Spectroscopic Investigation of Species Arising from CO Chemisorption on Titania-Supported Manganese

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The nature of manganese species on the surface of TiO_2 (anatase) has been investigated by means of XPS, visible absorption spectroscopy, and FTIR spectroscopy of adsorbed CO. The catalysts were prepared by ion-exchange from aqueous manganese(II) chloride solution and impregnation. The application of ion-exchange results in a loading of manganese oxide phase corresponding to a monolayer coverage. On the surface of the ion-exchanged sample two kinds of Mn^{3+} ions are stabilized, differing in their co-ordinative saturation and localization. The Mn^{3+} ions form two kinds of linear carbonyls characterized by absorption at 2194 and 2187 cm^{-1}, respectively. The impregnated catalyst contains a mixture of Mn^{3+} and Mn^{2+} species. The latter ions produce a carbonyl band at 2114 cm^{-1}. The adsorption of CO at room temperature on the catalysts studied results in formation of formate, carbonate, and hydrogen carbonate structures as well. It is found that the formation of formate species is associated with the Mn^{3+} ions and the possible mechanism is discussed. The stabilization of the hydrogen carbonates is favored by Mn^{2+} ions. The reduction of the catalyst studied with hydrogen strongly suppresses the adsorption of CO and is indicative of the occurrence of a strong metal–support interaction. © 2000 Academic Press

Key Words: titania-supported manganese; XPS, visible absorption spectroscopy; FTIR of adsorbed CO.

INTRODUCTION

Manganese-containing oxide catalysts have wide application and potential use in a variety of catalytic processes of industrial importance. The nature of the manganese species in the catalysts is strongly influenced by the preparation conditions, such as the metal precursor, support used, loading, and calcination temperature (1–4), and several oxidation states may coexist.

The extensive surface studies previously reported concern mostly manganese oxides supported on alumina and different spectroscopic methods, such as XRD, XPS, ISS, Raman and IR, TPD, and TPR, have been used (1–14) for their structural elucidation.

The IR spectroscopy of adsorbed CO is a useful technique applied for investigation of the surfaces of bulk and supported metal oxides (15). However, only a few studies (10, 13–20) (compared, for example, to those devoted to the catalytic performance) have appeared on the characterization of manganese oxide catalysts by this method. The reason for this could be the fact that manganese forms very complex species with oxygen, making characterization of manganese catalysts very difficult. For example, on the surface of MnO_2 no carbonyls have been detected because of oxidation of CO to carbonates (16). For this reason, in some experiments low-temperature adsorption of CO has been applied (14, 17). Difficulties might arise from determination of the oxidation state of manganse by XPS due to the fact that it cannot be elucidated from the binding energy of either of the manganese main peaks ($2p$ or $3p$) (21). In order to determine the oxidation state of manganese by this technique, the best approach (22) is to use the magnitude of Mn $3s$ splitting due to the coupling of the unpaired valence electrons with the core hole. Foord *et al.* (23) measured and tabulated the Mn $2p_{3/2}$ binding energies and the O $1s$:Mn $2p_{3/2}$ intensity ratios as well as $3s$ multiplet splittings for stable MnO_x species. Detailed values of binding energies and the splitting of Mn $3s$ for different manganese oxides were summarized by Grzybek *et al.* (1) as well.

In this paper FTIR results on the interaction of CO at room temperature with the surface of manganese–titania catalysts containing Mn^{3+} and Mn^{2+} ions are presented. The oxidation state of the deposited manganese ions was determined by XPS taking into account the above considerations. The catalysts were characterized by visible absorption spectroscopy as well.

EXPERIMENTAL

The support TiO_2 (anatase) used is a commercial product (Degussa P 25, surface area 52 m^2/g) containing 90% anatase and 10% rutile.

The ion-exchanged sample was prepared by suspending the support powder in a 0.2 M aqueous solution of $MnCl_2$ for 2 h followed by alkalization (pH 13) of the mixture with

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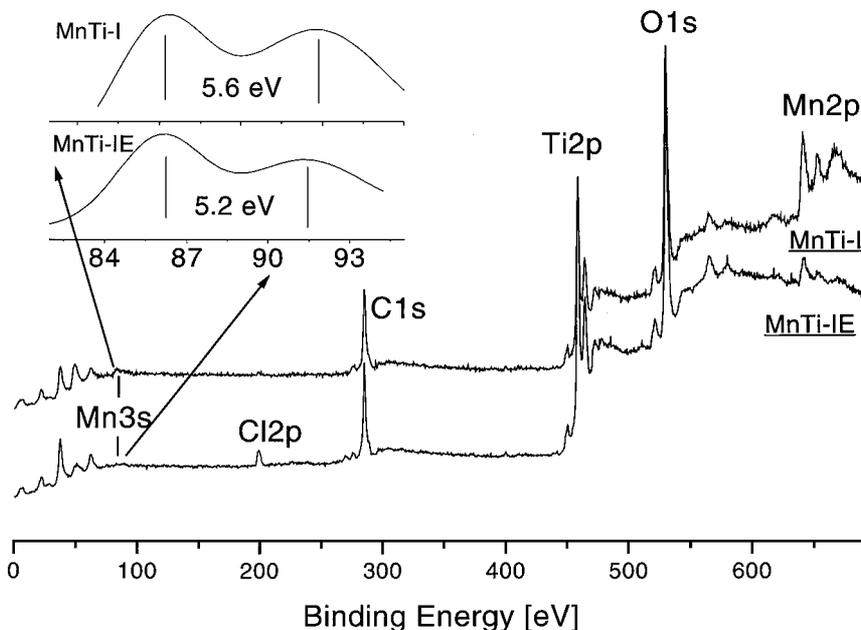
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FIG. 1. X-ray photoelectron spectra of the catalysts studied.

aqueous ammonia (1 : 1) and immediate filtration. Then the product was washed with deionized water, dried in air at 383 K, and calcined for 1 h at 623 K and then for 1 h at 723 K. This sample is denoted by MnTi-IE.

The impregnated sample was obtained by the incipient wetness technique (4 wt% of nominal manganese content) using $MnCl_2$ solution which was alkalized with ammonia to pH 13 in the last stage of the preparation procedure. The calcination procedure was the same as that used for the ion-exchanged catalyst. For this sample the notation MnTi-I is used. The chemical analysis of manganese was performed by flame atomic absorption spectrometry at the respective resonance wavelength. The manganese content in the ion-exchanged catalyst is 1.9 wt%.

The XPS spectra were taken with a KRATOS ES300 spectrometer equipped with a Mg $K\alpha$ radiation source. The visible absorption spectra were recorded with a Cary 5E UV–vis–NIR spectrometer. The reference substance was the catalyst support, titania. The FTIR spectra were recorded with a Bomem-MB102 (Hartmann & 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[2] of oxygen for 1 h at 673 K, and evacuation for 1 h at the same temperature.

Partial deuteroxylation of the manganese-containing samples was achieved by introduction to the evacuated IR cell of D_2O (99.9%) vapor at 3 Torr for 15 min at 673 K and evacuation for 30 min at the same temperature. This procedure was repeated two times. Then the activation procedure described above was employed. The reduction of the catalysts was performed with hydrogen (200 Torr, 673 K, for 30 min) and after that the samples were evacuated at the same temperature for 30 min. This procedure was repeated two times. After the final reduction, the samples were evacuated at 673 K for 1 h. The spectra of the catalysts thus activated were taken at ambient temperature and used as a background reference.

The carbon monoxide (99.95%) used was passed through a trap cooled by liquid nitrogen before admission to the IR cell.

RESULTS

1. XPS

The XPS spectra of the MnTi-I and MnTi-IE samples are shown in Fig. 1. In order to differentiate between the different oxidation states of manganese, the magnitude of 3s multiplet splitting is used as already mentioned. The values are 5.6 and 5.2 eV for the impregnated and ion-exchanged samples, respectively. Based on this, we can determine (1, 22, 23) that a mixture of Mn^{2+} and Mn^{3+} ions is present on the surface of the MnTi-I sample and only Mn^{3+} ions are present on the MnTi-IE catalyst. The Mn $2p_{3/2}$ binding energy has a value of 642 eV for both catalysts which is similar to those of bulk manganese oxides (640.5–643 eV)
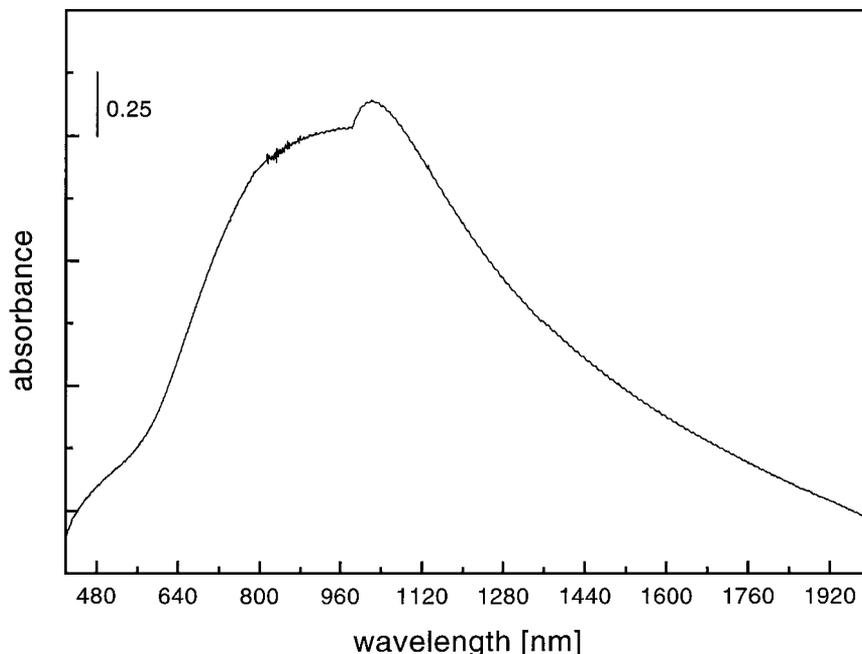
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[2] 1 Torr $= 133.3$ N m^{-2}.

FIG. 2. Absorption spectrum in the visible range of catalyst MnTi-IE taken under ambient conditions.

(1, 23). From this value it is difficult to estimate the degree of interaction of the deposited manganese ions with the surface of the support.

2. Visible Absorption Spectroscopy

The visible absorption spectrum of the catalyst MnTi-IE taken in the 300–2000-nm region displays a broad step curve with a large overall absorption due to the dark color of the sample (Fig. 2). Two distinct maxima between 700–900 and at about 1025 nm are observed which correspond to different d–d transitions of Mn^{3+} ions (24).

It was not possible to obtain the visible absorption spectrum of the catalyst MnTi-I by application of the same technique because of the very strong absorption of this sample.

3. FTIR Spectra of the Activated Samples

Figure 3 shows the FTIR spectra in the OH stretching region of the activated catalysts and the support TiO_2. In the same figure the spectrum of the catalyst MnTi-IE obtained after reduction with hydrogen at 673 K is also given. A series of bands between 3735 and 3640 cm^{-1} characteristic for anatase (25) are observed in the spectrum of the support. The band at 3745 cm^{-1}, according to some authors (26, 27), is due to presence of silicon. The extent of the participation of the surface OH groups of the support in the process of manganese deposition depends on the method of preparation used. The low-frequency (i.e., the more acidic) OH groups of the support are involved to a larger extent in the impregnation process whereas the reverse is observed in the ion-exchange process. The MnTi-I catalyst exhibits
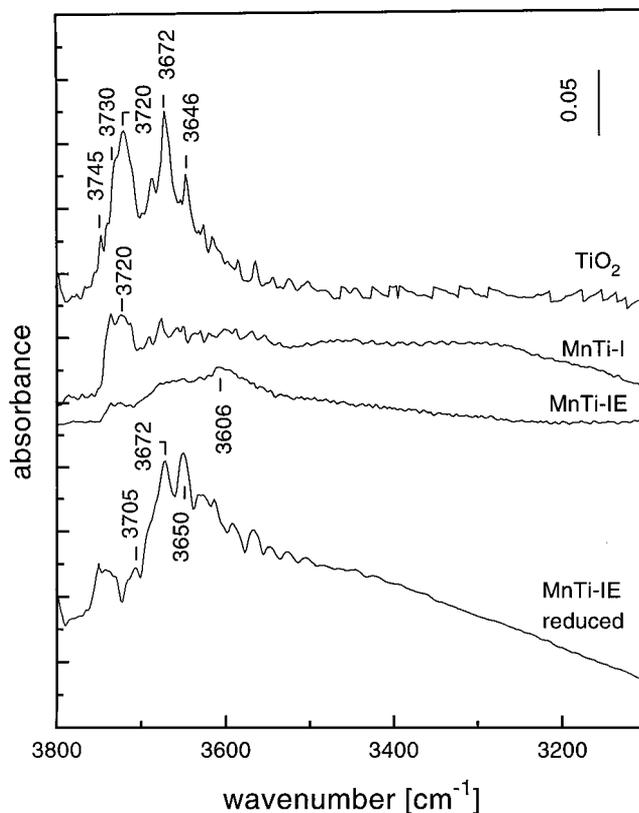

FIG. 3. FTIR spectra of the catalysts studied in the OH stretching region.

a broad band between 3550–3200 cm^{-1} which indicates the presence of H-bonded hydroxyl groups. A certain amount of hydrogen-bonded hydroxyls are observed also on the MnTi-IE sample. From these experimental data it is difficult to determine if the residual OH groups of the manganese-containing catalysts are of Ti^{4+}–OH type or are coordinated to manganese ions. No other bands are detected at lower wavenumbers.

The reduction of MnTi-IE catalyst causes significant changes in the spectrum in the OH stretching region. It seems that part of the original OH groups of the support are restored. In addition, there is a considerable amount of H-bonded OH groups.

4. FTIR Spectroscopy of Adsorbed CO

4.1. The support TiO$_2$.
CO adsorption (30 Torr) at room temperature on the TiO$_2$ sample leads to the appearance of two bands with maxima at 2206 and 2188 cm^{-1} (Fig. 4). They are characteristic of the CO stretching modes of two kinds of Ti^{4+}–CO surface carbonyls, formed with the participation of the strong (α) and weak (β') Lewis acid sites, respectively (25, 28–30). The intensities of these bands do not change with the time at constant CO pressure and the surface Ti^{4+}–OH groups are not affected by the adsorbed CO. No other adsorbed species are observed under these conditions.

4.2. The MnTi-IE sample.
The adsorption of CO at 30 Torr (room temperature) on the activated MnTi-IE catalyst (Fig. 4) leads to formation of two types of Mn^{3+}–CO carbonyls (FTIR bands at 2194 and 2187 cm^{-1}, respectively). The higher frequency and stability of the carbonyl manifesting band at 2194 cm^{-1} (which is present in the spectrum taken at 1 Torr of CO) are indicative of the greater acidity of the respective adsorption sites. The ν(CO) stretching frequencies of the corresponding carbonyls are very close to those observed on the anatase surface. The arguments for assignment of the bands at 2194 and 2187 cm^{-1} to two different kinds of Mn^{3+}–CO carbonyls are based on the XPS results, the behavior of these species in a CO atmosphere (see below), and the band intensities (about 5 times more intense than the Ti^{4+}–CO carbonyl bands).

The spectrum of the MnTi-IE catalyst in the carbonyl region is characterized by another weak absorption at 2140 cm^{-1}. This band can be associated with Mn^{2+} ions, whose amount is low and below the XPS detection limits. Another possibility could be the formation of these species during CO adsorption. All the carbonyls detected are unstable and disappear from the spectrum upon evacuation of CO at room temperature.

The adsorption of CO on the manganese-containing samples is a time-dependent process. In order to follow better the behavior of the surface hydroxyl groups after admission of CO into the IR cell, a partially deuteroxylated MnTi-IE sample was used. The development of the spectra with the time at constant CO pressure (30 Torr) is shown in Fig. 5. The increase in the time of CO adsorption causes a gradual increase of the bands in the carbonate–carboxylate region (2000–1040 cm^{-1}). Simultaneously, the bands detected in the carbonyl region, at 2194 and 2187 cm^{-1}, decrease in intensity. It should be pointed out that the carbonyl bands of the partially deuteroxylated sample have a different intensity ratio compared to that of the hydroxylated sample. Obviously, the reason for this is the high-temperature treatment with D$_2$O vapor which causes some structural changes. The decrease in the intensity of the carbonyl bands is accompanied by a strong enhancement of the adsorption in the 2400–2300-cm^{-1} region. The band at 2347 cm^{-1} is due to adsorbed CO$_2$ (31) and its growth with the time indicates that oxidation of CO to CO$_2$ occurs. In the OH/OD stretching region (3650–3000/2740–2500 cm^{-1}), with the increase of the CO contact time, the absorption due to H/D-bonded OH/OD groups rises in intensity. At the same time the negative band at 3730/2750 cm^{-1} due to isolated Ti^{4+}–OH/Ti^{4+}–OD groups gradually grows. The appearance of a positive absorption at 2668 and 3616 cm^{-1}, respectively, which is enhanced with time, is clearly observed. After 67 min of CO adsorption, the completely hydroxylated sample (spectrum f in Fig. 5) displays the same bands
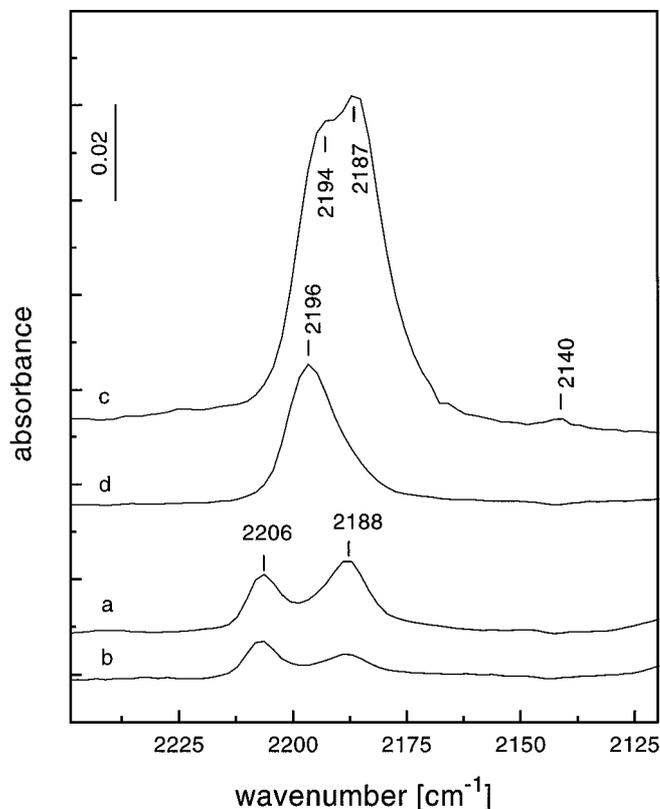

FIG. 4. FTIR spectra in the carbonyl region of adsorbed CO at room temperature on TiO$_2$ (anatase) at 30 Torr (a) and 1 Torr (b), and on MnTi-IE catalyst at 30 Torr (c) and 1 Torr (d).
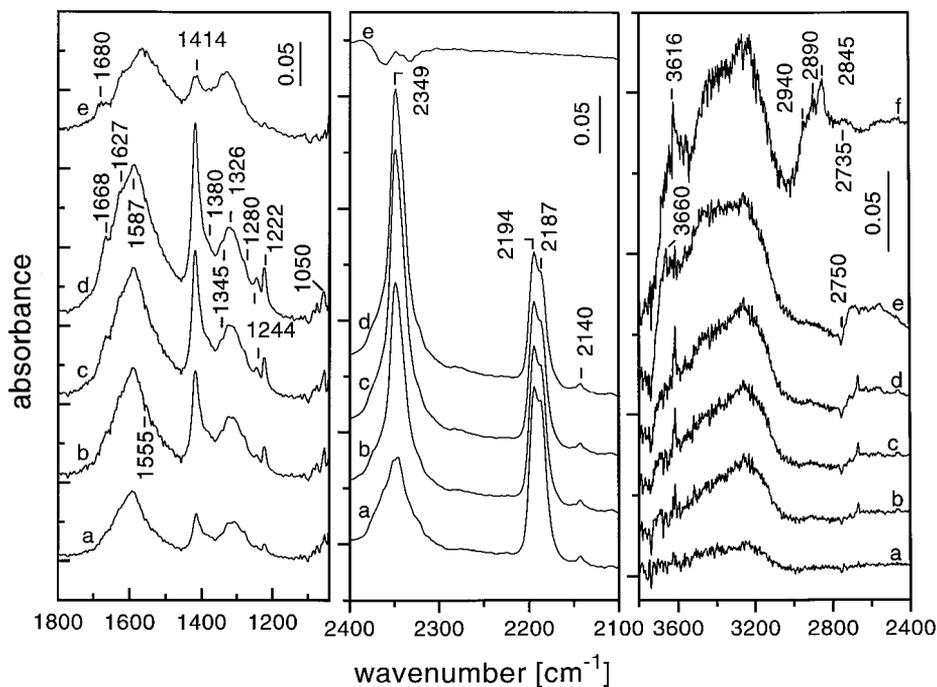
FIG. 5. FTIR spectra of adsorbed CO (30 Torr) at room temperature on partially deuteroxylated MnTi-IE catalyst for various times: immediately after admission of CO to the IR cell (a); after 10 min (b); after 42 min (c); after 67 min (d); and after evacuation at room temperature for 10 min (e). The spectrum of hydroxylated MnTi-IE catalyst in the OH stretching region after 67 min in CO (30 Torr) is also shown (f).

detected in the partially deuteroxylated MnTi-IE catalyst in the OH portion of the spectrum. However, a group of bands at 2940, 2890, and 2845 cm^{-1} together with the broad and weak absorption at about 2735 cm^{-1} are detected in the CH stretching region. The corresponding CD stretching vibrations are not observed because they fall in the region of the strong carbonyl bands (2230–2160 cm^{-1}).

After evacuation for 10 min at room temperature the carbonyl bands and the band due to adsorbed CO_2 disappear from the spectrum. The bands in the CH stretching (not shown in the Fig. 5) and carbonate–carboxylate regions are observed with reduced intensities. Under these conditions new bands at about 1680 and 3660 cm^{-1} emerge in the spectrum.

The species in the carboxylate–carbonate region obtained upon CO adsorption display low thermal stability: the intensities of the corresponding bands decrease strongly and almost simultaneously after evacuation for 5 min at 373 K. The heating at 423 K leads to complete desorption.

Figure 6 compares the spectra of adsorbed CO (30 Torr) 67 min after its admission to the IR cell on the reduced and oxidized MnTi–IE samples. After reduction the spectrum in the carbonate–carboxylate region becomes simpler and the absorption in the carbonyl region is considerably weaker. It is difficult to determine if the carbonyl band at 2189 cm^{-1} is due only to unreduced Mn^{3+} ions or if there is a contribution from the exposed β'-Ti^{4+} ions. The possibility of assigning this absorption only to exposed Ti^{4+} ions

can be ruled out because of the appearance of carbonate–carboxylate structures—a situation similar to that already observed with the oxidized MnTi-IE sample. As in the latter case, a weak absorption at about 2140 cm^{-1} is also detected. The simultaneous decrease of the bands at 1414 and 1222 cm^{-1} after reduction indicates that they belong to the same surface species. The complex and intense bands centered at about 1550 and 1340 cm^{-1} resemble part of the spectrum observed on the oxidized sample, but with lower band intensities. The absorption in the OH and CH stretching regions detected after CO admission is similar to that of the oxidized sample but less intense.

4.3. The MnT-I sample. The adsorption of CO was also performed over a partially deuteroxylated sample. In this case, however, the establishment of the equilibrium between the gas phase and the adsorbed species was slower. The complex band in the carbonyl region at 2186 cm^{-1} reached maximum intensity 10 min after admission of CO (30 Torr) into the IR cell.

Under the conditions described, together with the band at 2186 cm^{-1} (which has a shoulder at about 2194 cm^{-1}), two weak bands at 2144 and 2114 cm^{-1} are observed in the carbonyl region (Fig. 7). The absorption at 2144 cm^{-1} cannot be assigned to the ν(CD) stretching mode because it is detected also in the hydroxylated MnTi-IE and MnTi-I samples. Taking into account the XPS results on the MnTi-I catalyst and the FTIR data on the MnTi-IE sample, the
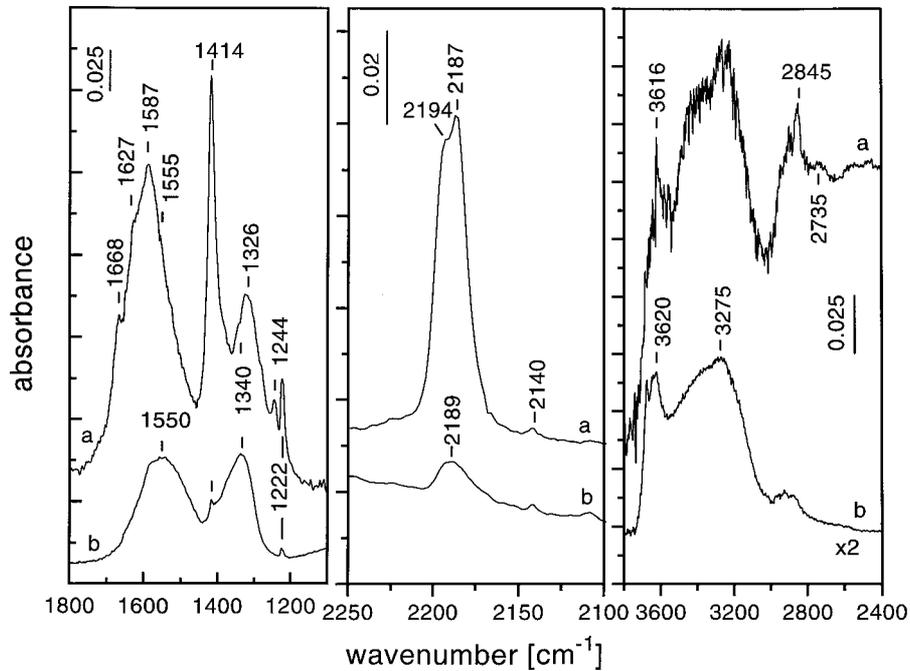
FIG. 6. FTIR spectra of adsorbed CO (30 Torr) at room temperature on MnTi-IE catalyst (a) and after reduction with hydrogen at 673 K (b).

complex adsorption with the maximum at 2186 cm^{-1} can be attributed to the two types of Mn^{3+}–CO carbonyls, whereas the two weak bands are assigned to different kinds of Mn^{2+}–CO species.

With an increase in contact time, the intensity of the unresolved band due to the Mn^{3+}–CO carbonyls gradually decreases, whereas the population of the Mn^{2+}–CO carbonyls showing absorption at 2114 cm^{-1} is enhanced
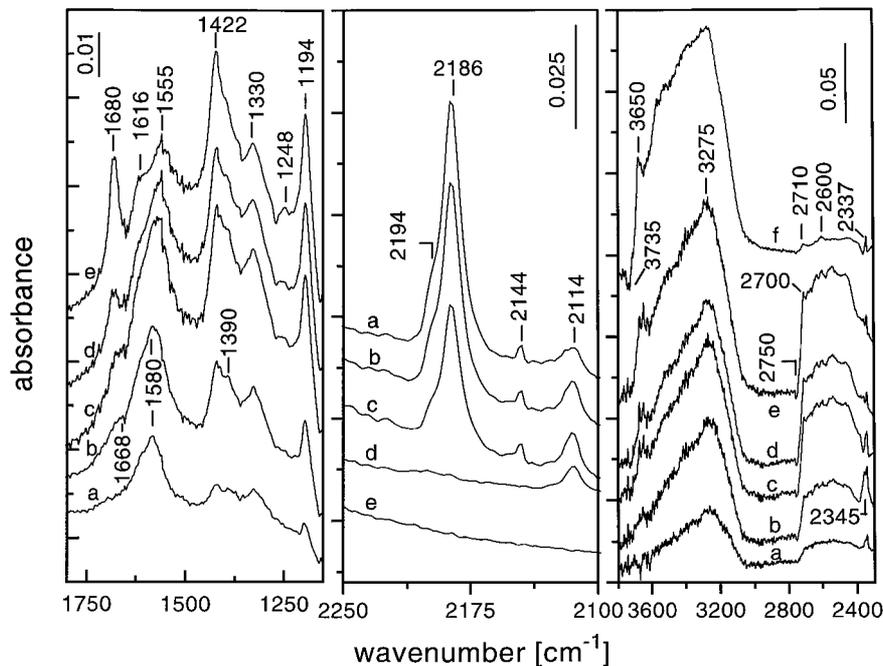

FIG. 7. FTIR spectra of adsorbed CO (30 Torr) at room temperature on partially deuteroxylated MnTi-I catalyst for various times: after 10 min (a); after 50 min (b); after 100 min (c); and after evacuation at room temperature for 2 min (residual pressure, $p = 3.5 \times 10^{-1}$ Torr) (d) and for 10 min ($p = 3.3 \times 10^{-3}$ Torr) (e). The spectrum of hydroxylated MnTi-I catalyst in the OH stretching region after 67 min in CO (30 Torr) is also shown (f).

almost 2 times after 100 min. The intensity of the band corresponding to Mn^{2+}–CO carbonyls represented by the absorption at 2144 cm^{-1} seems not to be affected by time. In the carbonate–carboxylate region, with increase of exposure time numerous bands develop, which can be grouped as follows (see the arguments below): (i) the set of bands with maxima at 1650–1500 and 1400–1250 cm^{-1} and (ii) the bands at 1680, 1422, and 1194 cm^{-1}.

As in the case of the MnTi-IE catalyst the absorption due to H/D-bonded OH/OD groups (3800–2400 cm^{-1}) grows in intensity with extent of contact time. This is accompanied by appearance of a negative OD band at 2750 cm^{-1} indicating that consumption of isolated Ti^{4+}–OD groups takes place. A sharp band at 2700 and 3650 cm^{-1}, respectively, corresponding to formation of isolated OD/OH groups increases in intensity. Here again, evolution of CO_2 is observed, which is detected by the appearance of two bands between 2400 and 2300 cm^{-1} due to adsorbed CO_2. These bands reached maximum intensity after 30 min of contact with CO (not shown in Fig. 7) and started to decay at more prolonged (50 min and above) adsorption times. This is an indication that transformation of the adsorbed CO_2 into other surface forms occurs.

Figure 7 shows also the spectrum of hydroxylated MnTi-I catalyst in the OH stretching region taken after 67 min of CO adsorption (spectrum f). It is characterized by the same spectral features in the OH stretching region observed for the deuteroxylated sample. In addition, it contains two weak bands at 2710 and 2600 cm^{-1} which correspond to ν(CH) stretching modes.

The evacuation of the deuteroxylated sample at room temperature to different residual pressures (Fig. 7, spectra d and e) causes the following changes in the IR spectra:

(i) Gradual increase is observed in the intensity of the H/D-bonded OH/OD groups and that of isolated OH/OD groups characterized by the absorption at 3650/2700 cm^{-1}.

(ii) The absorption corresponding to Mn^{3+}–CO species and the band at 2144 cm^{-1} disappear from the spectrum at a residual pressure of 3.5×10^{-1} Torr. The carbonyl species characterized by the ν(CO) stretching frequency at 2114 cm^{-1} resist the short evacuation which is consistent with their assignment to Mn^{2+}–CO carbonyls.

(iii) In the carbonate–carboxylate region the set of bands at 1680, 1422, and 1194 cm^{-1} increases in intensity. This increase is at the expense of the complex bands centered at 1580 and 1330 cm^{-1} and is more pronounced at a residual pressure of 3.3×10^{-3} Torr. This is an indication that under these conditions transformation of some surface species into others takes place.

The changes described in the spectra are more clearly visible in the subtraction spectra (Fig. 8) obtained from the spectra recorded after 10 min ($p = 3.3 \times 10^{-3}$ Torr) and 4 min of evacuation ($p = 5.5 \times 10^{-3}$ Torr), respec-
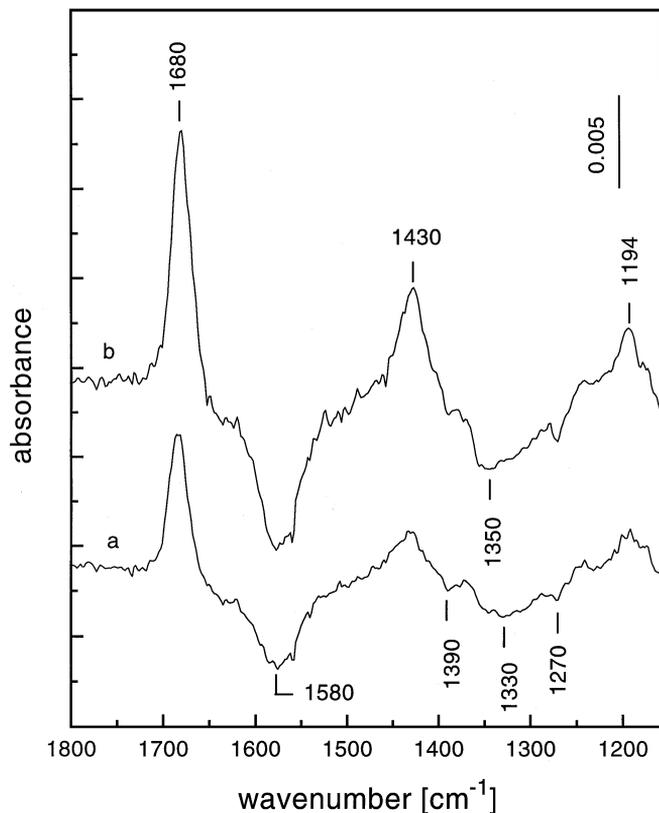

FIG. 8. FTIR spectra of partially deuteroxylated MnTi-I catalyst in the carbonate–carboxylate region obtained by subtraction of the spectrum of adsorbed CO (30 Torr) followed by evacuation for 2 min at room temperature ($p = 3.5 \times 10^{-1}$ Torr) from the spectrum after 4 min of evacuation ($p = 5.5 \times 10^{-3}$ Torr) (a) and from the spectrum after 10 min of evacuation ($p = 3.3 \times 10^{-3}$ Torr) (b).

tively, minus that taken after 2 min of evacuation ($p = 3.5 \times 10^{-1}$ Torr). The constant intensity ratio between the bands at 1680, 1430, and 1194 cm^{-1} which is observed at different evacuation times and different residual pressures in the IR cell, respectively, indicates that these bands belongs to the same surface species. Similarly, it is concluded that the absorption in the 1650–1500-cm^{-1} region together with the complex band centered at 1330 cm^{-1} characterizes another surface species.

After reduction of the MnTi-I sample no bands in the carbonyl and carbonate–carboxylate region are detected upon CO adsorption.

5. Room-Temperature Adsorption of Formic Acid on the MnTi-IE Sample

The FTIR spectrum of the formic acid used in the adsorption experiments is characterized by the following bands: a broad and intense absorption with a maximum at 3430 cm^{-1} due to ν(OH) of H-bonded OH groups, bands with maxima at 2947 (ν(CH)) and 1718 cm^{-1} (ν(C=O)), a group of bands at 1396 and 1380–1320 cm^{-1} both due to coupling
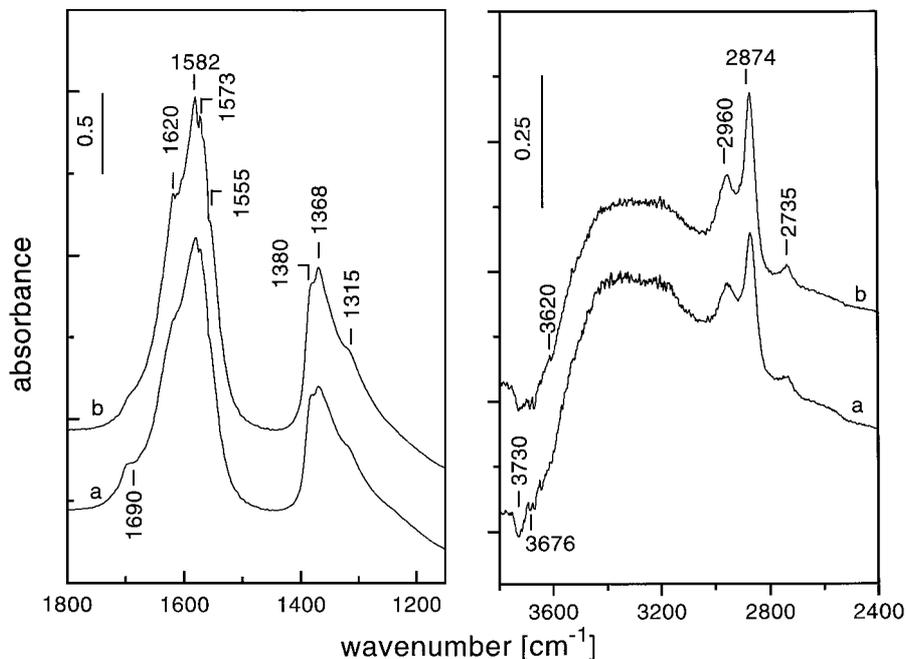
FIG. 9. FTIR spectra of adsorbed formic acid (0.5 Torr) on MnTi-IE catalyst (a) and after 10 min of evacuation at room temperature (b).

between in-plane O–H bending and C–O stretching of the dimer, and absorption at 1190 cm^{-1} (ν(C–O)). The unresolved absorption observed at about 1630 cm^{-1} is due to the δ(HOH) mode of water used for stabilization of the formic acid. The two bands with maxima at about 2714 and 2560 cm^{-1} are due to the presence of the formate moieties. This spectrum is consistent with the literature data (32, 33) for the prevailing dimeric form of the acid.

The FTIR spectra of HCOOH (0.5 Torr) adsorbed at room temperature on the surface of the MnTi-IE catalyst and after 10 min of evacuation are shown in Fig. 9. The spectra differ from the spectrum of the free acid indicating an interaction of the latter with the catalyst surface. Bands typical for formate species (31, 34, 35) are detected at 2960 ($\nu_{as}(CO_2^-) + \delta$(CH)), 2874 ($\nu$(CH)), and 2735 cm^{-1} ($\nu_s(CO_2^-) + \delta$(CH)). To these species belongs the group of bands with maxima at 1582, 1573, and 1555 cm^{-1} due to $\nu_{as}(CO_2^-)$ and the absorptions at 1368 and 1315 cm^{-1} which correspond to the $\nu_s(CO_2^-)$ mode of the formate ions, respectively. The splitting in the CO_2^- stretching vibrations suggests different types of coordination and/or different adsorption centers (31, 34, 35). The band at 1380 cm^{-1} can be attributed to the deformation vibration, δ(CH). This experimental fact shows that the adsorption of formic acid on the surface of the MnTi-IE catalyst is mainly dissociative, leading to formation of H-bonded OH groups (an intense and broad band between 3500 and 3000 cm^{-1} in the IR spectrum). The water present in the acid contributes also to this absorption. The band at about 1620 cm^{-1} is attributed to the δ(HOH) mode of the adsorbed water molecules although

the existence of formate species with the same $\nu_{as}(CO_2^-)$ frequency cannot be excluded. The weak band at 1690 cm^{-1} (ν(C=O)) together with the unresolved weaker absorption in the OH stretching region at about 3620 cm^{-1} (ν(OH)) suggests the presence of some undissociated formic acid on the catalyst surface. The former band is red-shifted compared to its position in the spectrum of the free acid which indicates that HCOOH is coordinated through the carbonyl oxygen to a Lewis acid site. The surface species formed are stable toward evacuation at room temperature for 10 min. The increased intensity of the bands in the 1580–1300-cm^{-1} region suggests formation of an additional amount of formate species. Finally, the weak negative bands at 3730–3670 cm^{-1} in the OH stretching region indicate that the isolated OH groups in the catalyst are altered during the adsorption of formic acid.

DISCUSSION

1. Coordination Number of Deposited Manganese Ions

According to the XPS data the ion-exchanged catalyst, MnTi-IE, contains only Mn^{3+} ions. Manganese(III) usually forms six- and five-coordinated complexes (24). The six-coordinated Mn^{3+} complexes are subject to Jahn–Teller effects (24, 36, 37) and the absorption spectra are difficult to interpret. The analysis of the literature data (24) shows that five- and six-coordinated Mn^{3+} ions in bulk coordination compounds have an overlapping region in the visible absorption spectra between 500 and 650 nm when the

ligating atom is oxygen. However, they can be distinguished by the adsorption at 1050–1100 nm ($^5A_{1g} \rightarrow {}^5B_{1g}$) for six-coordinate Mn^{3+} ions and by that at 730–830 nm for five-coordinated species. Based on this, it is possible to conclude that the catalyst MnTi-IE contains both five- and six-coordinate Mn^{3+} ions: the wide unresolved absorption with a maximum at about 850 nm is attributed to the *d–d* transition of five-coordinated Mn^{3+} ions whereas the band at about 1015 nm can be assigned to the transition $^5A_{1g} \rightarrow {}^5B_{1g}$ of six-coordinated species which are subject to Jahn–Teller distortion. Probably the concentration of six-coordinated Mn^{3+} ions is higher. This conclusion is drawn by comparison of the molar absorptivities for the two transitions. The molar absorptivity for the transition $^5A_{1g} \rightarrow {}^5B_{1g}$ in the six-coordinated complexes is lower by approximately one order of magnitude than that for the transition at 730–850 nm in the case of five-coordinated species (24).

2. Localization of the Supported Manganese Ions on the Surface of Titania

According to the chemical analysis the ion-exchanged catalyst, MnTi-IE, contains 1.9 wt% of manganese which corresponds to a surface concentration of 4 Mn^{3+} ions/nm^2. On the anatase surface there are 4–7 Ti^{4+}/nm^2 and the concentration of the isolated Ti^{4+}–OH groups is not more than 0.5 OH group/nm^2 (28, 29). If the anchoring sites are the hydroxyl groups and in the vicinity of the coordinatively unsaturated (cus) Ti^{4+} ions (assuming one Mn^{3+} ion per two Ti^{4+} ions), a monolayer coverage would be reached at maximum 1.9 wt% of manganese. Hence, the experimentally determined manganese loading in the ion-exchanged catalyst corresponds to a monolayer coverage.

The adsorption of CO on the activated MnTI-IE sample revealed the presence of two types of Mn^{3+} ions, which form two kinds of linear Mn^{3+}–CO carbonyls with ν(CO) stretching frequencies at 2194 and 2187 cm^{-1}, respectively. These two adsorption sites differ in their strength, the former being stronger; i.e., they are characterized by a lower coordinative saturation. Based on the loading determined by the chemical analysis, it is reasonable to assume that Mn^{3+} ions are localized mainly in the vicinity of the cus Ti^{4+} ions. Several types of cus titanium ions exist on the surface of anatase but only α- and β'-Ti^{4+} centers can be detected by adsorption of CO at room temperature (25, 28–30). The so-called β''- and γ-Ti^{4+} ions possess low electrophilicity and can be monitored only in low-temperature experiments (25, 30). The surface concentration of the α-sites is the lowest (29). Consequently, a higher concentration of Mn^{3+} ions localized in the vicinity of β- and γ-Ti^{4+} ions than that of those ions situated in the proximity of the α-Ti^{4+} sites can be expected. According to visible spectroscopy, the Mn^{3+} ions are five- and six-coordinate species, the latter being more abundant. The CO adsorption experiments show that only monocarbonyls are formed; i.e., the

manganese species contain only one coordination vacancy. Since the electronic spectra are taken under ambient conditions, it is possible to conclude that after the catalyst activation four- and five-coordinated Mn^{3+} ions are formed. Hence, the following localization of the cus Mn^{3+} ions can be proposed:

(i) The vicinity of the β- and γ-Lewis acid sites on anatase (which represent five-coordinated Ti^{4+} ions (28, 29)) is occupied by five-coordinated Mn^{3+} ions (type I). The carbonyls formed with their participation are characterized by the absorption at 2187 cm^{-1}.

(ii) Four-coordinated Mn^{3+} ions (type II) block the α-Lewis sites of the support (four-coordinated Ti^{4+} ions (28, 29)) and form carbonyls with the ν(CO) stretching frequency at 2194 cm^{-1}.

Finally, the existence of five-coordinate Mn^{3+} ions localized on the sites which correspond to surface Ti^{4+}–OH groups participating in the deposition process should be taken into account also. It is believed (29, 30) that the Ti^{4+} ions, to which the residual OH groups are bound, are five-coordinated.

No exposed Ti^{4+} ions are expected on the surface of the MnTi-IE catalyst. However, this suggestion cannot be proved unambiguously by room-temperature adsorption of CO. In addition, the close frequencies and the strong absorption of Mn^{3+}–CO carbonyls hinder the detection of Ti^{4+}–CO carbonyls eventually formed at room temperature.

According to the XPS data and FTIR spectroscopy of adsorbed CO the impregnated MnTi-I catalyst originally contains Mn^{2+} in addition to the two types of cus Mn^{3+} ions. Probably, the vicinity of the cus Ti^{4+} sites of the support is partially occupied by Mn^{2+} ions as well. The carbonyl band at 2114 cm^{-1} is assigned to these species. The presence of a high-frequency shoulder to this band indicates that the Mn^{2+} ions are of two kinds, like the Mn^{3+} ions. The Mn^{2+} ions characterized by the carbonyl band at 2144 cm^{-1} are envisaged as products of the CO adsorption. The difference of 30 cm^{-1} in the stretching frequencies of the corresponding carbonyls is probably due to a difference in the σ component of the bond between Mn^{2+} and CO (38). The carbonyl band at 2114 cm^{-1} present in the spectrum after short evacuation (i.e., the corresponding carbonyls are more stable) can be attributed to Mn^{2+} ions which form a bond with CO with a considerable π contribution. The behavior of the carbonyls characterized by the adsorption at 2144 cm^{-1} (not observed at low equilibrium pressures of CO) indicates that the adsorption centers are weak.

During the adsorption, CO is oxidized to CO_2 which further interacts with the basic surface sites, i.e., O^{2-} ions and OH groups producing surface carbonates and hydrogen carbonates (see below). The CO_3^{2-} and HCO_3^- ions can attract electron density via an inductive effect from the neighboring Mn^{2+} ion formed during the reduction. As a result the

electrophilicity of the Mn^{2+} ions increases. This leads to an enhancement of the σ component of the bond between CO and the metal cation. As a result the C–O stretching frequency is increased. A similar effect was reported by Saussey *et al.* (39): the C–O stretching frequencies of CO adsorbed on ZnO before and after CO_2 adsorption differ by about 30 cm^{-1}.

Probably the ion-exchanged and impregnated catalysts have different morphologies which affects the rate of CO chemisorption. This process is much slower for the impregnated catalyst. The reason for this could be the preferential CO adsorption on sites near the surface of the pellet. This suggests the presence of MnO_x particles which are not covered by CO immediately after CO admission on the MnTi-I catalyst.

3. CO Chemisorption

The Mn^{3+}–CO carbonyls produced on the surface of the catalysts studied are not stable in a CO atmosphere. This is shown by the decrease in the intensity of the corresponding carbonyl bands and by the appearance of absorption typical for linearly bonded CO_2 and various carbonate–carboxylate structures. The formation of CO_2 from CO is associated with the oxidizing properties of Mn^{3+} ions (40). The involvement of surface OH groups and the appearance of a series of bands in the carbonate–carboxylate region suggest formation of hydrogen carbonate or/and formate species.

The similarity of the FTIR spectra of adsorbed formic acid to the spectra in the carbonate–carboxylate region obtained during CO adsorption on the surface of the MnTi-IE catalyst implies the existence of similar adsorption forms in both cases. The adsorption of formic acid on this catalyst is dissociative, resulting in the appearance of formate species characterized by complex bands in the 1630–1550- and 1400–1250-cm^{-1} regions. A similar set of bands, between 1630 and 1550 cm^{-1} and the complex absorption at 1350–1250 cm^{-1}, is observed upon CO adsorption on the MnTi-IE catalyst. This allows us to attribute these bands to $\nu_{as}(CO_2^-)$ and $\nu_s(CO_2^-)$ stretching vibrations of formate species, respectively, which are formed during the reactive adsorption of CO. This assignment is supported by the appearance of weak bands at 2940, 2890, 2845, and 2750 cm^{-1} on the sample containing OH groups with the natural isotopic content of hydrogen, their absence in the spectra of a deuteroxylated sample, and the appearance in the latter of a weak absorption at 1050 cm^{-1}. The bands at 2940 and 2750 cm^{-1} are typical for formate ions (31, 35) and are due to the Fermi resonance between the $\nu(CH)$ fundamental (at 2890 cm^{-1}) and combinations or overtones of the bands in the carboxylate region (see Table 1). The band at 1050 cm^{-1} is characteristic for the $\delta(CD)$ mode of the DCO_2^- ion (31). The pair of bands at 1414 and 1222 cm^{-1} can be assigned to the splitting of the ν_3 vibration of monodentate carbonate ($\Delta\nu_3 < 300$ cm^{-1}) (31) whose ν_1 stretching mode is positioned at 1075 cm^{-1}. The bands at 1668 ($\nu(C=O)$) and 1244 cm^{-1} ($\nu(C-O)$) together with the sharp band at 3616/2668 cm^{-1} ($\nu(OH)/\nu(OD)$) are attributed to formic acid formed on the surface of the catalyst MnTi-IE. The band assignment is presented in Table 1.

TABLE 1

Assignment of the FTIR Bands Observed in the Carbonate–Carboxylate Region during Adsorption of 30 Torr of CO at Room Temperature on the Catalysts Studied

Catalyst	Frequency (cm^{-1}) and mode	Possible assignment	Refs.
MnTi-IE	2940 ($\nu_{as}(CO_2^-) + \delta(CH)$) 2890, 2845 ($\nu(CH)$) 2735 ($\nu_s(CO_2^-) + \delta(CH)$) 1630–1550 ($\nu_{as}(CO_2^-)$) 1380 ($\delta(CH)$), 1350–1250 ($\nu_s(CO_2^-)$)	Formate species coordinated to Mn^{3+} ions	31, 34, 35
	3616 ($\nu(OH)$) 1668 ($\nu(C=O)$), 1244 ($\nu(C-O)$)	Adsorbed formic acid	This work
	1414, 1222 (splitting of ν_3 vibration)	Monodentate carbonate ($\Delta\nu_3 < 300$ cm^{-1})	31, 34
MnTi-I	2710 ($\nu_s(CO_2^-) + \delta(CH)$) 2600 (comb. $1270 + 1330$) 1630–1500 ($\nu_{as}(CO_2^-)$) 1390 ($\delta(CH)$), 1350–1250 ($\nu_s(CO_2^-)$)	Formate species coordinated to Mn^{3+} ions	31, 34, 35
	3616 ($\nu(OH)$) 1668 ($\nu(C=O)$), 1248 ($\nu(C-O)$)	Adsorbed formic acid	This work
	3650 ($\nu(OH)$), 1860 ($\nu_{as}(C=O)$) 1422 ($\nu_s(C=O)$), 1194 ($\delta(OH)$)	Hydrogen carbonate species	31

Similar arguments for the interpretation of the bands observed in the carbonate–carboxylate region are applied to the catalyst MnTi-I (see Table 1 and Fig. 7). However, this sample displays different behavior during the evacuation at room temperature, allowing the bands at 1680 (ν_{as}(C=O)), 1422 (ν_s(C=O)), and 1194 cm^{-1} (δ(OH)) to be attributed to hydrogen carbonate species (31). The absorption at 3650/2700 cm^{-1} (which increases simultaneously with the bands cited above during the evacuation) is also assigned to these species. The latter band corresponds to the ν(OH/OD) stretching frequency of the hydrogen carbonate ion.

The positive absorption due to H/D-bonded OH/OD groups which develops simultaneously with the bands in the carbonate–carboxylate region and which is observed on both catalysts is an indication of interaction of the adsorbed forms (formates, carbonates, and/or hydrogen carbonates) with the surface OH/OD groups originally present in the catalysts. However, the alteration of the latter cannot be observed because the expected negative OH/OD bands fall in the same region of the strong positive band between 3700–3000 and 2700–2400 cm^{-1}, respectively.

The complex shape of the bands assigned to formate ions implies the existence of at least three kinds of formate species differing in their structure and type of coordination site, e.g., two types of Mn^{3+} ions and probably some exposed Ti^{4+} ions. However, exact determination of the coordination type and site(s) is difficult due to the simultaneous development of the corresponding bands during the CO adsorption and the comparable stabilities of the formate structures toward evacuation at ambient and higher temperatures. The reduced MnTi-IE catalyst displays a less complex spectrum in the carbonate–carboxylate region and the formate species characterized by the absorption at 1550 (ν_{as}(CO$_2^-$)) and 1340 cm^{-1} (ν_s(CO$_2^-$)) can be tentatively described as a bridged species ($\Delta\nu = 210$ cm^{-1} (31)) coordinated to the Mn^{3+} ions of type I. The argument for this is that part of the Mn^{3+} ions are left unreduced and produce a carbonyl band at 2189 cm^{-1}.

It is known (2, 41) that bulk Mn$_2$O$_3$ reduced with hydrogen at temperatures above 523 K is in equilibrium with the product MnO. According to the TPR results (3) on highly dispersed manganese oxides deposited on the surface of γ-Al$_2$O$_3$, the major reduction process of Mn^{3+} to Mn^{2+} at low loading (up to 2 wt%) is between 500–700 K and occurs in one step. In the case of catalysts with lower dispersion and higher manganese content a two-step reduction via intermediate formation of Mn$_3$O$_4$ phase is observed. The ESCA investigations (2) on Mn/Al$_2$O$_3$ catalysts that have been reduced with hydrogen (773 K, 5 h) showed formation of bulk MnO. Our results show a strong decrease in the population of Mn^{3+} ions in the ion-exchanged catalysts after reduction with hydrogen. However, the amount of Mn^{2+} ions detected by adsorption of CO at room tem-

perature is very low and does not differ from that in the oxidized catalyst (Fig. 6). As already discussed, it probably arises from the interaction of some unreduced Mn^{3+} ions with the adsorbate. The reduced MnTi-I catalyst is inactive toward CO adsorption. It is possible that, due to agglomeration, the reduced phase does not contain cus Mn^{2+} ions (or their amount is very low) and thus cannot be detected by CO adsorption. However, we prefer to interpret the drastic decrease in the CO chemisorption after the reduction with hydrogen in terms of the strong metal–support interaction (SMSI) (42). The presently accepted explanation (43, 44) for SMSI in supported titania catalysts reduced at temperatures above 573 K is associated with migration of suboxide titania phase onto the particle of the active phase. Thus, part of the manganese oxide phase is partially covered by TiO$_x$ and is not accessible to CO adsorption. Evidence that such structural changes are induced by the reduction is the similarity between the spectra in the OH region of the reduced MnTi-IE catalyst and the support. It is believed that the suboxide titania phase is a strong reducer and is oxidized by CO (25, 29). This means that the carbonyl band detected at 2189 cm^{-1} might be due to both unreduced Mn^{3+} and reoxidized Ti^{4+} ions. From these experimental results it is difficult to judge if reduction of Mn^{3+} ions has occurred and the MnO and/or Mn$_2$O$_3$ phases are encapsulated by the suboxide phase. Further investigations are needed.

The formation of formate species during the CO adsorption can be described (34) as a nucleophilic attack of basic OH group on the carbonyl carbon of a coordinated CO molecule (Scheme 1). The surface OH groups which are involved in this reaction are the Ti^{4+}–OH groups characterized by the absorption band at 3730 cm^{-1} (shifted to 2750 cm^{-1} after the deuteroxylation). The participation of hydroxyls with lower OH stretching frequencies is not excluded but it could not be monitored. The observed decrease in the intensity of the bands corresponding to the
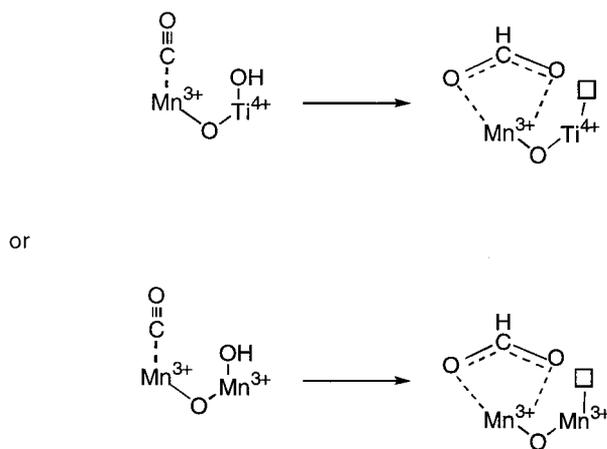
SCHEME 1
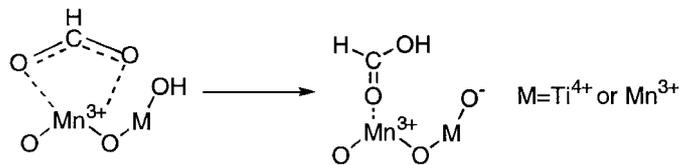
SCHEME 2

Mn^{3+}–CO carbonyls and the respective Ti^{4+}–OH groups and the parallel growth of the bands due to the formate species support the proposed reaction scheme.

Some molecularly adsorbed formic acid is detected on the surface of the catalyst MnTi-IE. The formation of HCOOH can be explained by coordination of a proton from the acidic OH group with a formate species (Scheme 2).

The experimental results show that the appearance of the formate species is associated only with the Mn^{3+} ions: the band at 2114 cm^{-1} due to Mn^{2+}–CO carbonyls (catalyst MnTi-I) does not decrease in intensity during the CO adsorption at constant pressure. In contrast, there is an enhancement of its intensity after prolonged (100 min) contact of the catalyst with CO; i.e., part of the Mn^{3+} ions are reduced to Mn^{2+} in the CO atmosphere. The CO_2 produced is coordinated on the surface and forms carbonates (MnTi-IE catalyst) and hydrogen carbonates (MnTi-I catalyst). The stabilization of the hydrogen carbonate species on the surface of the impregnated catalyst probably is favored by the Mn^{2+} ions. This suggestion is confirmed by the experimental fact that a similar process occurs to a much smaller extent on the surface of the MnTi-IE catalyst which contains originally only Mn^{3+} ions.

The importance of Mn^{3+} ions for formate formation is also demonstrated by the adorption of CO on the reduced MnTi-IE catalyst. The decrease in the amount of exposed cus Mn^{3+} causes a significant decrease in the population of the formate species.

Finally, it should be noted that the frequencies of the formate species produced during the CO adsorption differ slightly from those obtained from formic acid. The reason is the different mechanism of formation of these surface forms which influences their structure. During the CO adsorption, the surface OH groups and Mn^{3+}–CO carbonyls are involved, whereas in the case of HCOOH the formation of HCO_2^- species is a result of dissociation of the acid. Variation of the frequencies of the formate ions produced by adsorption of formaldehyde, formic acid, or methanol oxidation on different oxide surfaces is reported also by other authors (35, 45).

CONCLUSIONS

The results of the present investigation show that the application of ion-exchange for deposition of managanese ions on titania (anatase) from manganese(II) chloride solution ensures a coverage by manganese oxide phase which corresponds to a monolayer. The catalyst prepared by this method contains two kinds of Mn^{3+} ions differing in their coordinative saturation: five-coordinated Mn^{3+} ions located in the vicinity of the weaker Lewis acid sites and four-coordinated Mn^{3+} ions which block the stronger Lewis acid sites of the support. A small amount of the deposited managanese ions occupies part of the sites of the residual OH groups of the support participating in the synthesis process. The impregnated catalyst contains a mixture of Mn^{3+} and Mn^{2+} species.

The adsorption of CO at room temperature on the catalysts studied results in the appearance of formate, carbonate, and hydrogen carbonate structures. It is found that the formation of formate species is associated with the Mn^{3+} ions. The stabilization of the hydrogen carbonates is favored by Mn^{2+} ions. The reduction of the catalyst studied with hydrogen strongly suppresses the adsorption of CO and is indicative of the occurrence of a strong metal–support interaction.

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