradual decrease in the intensities of the bands, corresponding to the adsorbed hydrocarbon and NO₃⁻ species (the spectra are taken after cooling the cell to room temperature). This result indicates that interaction between the decane and nitrate species adsorbed on the surface of the catalyst has occurred. The spectrum detected after heating at 373 K contains strong absorption in the $\nu(\text{OH})$ stretching region, with a maximum at 3600 cm⁻¹ (Fig. 7). Obviously, oxidation of the hydrocarbon starts already at this temperature. The treatment at 473 K causes the band at 3600 cm⁻¹ to vanish, and a weak, broad band between 3550 and 3100 cm⁻¹ is detected. The only species which appears with significant intensity in the 1700–1100 cm⁻¹ region after interaction at 473 K is the one characterized by a band at 1575 cm⁻¹. This species could be associated with a carbonate–carboxylate structure and/or a less-reactive bidentate nitrate whose low-frequency component is not resolved in the full spectra but appears in the subtraction

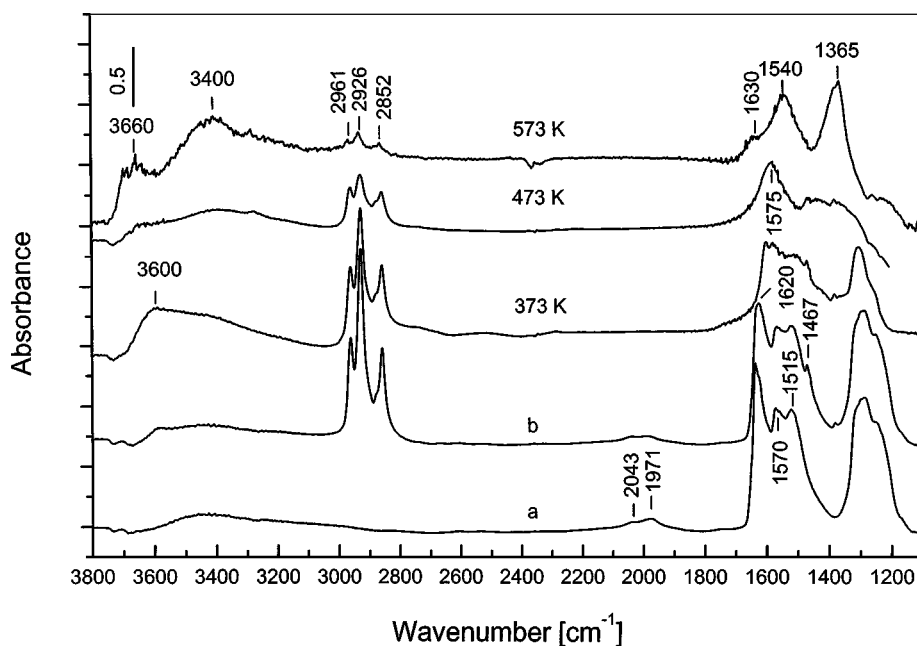


FIG. 7. FTIR spectra of the catalyst MnT-IE taken after adsorption of NO/O₂ mixture (40 Torr, NO : O₂ = 1 : 4) at room temperature followed by evacuation for 10 min (a), after adsorption of decane (0.6 Torr) on the NO_x precovered catalyst followed by evacuation for 10 min at room temperature (b), and after heating the closed IR cell for 10 min at the indicated temperatures.

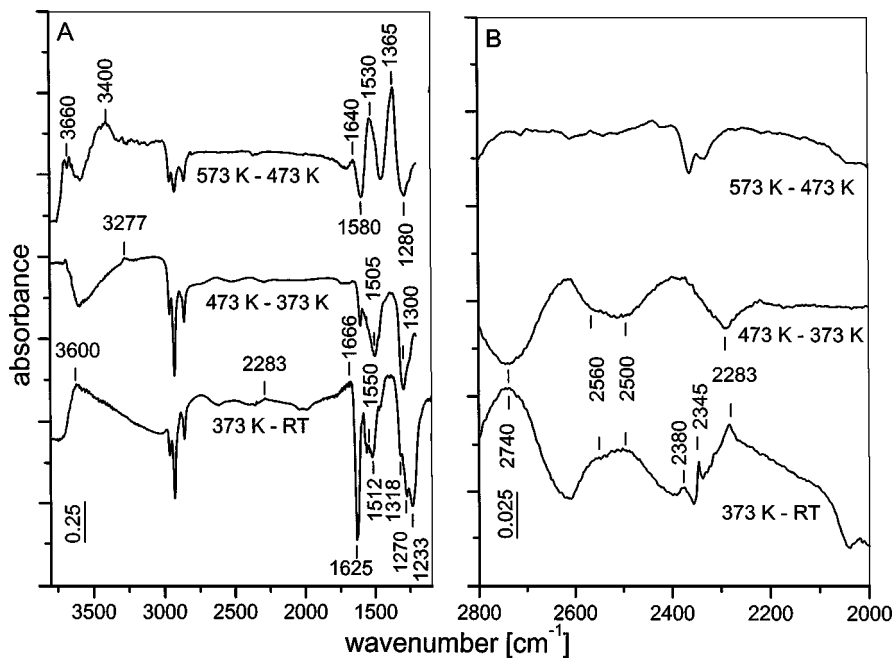


FIG. 8. FTIR subtraction spectra of the catalyst MnT-IE obtained from the spectra shown in Fig. 7; spectrum RT corresponds to spectrum (b) in Fig. 7.

spectrum at 1280 cm^{-1} (see Fig. 8, spectrum 573 K–473 K). After heating at 573 K, the bands characteristic of the adsorbed hydrocarbon appear with strongly reduced intensities and the band at 1575 cm^{-1} is not observed. Under these conditions, new bands at 1630, 1540, and 1365 cm^{-1} are detected. This indicates that the absorption at 1575 cm^{-1} is associated with nitrate species.

Figure 8 shows the spectra obtained by subtraction of the spectrum detected after the preceding thermal treatment from the spectrum taken after heating at a given temperature. The spectra contain strong negative bands, indicating simultaneous decrease in the surface concentrations of the hydrocarbon and the nitrate species. The following important observations should be noted.

1. The reactivity of the surface nitrates depends on the temperature (Fig. 8A). After heating at 373 K the bridged nitrates (1625 and 1233 cm^{-1}) are altered to a larger extent than the monodentate nitrates (1550 and 1270 cm^{-1} and 1512 and 1318 cm^{-1}). This means that the former species are the most reactive. At 473 K mainly the monodentate nitrates (1505 and 1300 cm^{-1}) are involved in the interaction with the hydrocarbon. The bidentate nitrates giving rise to the bands at 1580 and 1280 cm^{-1} possess the lowest reactivity—they disappear after heating at 573 K.

2. In the $2800\text{--}2100\text{ cm}^{-1}$ region, the bands at 2380 and 2345 cm^{-1} detected after heating at 373 K (Fig. 8B, spectrum 373 K–273 K) are due to adsorbed CO_2 (14). The bands at 2740 and at $2560\text{--}2500\text{ cm}^{-1}$ are typical of formate ions adsorbed on the MnT-IE catalyst (14) and are due to

Fermi resonance between the $\nu(\text{CH})$ fundamental and combinations or overtones of bands in the carboxylate region. The spectrum in the OH region (Fig. 8, spectrum 373 K–RT) contains the positive band at 3600 cm^{-1} . Based on the data in Ref. (14), the band at 3600 cm^{-1} is assigned to $\nu(\text{OH})$ stretching modes of adsorbed formic acid. The $\nu(\text{C}=\text{O})$ stretching frequency is positioned at 1666 cm^{-1} and is partially masked by the strong negative band at 1625 cm^{-1} . After heating at 473 K, the bands at 3600 , 2740 , $2560\text{--}2500$, and 1666 cm^{-1} decrease in intensity (negative bands at the corresponding positions in the spectrum 473 K–373 K, Fig. 8B). These experimental facts suggest that the formic acid produced during the oxidation of the hydrocarbon by the surface nitrates undergoes decomposition or further interaction with the nitrate species. The weak band at 3277 cm^{-1} has been observed previously on CO adsorption (14) with much stronger intensity and has been attributed to H-bonded OH groups arising from interaction of the formate species with the isolated OH groups of the catalyst. The alteration of the corresponding surface hydroxyls cannot be observed because the expected negative bands overlap with the negative band at 3600 cm^{-1} . Increase in the temperature to 573 K (Fig. 8, spectrum 573 K–473 K) causes involvement of the least reactive surface nitrates in the interaction with the hydrocarbon. Positive bands probably due to adsorbed water [3660 ($\nu_{\text{as}}(\text{OH})$), 3400 ($\nu_{\text{s}}(\text{OH})$), and 1640 cm^{-1} ($\delta(\text{H}_2\text{O})$)] and carbonate species at 1530 and 1365 cm^{-1} (split ν_3 mode (27)) are observed. Homogeneous interaction between the hydrocarbon and NO_2 (which could arise from thermal decomposition of the

nitrates) should be excluded because the interaction of decane and NO + O₂, respectively NO₂ in the gas phase, occurs at about 673–713 K (28). The facts reported present evidence that the adsorbed decane is oxidized by the surface nitrate species.

3. The weak band at 2283 cm⁻¹, which decreases in intensity with increases in reaction temperature (Fig. 8B, spectra (373 K–RT) and (473 K–373 K)), is attributed to isocyanate, NCO⁻, species. The literature data (26) on organic isocyanates show that the $\nu_{\text{as}}(\text{N}=\text{C}=\text{O})$ band normally occurs in the range 2290–2255 cm⁻¹. In the complex [Mn(NCO)₄]²⁻ the isocyanate group is characterized by a band at 2222 cm⁻¹ (16). In the case of oxide surfaces, the NCO⁻ species absorb in the 2300–2180 cm⁻¹ region (13). To the best of our knowledge, no data are available for surface NCO⁻ species coordinated to manganese or titanium ions. It is possible that the band at 2283 cm⁻¹ is due to organic isocyanate.

MnT-I

The reactivity of nitrate species toward the hydrocarbon is followed by an identical experiment, described above. The results are shown in Fig. 9. As in the case of the ion-exchanged sample, the concentration of the surface nitrates and that of the adsorbed hydrocarbon decrease with an increase in temperature. A noticeable difference is that compared to the MnT-IE catalyst, the relative changes in the intensities of the bands in the 3000–2800 cm⁻¹ region due to

the adsorbed decane are considerably lower for the MnT-I catalyst. The reason for this could be the lower concentration of the reactive surface nitrates on the latter sample.

The behavior of the absorption bands (consumed and produced) in the whole region is similar to that already observed for the MnT-IE catalyst, which is illustrated by the subtraction spectra (Fig. 10). The sequence in the interaction of the surface nitrates with decane after heating at 373 K is similar to that observed for the ion-exchanged sample. Bands (Fig. 10A, spectrum 373 K–RT) typical of adsorbed formic acid (14) are detected on the MnT-I catalyst: 3625 ($\nu(\text{OH})$), 3394 (hydrogen bonded hydroxyls), and 1680 cm⁻¹ ($\nu(\text{C}=\text{O})$). Heating at 573 K (Fig. 10A, spectrum 573 K–373 K) causes disappearance of the formic acid (negative bands at 3625 and 1690 cm⁻¹) and additional oxidation of the hydrocarbon (small decrease in the intensity of the decane bands). New bands at 3275, 1588, 1426, and 1375 cm⁻¹ are detected together with an absorption in the 2800–2500 cm⁻¹ region (Fig. 10B). The latter is characteristic of formate species. Most probably, the formate species are produced during room-temperature interaction of small amounts of CO (formed as a product of incomplete oxidation of the hydrocarbon or by decomposition of the formic acid) with the catalyst surface, according to the process described earlier (14). The presence of formate species contributes to the absorption at 1588 and 1375 cm⁻¹. The group of bands at 1588, 1426, and 1375 cm⁻¹ can be attributed to the $\nu_{\text{as}}(\text{CO}_2^-)$, $\nu_{\text{s}}(\text{CO}_2^-)$, and $\delta_{\text{s}}(\text{CH}_3)$ modes of acetate species, respectively (29). The origin of the sharp

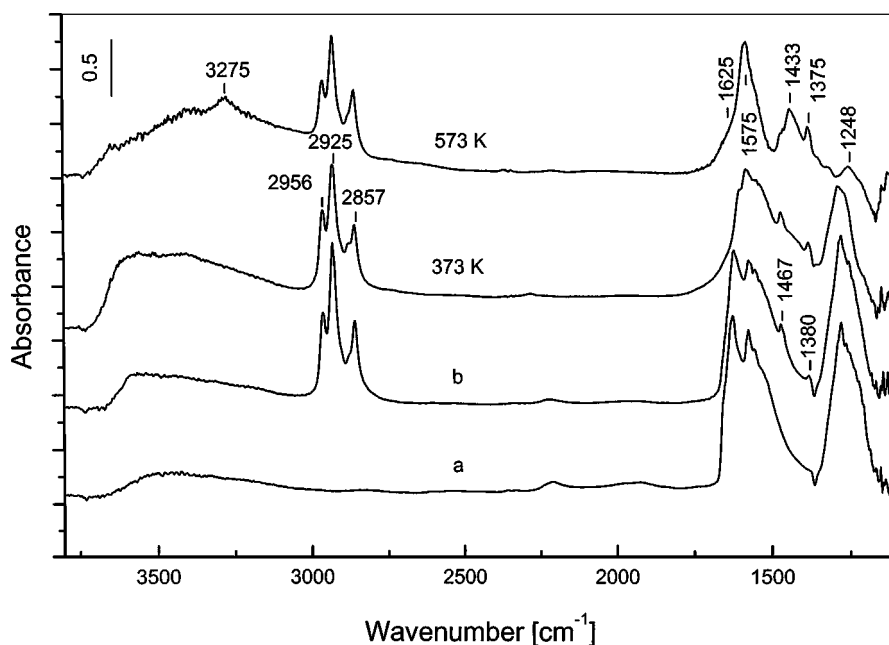


FIG. 9. FTIR spectra of the catalyst MnT-I taken after adsorption of NO/O₂ mixture (40 Torr, NO:O₂ = 1:4) at room temperature followed by evacuation for 10 min (a), after adsorption of decane (0.6 Torr) on the NO_x precovered catalyst followed by evacuation for 10 min at room temperature (b), and after heating the closed IR cell for 10 min at the indicated temperatures.

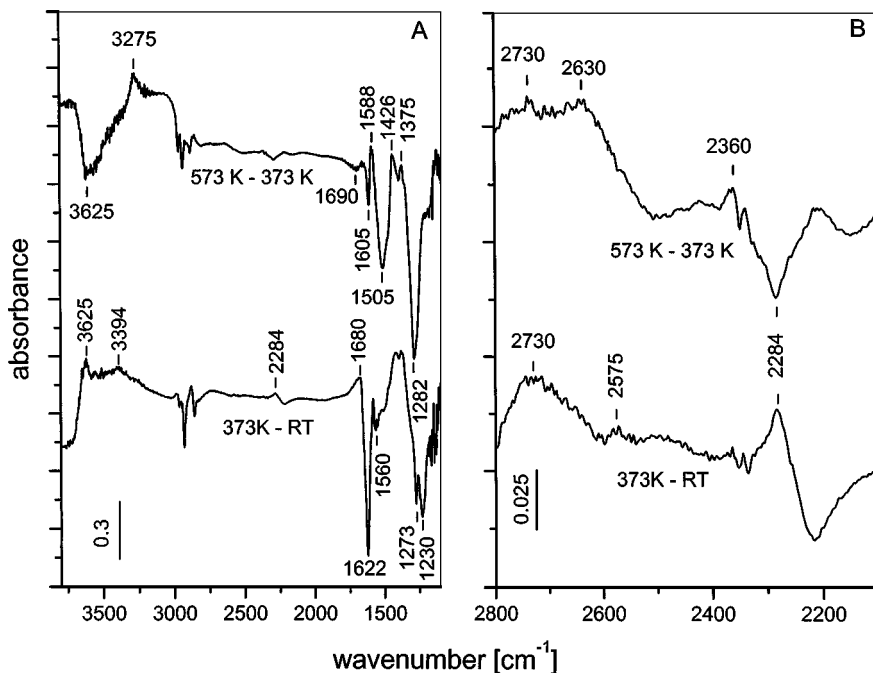


FIG. 10. FTIR subtraction spectra of the catalyst MnT-I obtained from the spectra shown in Fig. 9; spectrum RT corresponds to spectrum (b) in Fig. 9.

band at 3275 cm^{-1} has been explained above. There is a noticeable difference in the reactivity of the surface nitrates formed on the ion-exchanged and impregnated catalysts. Contrary to the ion-exchanged sample, the concentration of the surface nitrates on the catalyst MnT-I characterized by the bands at 1575 and 1248 cm^{-1} does not change after the treatment at 573 K (compare Figs. 8A and 10A). It can be concluded that the corresponding absorption bands belong to bidentate nitrates coordinated to the titanium(IV) site.

As in the case of the ion-exchanged sample, the band at 2284 cm^{-1} is associated with NCO^- species. Here again, the intensity of this band decreases with an increase in temperature.

TiO_2

The reactivity of NO_x species on titania is considerably lower than that for the MnT-IE catalyst and is comparable to that of the impregnated sample. This conclusion is made from the relative changes in the intensities of the bands of the adsorbed hydrocarbon in the $\nu(\text{CH})$ stretching region (Figs. 7, 9, and 11). As illustrated by the subtraction spectrum in Fig. 12A, after heating at 573 K the concentration of the bridged (1636 , 1625 , and 1275 cm^{-1}) and the monodentate nitrates associated with the band at 1530 – 1517 cm^{-1} on the surface of titania decreases simultaneously with that of the adsorbed hydrocarbon. The negative bands at 2200 cm^{-1} and at 1972 and 1902 cm^{-1} indicate that a transformation of the NO^+ ion and the nitrosyl species coordinated to titanium(IV) sites during interaction with the decane takes place. The positive bands at 2740 – 2600 cm^{-1}

and about 2575 and 2480 cm^{-1} (Fig. 12B) reveal the presence of formate moieties, and the absorption at 3650 and 3415 cm^{-1} together with the bands at 1740 and 1712 cm^{-1} (Fig. 12A) are attributed to undissociated formic acid (14). The sharp band at 2348 cm^{-1} is due to adsorbed CO_2 (Fig. 12B). No bands which can be assigned to NCO^- species coordinated to titanium(IV) cations are detected. In the low-frequency region (Fig. 12A), new bands at 1430 and 1358 cm^{-1} are formed, which are assigned to surface carbonates. The formation of adsorbed formic acid, CO_2 , and carbonate species indicates that the bridged and monodentate nitrates coordinated to the titania surface are able to oxidize the adsorbed decane. Since the bands at 1605 , 1575 , and 1550 cm^{-1} , which correspond to bidentate nitrates (Fig. 11), do not appear as negative bands in the subtraction spectrum in Fig. 12, the latter species do not interact with the hydrocarbon. This confirms the conclusion made above that the unreactive nitrate species observed on the MnT-I catalysts and characterized by the band at 1575 cm^{-1} is associated with the support.

Interaction of the Adsorbed Decane with the Surfaces of MnT-IE Catalyst and TiO_2

The spectrum of adsorbed decane (0.6 Torr, followed by a 15-min evacuation at room temperature) on the MnT-IE catalyst is shown in Fig. 13. The absorption in the 3670 – 3500 cm^{-1} region and the weak band at 1610 cm^{-1} are associated with small amounts of water contained in the hydrocarbon. The heating of the closed IR cell at 398 K for 10 min leads to a decrease in the intensities of the absorption bands,

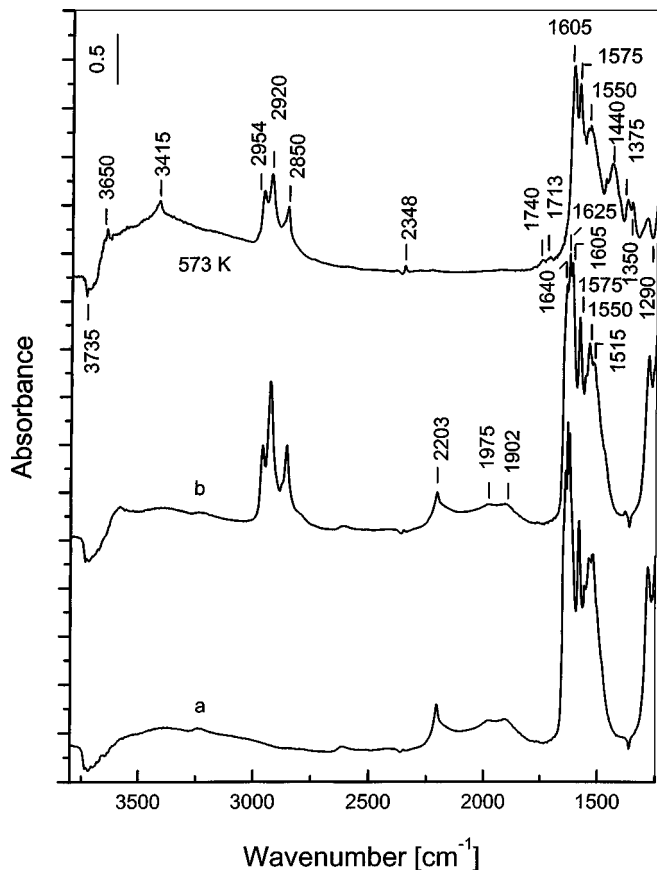


FIG. 11. FTIR spectra of the sample TiO₂ taken after adsorption of NO/O₂ mixture (40 Torr, NO:O₂ = 1:4) at room temperature followed by evacuation for 10 min (a), after adsorption of decane (0.6 Torr) on the NO_x precovered surface followed by evacuation for 10 min at room temperature (b), and after heating the closed IR cell for 10 min at 573 K.

corresponding to the adsorbed hydrocarbon and the appearance of a weak band at 1685 cm⁻¹ which falls in the carboxylate region (26, 27). This combined with the fact that there is an enhancement in the absorption in the $\nu(\text{OH})$ stretching region (absorption band at 3590 cm⁻¹) leads to the conclusion that under these conditions, partial oxidation of the adsorbed decane to carboxylic acid(s) has occurred. The spectrum taken after 10 min of heating at 483 K contains a sharp band at 1578 cm⁻¹ and the absorption at 1685 cm⁻¹ is no longer present. The former band is attributed to the $\nu_{\text{as}}(\text{CO}_2^-)$ mode of acetate ion (29). There are no changes in the intensities of the bands in the $\nu(\text{CH})$ stretching region, which indicates that under these conditions, only dissociation of the carboxylic acid (probably CH₃COOH) has occurred, leading to formation of acetate ions. The prominent band at 3275 cm⁻¹ is due to H-bonding between surface OH groups and carbonate/carboxylate structures (14). After the treatment at 573 K, additional decrease in the intensities of the bands in the $\nu(\text{CH})$ stretching region is observed. In the low-frequency region, two new bands at 1530 and 1343 cm⁻¹

are detected, which can be attributed to carbonate species. It seems that under these conditions, the predominant process is the decomposition of the acetate species to carbonates and water (absorption bands at 3645, 3420, and about 1620 cm⁻¹) and probably no further oxidation of the hydrocarbon takes place. Since the experiment is performed under anaerobic conditions, the observed oxidation of the hydrocarbon after the heating at 398 K is caused by surface oxide ions coordinated to the manganese(III) sites.

It should be pointed out that the same experiment with pure titania did not cause any considerable changes in the intensities of the bands due to the adsorbed hydrocarbon, and no oxidized hydrocarbon products were detected.

Summary of the Results on the Reactivity of the Adsorbed Nitrate Species

The data reported show that the activated MnT-IE catalyst possesses some activity for oxidation of the adsorbed decane. However, after modification of the catalyst surface by adsorbed NO₃⁻ species, the oxidation of the adsorbed hydrocarbon in the absence of gaseous oxygen is almost complete. This experimental fact demonstrates the role of surface nitrate species (obtained by NO/O₂ coadsorption) as key intermediates in the reduction of NO by decane. This conclusion is in agreement with the results of some recent reports (12, 30–39) on the importance of various surface NO_x species ($x > 1$) in the SCR process.

During interaction of the adsorbed hydrocarbon with the nitrate species coordinated on the surface of manganese-containing catalysts and the support, various oxidized hydrocarbon compounds (formic acid, formate and acetate species, NCO⁻), CO₂, and carbonates are detected. The fact that formation of oxidized hydrocarbons is observed on the NO₃⁻ precovered TiO₂ and that there is no oxidation of the decane in the absence of adsorbed NO₃⁻ species suggests that the bridged and monodentate nitrates interact directly with the hydrocarbon. These species are the most reactive ones in the case of manganese-containing catalysts and are able to oxidize the hydrocarbon at 373 K to formic acid and isocyanate ions. The bidentate nitrates on titania show no reactivity toward the adsorbed hydrocarbon. However, the presence of manganese(III) cations (MnT-IE catalyst) promotes the reactivity of the bidentate NO₃⁻ species, and their participation in the process starts at 473 K (Fig. 8). This means that the reactivity of surface nitrates depends not only on the mode of their coordination but also on the nature of the surface site(s). The catalyst MnT-IE does not contain exposed (cus) titanium(IV) cations detectable by room-temperature adsorption of CO (14) and NO (this paper). It can be concluded that the high reactivity of the surface nitrates on this catalyst is associated with the formation of Mn³⁺-NO₃⁻ species on NO/O₂ coadsorption and the absence of nitrates coordinated to titanium(IV) cations.

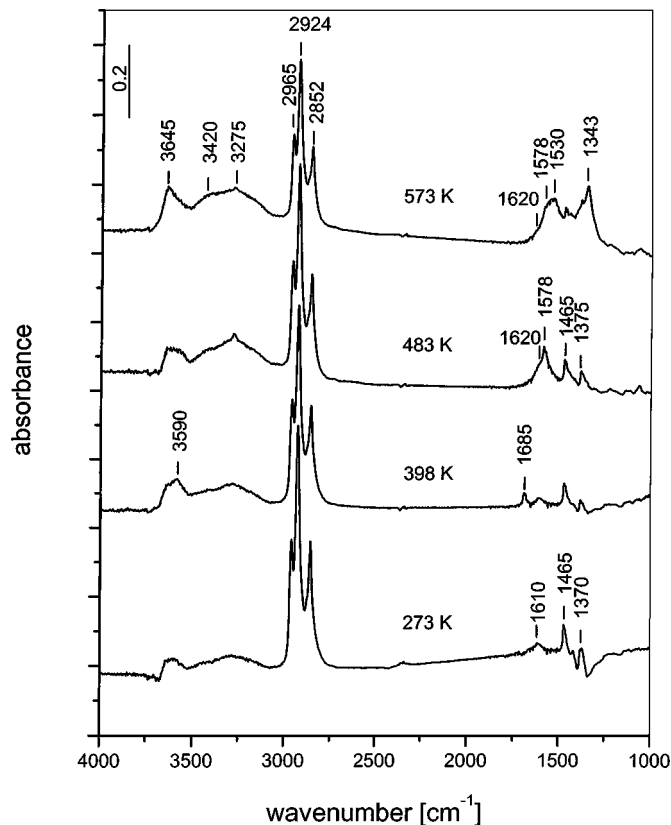


FIG.13 FTIR spectra of the MnT-IE catalyst taken after adsorption of decane (0.6 Torr) at room temperature followed by evacuation for 10 min (RT), and after heating the closed IR cell for 10 min at the indicated temperatures.

are not formed. This catalyst is promising for the selective catalytic reduction of NO by longer chain saturated hydrocarbons.

CONCLUSIONS

1. The nature of the NO_x species obtained on NO adsorption and its coadsorption with O₂ at room temperature, their stability, and the mechanisms of their formation on TiO₂ and MnO_x/TiO₂ catalysts have been studied. The adsorption of NO on the support and the catalysts leads to disproportionation of NO to anionic nitrosyl, NO⁻, its protonated form, NOH, and NO₂. On coadsorption of NO and O₂ at room temperature, various kinds of surface nitrates are observed differing in the mode of their coordination. No anionic nitrosyls are present. The nitrates on the manganese-containing samples are characterized by significantly lower thermal stability than those on the pure support, titania.

2. The difference in the thermal stability of the nitrates parallels their reactivity toward the reducer (decane). The monodentate and bridged nitrates formed on the manganese catalysts studied are able to oxidize the adsorbed

hydrocarbon at temperatures as low as 373 K and are important intermediates in the SCR of NO by hydrocarbons.

3. Formic acid, formate and acetate species, carbonates, and adsorbed CO₂ are identified as products of the interaction of the nitrates with the adsorbed decane. Formation of isocyanate species on the surface of manganese-titania catalysts is detected. It is proposed that the surface nitrates and NCO⁻ species react, leading to production of N₂ and CO₂.

4. The concentration of the reactive surface nitrates on the MnO_x/TiO₂ catalyst with manganese content corresponding to a monolayer is considerably greater than that on the sample with higher manganese loading. The former catalyst is promising for the SCR of NO by longer chain saturated hydrocarbons.

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