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Formation of carbonyl and nitrosyl complexes on titania- and zirconia-supported nickel: FTIR spectroscopy study

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Abstract

Adsorption of CO on Ni/TiO_2 sample results in the formation of Ni^{2+}–CO and Ti^{4+}–CO species which are observed in the 2210–2185 cm^{-1} region and are characterized by similar stabilities. This makes unambiguous assignment of the carbonyl bands problematic. An analogous situation is found with Ni/ZrO_2 sample (carbonyls in the 2190–2155 cm^{-1} region), where distinguishing between Ni^{2+}–CO and Zr^{4+}–CO species is even more difficult. Some Ni^{+} sites were easily monitored on both samples by bands in the 2135–2110 cm^{-1} region. Adsorption of NO on Ni/TiO_2 results in the formation of Ni^{3+}–NO (1932 cm^{-1}, negligible amount), Ni^{2+}–NO (1878 cm^{-1}), $Ni^{2+}(NO)_2$ (1897 and 1851 cm^{-1}), and Ni^{+}–NO (1855 cm^{-1}) complexes. Only Ni^{2+}–NO (1840 cm^{-1}) and Ni^{+}–NO (1815 cm^{-1}) species are detected after NO adsorption on the Ni/ZrO_2 sample. In this case, however, formation of surface nitrates as a result of NO disproportionation (at high NO equilibrium pressures) strongly affects the Ni^{2+}–NO nitrosyls: their stretching frequencies are blue-shifted due to the enhanced acidity of the Ni^{2+} ions. It has been concluded that coadsorption of CO and NO permits simultaneous and selective registration of (i) Ni^{2+} and Ti^{4+} (Zr^{4+}), and (ii) Ni^{2+} and Ni^{+} surface cations. This is based on the fact that CO is adsorbed more strongly on Ti^{4+}, Zr^{4+}, and Ni^{+} ions while NO forms a stronger bond with Ni^{2+} ions.

Keywords: Adsorption; Coadsorption; Carbon monoxide; Nitrogen monoxide; FTIR spectroscopy; Nickel catalysts

1. Introduction

Nickel-containing catalysts have found a wide application due to their high activity and relatively low price. Although in most cases nickel is used as a metal, there are also many catalytic reactions proceeding with the participation of oxidized nickel sites. Thus, supported nickel oxide, mixed oxides containing nickel, and nickel-exchanged zeolites are active in oxidation reactions (of CO, NO, organic compounds), ozone decomposition, conversions of hydrocarbons, CO conversion with water vapor, reduction of NO_x with ammonia or hydrocarbons, etc. [1–5]. For designing new effective catalysts and for understanding the mechanisms of the catalytic reactions it is important to know the oxidation and coordination state of the cations from the active phase. IR spectroscopy of probe molecules is one of the most used techniques for characterization of coordinatively unsaturated surface (c.u.s.) metal cations and atoms [6–12]. The most used probe molecule is CO [8–10,12]. With supported nickel catalysts it permits separate detection of Ni^{2+}, Ni^{+}, and Ni^{0} [8–10,12]. In some cases, however, e.g., with Ni/TiO_2, Ni/ZrO_2 and Ni/Al_2O_3 [10,13–15], the use of CO is accompanied by a series of difficulties. In all these cases the Ni^{2+}–CO species are registered in the spectral region where carbonyls formed with the participation of the supports are detected. Besides, the carbonyls of the supported ions and those of the support have comparable stabilities, which create additional problems with distinguishing between them.

A similar situation is also observed with other systems. Thus, it is very difficult to distinguish between the carbonyls of Me^{n+} (e.g., V^{4+}, V^{3+}, W^{5+}, W^{4+}, Cr^{3+}) and those of Ti^{4+}–CO or Zr^{4+}–CO species formed on the respective

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Me^{n+}/TiO_2 and Me^{n+}/ZrO_2 samples [16–20]. In these cases the use of NO as a probe molecule is advantageous [17–20]. As a rule, nitrogen oxide does not form nitrosyls with Ti^{4+} and Zr^{4+} cations at room temperature [21–23] but produces stable dinitrosyls with the above Me^{n+} ions [17–20].

In some cases it is appropriate to use a mixture of CO and NO in order to monitor selectively different surface cations. For instance, this permits simultaneous and selective determination of the oxidation state of copper cations (Cu^{2+} and Cu^{+}) on copper-containing samples [24,25]. Carbon monoxide is adsorbed selectively on Cu^{+} cations while NO, on Cu^{2+} cations. Recently it was demonstrated that coadsorption of CO and NO can be used for simultaneous and selective detection of Cr^{3+} and Ti^{4+} or Zr^{4+} on the surface of Cr/TiO_2 and Cr/ZrO_2 catalysts [20]. This is based on the fact that the Cr^{3+} cations adsorb more strongly nitrogen oxide as dinitrosyls, while the Ti^{4+} and Zr^{4+} ions form carbonyl complexes alone.

The Ni^{3+} ions are believed to form no carbonyl complexes [8,10]. The C–O-stretching modes of surface Ni^{2+}–CO compounds are usually observed at 2220–2180 cm^{-1} [8,10,12–15,26–40]. These surface compounds are registered at room temperature and are, as a rule, decomposed during evacuation. The absorption bands of linear Ni^{+}–CO complexes are, in general, detected at lower frequencies (2160–2110 cm^{-1}) [8,10,13,14,27,30–36,38,41,42]. Due to the π-backbonding and the synergism between the π- and the σ-bonds these species are much more stable than Ni^{2+}–CO carbonyls. In some cases, the linear Ni^{+}–CO carbonyls can be converted, under CO equilibrium pressures, into dicarbonyls (ν_s(CO) at 2145–2131 cm^{-1} and ν_{as}(CO) at 2100–2081 cm^{-1}) [8,31,35,41–43]. The bond between CO and Ni^0 has a pronounced π character due to which the carbonyls of metal nickel are generally observed below 2100 cm^{-1} [8,10, 12–15,24,27,30,44–46].

Some authors [8] are of the opinion that, owing to their high coordinative saturation, Ni^{3+} ions form no complexes with NO (as is the case of CO). Platero et al. [47], however, have observed low-intensity bands at 1875 and 1916 cm^{-1} on NiO and on a solid MgO–NiO solution, respectively, and have attributed them to Ni^{3+}–NO species. The N–O-stretching modes of the Ni^{2+}–NO species are usually found at 1910–1810 cm^{-1} [8,11,14,29,30,37,48–53]. In some cases, e.g., with the systems Ni/SiO_2, Ni-ZSM-5 [36], and Ni-MOR [37], NO adsorption produces two bands at 1905–1870 and 1870–1855 cm^{-1}. The high-frequency band is attributed to linear Ni^{2+}–NO complexes while the low-frequency bands are ascribed to ν_{as} vibrations of dinitrosyls. The ν_s modes are masked by the mononitrosyl band.

The data in the literature concerning Ni^{+}–NO type complexes are scarce [8,36]. After NO adsorption on reduced NiY, two bands with maxima at 1900 cm^{-1} (NO adsorbed on isolated Ni^{2+} ions) and 1870 cm^{-1} (Ni^{+}–NO complexes) have been observed [8]. Adsorption of NO on metal Ni particles produces bands with maxima at 1860–1840 cm^{-1} [54,55]. They have been attributed to Ni^0–NO-type linear complexes [48,54,55]. According to some authors [48,51], however, NO dissociates on the metallic nickel surface and the nitrosyls observed are formed on oxidized sites.

Analysis of the available literature data indicates that NO is adsorbed on Ni^{2+} ions more strongly than CO and displaces the latter from the corresponding carbonyls [29,36].

The adsorption of CO on titania and zirconia has been investigated by many authors [56–62]. Different carbonyl bands, disappearing after evacuation, have been detected in the 2208– 2185 cm^{-1} region after room temperature CO adsorption. Recent investigations show that adsorption of NO on pure titania and zirconia does not lead to formation of nitrosyl species [21–23].

On the basis of data from the literature it may be expected that the use of CO as a probe molecule for the study of the Ni/TiO_2 and Ni/ZrO_2 systems would be convenient for the determination of Ni^{+} cations but not suitable for determination of Ni^{2+} cations. It seems that the NO molecule would be more appropriate for detecting these cations.

The purpose of this work was to study the adsorption and coadsorption of CO and NO on Ni/ZrO_2 and Ni/TiO_2 and to draw some conclusions on the applicability of these probe molecules to the selective determination of Ni^{n+} and Ti^{4+} (Zr^{4+}) sites. The samples were prepared by grafting nickel ions on the support surface which ensures an almost atomic dispersion of the supported nickel-containing phase. This was evidenced by characterization by different techniques, such as TPR, DR UV–vis spectroscopy, and XPS [13,14].

2. Experimental

The supports used were prepared by hydrolysis of $TiCl_4$ ($ZrCl_4$) followed by calcination as described elsewhere [13,14]. Titania thus obtained consisted of anatase and had a specific surface area of 102 $m^2\,g^{-1}$. Zirconia was obtained in monoclinic form with a surface area of 57 $m^2\,g^{-1}$.

The preparation of Ni/TiO_2 and Ni/ZrO_2 samples by a grafting procedure was also described previously [13,14]. Briefly, 10 g of the support was suspended in 50 ml 0.1 M Ni^{2+} solution of $Ni(NO_3)_2$ containing 12.5 wt% ammonia (pH 12.3). After 10 min the liquid phase was removed and 100 ml of the initial solution was added again. A 50-min agitation followed, and then the precipitates were filtered, washed thoroughly with water (to remove the reversibly adsorbed cations), dried, and calcined for 1 h at 623 K. The nickel content of Ni/TiO_2 was 0.74 wt% while in Ni/ZrO_2 it was 0.40 wt%. The low nickel concentration and the preparation technique ensured a high dispersion of the nickel ions.

The FTIR spectra were recorded on a Nicolet Avatar-360 spectrometer at a spectral resolution of 2 cm^{-1} accumulating 64–128 scans. Self-supporting pellets were prepared from the samples and treated directly in the IR cell. The latter was connected to a vacuum-adsorption apparatus with a base pressure below 10^{-3} Pa. Prior to the adsorption measurements, the samples were activated by 1 h calcination at 723 K and 1 h evacuation at the same temperature.

Carbon monoxide (99.5%) was supplied by Merck, and nitrogen monoxide ($> 99.0\%$), by Messer Griesheim GmbH. Before adsorption, carbon monoxide was passed through a liquid nitrogen trap while NO was additionally purified by fraction distillation.

3. Results

3.1. Adsorption of CO

3.1.1. TiO_2

Since the absorption regions of Ni^{2+}–CO and Ti^{4+}–CO carbonyls overlap, the results obtained on the Ni/TiO_2 sample can be interpreted correctly only after studying CO adsorption on the pure support. Adsorption of CO on our titania sample leads, in agreement with the published data [13,56,57], to the appearance of two bands, at 2206 and 2187 cm^{-1} (not shown). They are produced by carbonyl complexes of two types of c.u.s. Ti^{4+} cations (α- and β-Ti^{4+}, respectively). The decrease in equilibrium pressure is accompanied by an intensity drop of the bands, the one at 2187 cm^{-1} being shifted to about 2190 cm^{-1}. Both bands vanish after evacuation, the compounds characterized by the higher frequency band being more stable. This is in agreement with the rule that carbonyls of a given cation formed by a σ and/or electrostatic binding are characterized by a higher frequency of the C–O vibration when they are more stable [63].

3.1.2. Ni/TiO_2

The background spectrum of the activated Ni/TiO_2 sample contains a series of bands at 2146, 2124, and about 1880–1850 cm^{-1}. These bands are of a very low intensity and most probably characterize small amounts of carbonyls (2146 and 2124 cm^{-1}) and nitrosyls (1880–1850 cm^{-1}) formed on reduced nickel sites. In the lower frequency region there are bands at 1391, 1361, and 1340 cm^{-1} which have a very low intensity and are assigned to $NO_x{}^-$ surface compounds [11]. Probably all these stable compounds are formed as a result of processes occurring during the sample activation.

Adsorption of CO (4.27 kPa equilibrium pressure) on Ni/TiO_2 causes the appearance of two main bands: at 2199 and 2186 cm^{-1} (Fig. 1, spectrum a). There is also a shoulder at about 2207 cm^{-1}. A decrease in equilibrium pressure and evacuation lead to a decrease in intensity and then to disappearance of the bands (Fig. 1, spectra b–f). Of the three bands, that at 2186 cm^{-1} shows the quickest decrease, i.e., it characterizes the less stable surface carbonyls. Simultaneously with the coverage decrease, the maximum of the band at 2186 cm^{-1} is shifted to about 2190 cm^{-1} whereas the maximum of the 2199 cm^{-1} band is coverage independent. In agreement with the results on pure TiO_2, the band at 2186 cm^{-1} is ascribed to the so-called β-Ti^{4+}–CO carbonyls while the shoulder at 2207 cm^{-1} is attributed to α-Ti^{4+}–CO compounds [13,56,57]. Since the 2199 cm^{-1} band has not been found with the pure support, and following literature data [8,10,13,14,27,30–36,38,41,42], it is assigned to Ni^{2+}–CO complexes. However, it might also be due to Ti^{4+}–CO carbonyls affected by the supported nickel phase. The results on CO + NO coadsorption (vide infra) confirm the first interpretation. The fact that ν(CO) of Ni^{2+}–CO is practically independent of the coverage indicates that it corresponds to isolated Ni^{2+} sites.

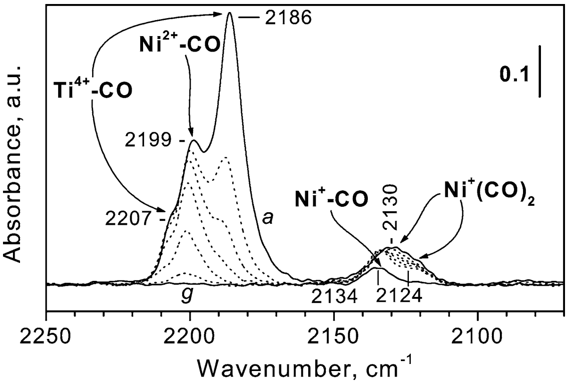

Fig. 1. FTIR spectra of CO adsorbed on Ni/TiO_2. Equilibrium pressure: 4270 (a), 1290 (b), 390 Pa (c), and 120 Pa (d), and after evacuation for 5 (e), 10 (f), and 30 min (g).

In addition to the above bands, CO adsorption leads to the formation of a low-intensity band at about 2130 cm^{-1} with a shoulder at 2124 cm^{-1}. The decrease in equilibrium pressure and evacuation results in an intensity drop of these bands and the appearance of a band at 2134 cm^{-1}. The latter is stable and disappears only after evacuation at 373 K. The bands in the 2140–2120 cm^{-1} region can in general be assigned to carbonyl complexes of Ni^{+} [8,10,13,14,27,30–36,38,41,42]. They may characterize carbonyl complexes of different Ni^{+} sites. However, the bands at 2130 and 2124 cm^{-1} are most probably due to the symmetric and antisymmetric modes of $Ni^{+}(CO)_2$ complexes [8,31,35,41–43] which are converted to linear Ni^{+}–CO carbonyls (2134 cm^{-1}) with decreasing coverage. Indeed, it was already noted that the band at 2134 cm^{-1} develops at the expense of the band at 2130 cm^{-1}. Due to their low charge and high d-electron density the Ni^{+} ions can form a back π-bond with CO. This and the synergism between the σ and π bonds determine the higher stability of the species as compared to Ni^{2+}–CO and Ti^{4+}–CO complexes. The formation of a π-back bond is also associated with a considerable rise of the extinction coefficient [64]. This and the relatively low intensity of the bands in the 2140–2120 cm^{-1} region indicate that only a small part of the nickel on the surface is present as Ni^{+} ions, while the prevailing oxidation degree is 2+. It should be noted that in the region of 2140–2120 cm^{-1}, Ti^{3+}–CO carbonyls may appear [56]. Indeed, the probability for the supported nickel to enhance the reducibility of titania should not be excluded. However, we believe that the bands under consideration characterize (di)carbonyls of Ni^{+} because of their behavior (vide supra).

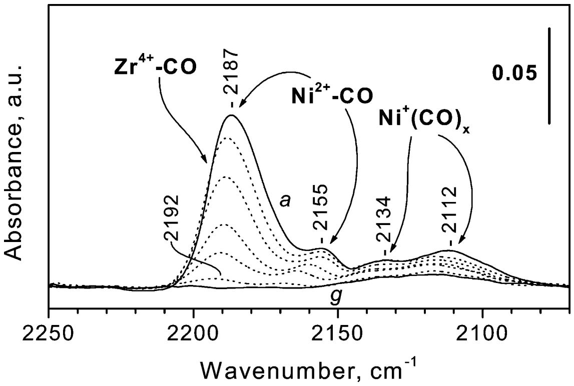

Fig. 2. FTIR spectra of CO adsorbed on Ni/ZrO_2. Equilibrium pressure: 4000 (a), 1200 (b), and 270 Pa (c), and after evacuation for 5 (e), 10 (f), and 30 min (g).

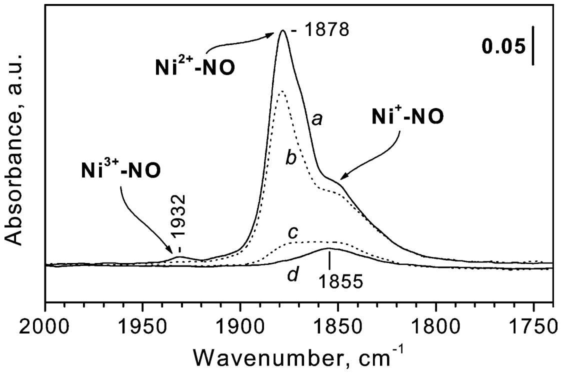

Fig. 3. FTIR spectra of NO adsorbed on Ni/TiO_2. Equilibrium pressure of ca. 70 Pa (a), and after evacuation at room temperature (b), 433 (c), and 463 K (d).

Another effect of CO adsorption is the appearance of low-intensity bands at 1582 and 1320 cm^{-1}, which, according to data from the literature [65], are attributed to bidentate carbonates and/or carboxylates. These results can be explained by oxidation of CO by Ni^{3+} and Ni^{2+} ions because the adsorption of CO on TiO_2 does not lead to formation of such compounds.

We reported recently [36] the generation of Ni^+ sites as a result of the reduction of Ni-ZSM-5 with CO. However, only metal clusters were formed under the same conditions on a Ni/SiO_2 sample. Similar to the latter case, all attempts to increase the population of Ni^+ cations on the Ni/TiO_2 sample by means of reduction with CO failed.

3.1.3. ZrO_2

Adsorption of CO on pure ZrO_2 produces, in agreement with the published literature data [56–62], a band at about 2190 cm^{-1} which is shifted to higher frequencies with decreasing pressure and vanishes after evacuation (spectra not shown). This band characterizes Zr^{4+}–CO complexes [58–60].

3.1.4. Ni/ZrO_2

No bands due to residual carbonyl, nitrosyl, or $NO_x{}^-$ species have been registered in the background spectrum of the Ni/ZrO_2 sample. The introduction of CO (4 kPa equilibrium pressure) to the activated sample leads to the formation of an intense band with a maximum at 2187 cm^{-1} and three more low-intensity bands at 2155, 2134, and 2112 cm^{-1} (Fig. 2, spectrum a). After evacuation, one broad band at about 2134–2112 cm^{-1} (Fig. 2, spectrum g) remains in the spectrum. The band at 2187 cm^{-1} can be due to both Zr^{4+}–CO [58–60] and Ni^{2+}–CO [8,10,12–15,26–38] species. Comparison with the spectra of CO adsorbed on the pure support shows that the band is more intense with the Ni/ZrO_2 sample. This shows that Ni^{2+}–CO species contribute to the band at 2187 cm^{-1}. In contrast to Ni/TiO_2, however, in this case it is practically not possible to establish which part of the 2187 cm^{-1} band is due to CO adsorbed on the support and which to CO on Ni^{2+} sites. The bands at 2134–2112 cm^{-1} are not found with the pure support and, by analogy with Ni/TiO_2, can be associated with (di)carbonyl complexes of Ni^+ [8,10,13,14,27,30–36,38,41,42]. The probability that the bands arise from Zr^{3+}–CO species cannot be totally ruled out. However, this interpretation is even less probable than is the case of Ni/TiO_2 (Ti^{3+}–CO complexes) because it is more difficult to reduce ZrO_2 than TiO_2. The band at 2155 cm^{-1} is not observed with the pure support either and is most probably due to CO adsorbed on a NiO-like phase. A similar band has been observed on bulk NiO after low-temperature CO adsorption [39,40,47]. The fact that we have found it at room temperature can be explained by an enhanced electrophilicity of the Ni^{2+} ions in a “NiO”-like phase due to the effect of the support. The presence of associated nickel ions is also confirmed by the significant chemical shift of the band at 2155 cm^{-1} (to 2168 cm^{-1}) with decreasing coverage.

It should be noted that CO adsorption on Ni/ZrO_2 shows a much more pronounced reduction effect than is the case of Ni/TiO_2. As a result, a series of intense bands are observed at 1780, 1708, 1629, 1555, 1426, 1321, 1300, 1220, 1058, and 1017 cm^{-1}. All these bands can, in general, be assigned to carbonate–carboxylate structures [65].

As with Ni/TiO_2, we were not able to produce additional Ni^+ ions by means of reduction of the sample with CO.

3.2. Adsorption of NO

3.2.1. TiO_2

The results concerning NO adsorption on our pure supports have already been reported [21,22]. Briefly, adsorption of NO on TiO_2 does not initially lead to formation of any nitrosyls. With time NO disproportionates to N_2O (2242 and 2231 cm^{-1}), NO^- (1170 cm^{-1}), $N_2O_2{}^{2-}$ (1335 cm^{-1}), and nitrates (1628, 1617, 1578, 1552, 1270, 1248, and 1223 cm^{-1}). The nitrates enhance the acidity of the Ti^{4+} cations in their neighborhood, as a result of which ($NO_3{}^-$)–Ti^{4+}–NO (1913 and 1848 cm^{-1}) complexes are formed.

3.2.2. Ni/TiO$_2$

After NO adsorption (ca 70 Pa equilibrium pressure) on Ni/TiO$_2$, an intense band with a maximum at 1878 cm^{-1} and a shoulder at 1855 cm^{-1} (Fig. 3, spectrum a) is observed. In addition, there are low-intensity bands at 2133, 1932, and 1619 cm^{-1}. After evacuation at room temperature the band at 1878 cm^{-1} becomes weaker, the shoulder at 1855 cm^{-1} being more resistant (Fig. 3, spectrum b). In addition, while the 2133 cm^{-1} band shows a slight intensity decrease, the band at 1619 cm^{-1} develops, and the band at 1932 cm^{-1} practically disappears. Evacuation at 433–463 K (Fig. 3, spectra c and d) causes a considerable decrease in intensity and vanishing of the band at 1878 cm^{-1}, the band at 1855 cm^{-1} only remaining in the spectrum. The bands at 2133 and 1619 cm^{-1} disappear successively. According to literature data [66], the band at 2133 cm^{-1} is attributed to NO$^+$ compounds. The band at 1619 cm^{-1} is assigned to water-bending modes. Indeed, H$_2$O could be formed along with NO$^+$ according to the reaction [66]:

$$2\text{NO} + \frac{1}{2}\text{O}_2 + 2\text{O}^{2-}\text{–H}^+ \rightarrow 2\text{O}^{2-}\text{–NO}^+ + \text{H}_2\text{O}. \qquad (1)$$

In agreement with data from the literature [8,11,14,29,30,37,48–53], the band at 1878 cm^{-1} is assigned to linear Ni^{2+}–NO complexes. The band at 1855 cm^{-1} characterizes another kind of more stable nitrosyl complexes. The high stability and low stretching frequency of these nitrosyls indicate a π-backbonding. Owing to their low charge, the Ni$^+$ ions can relatively easily donate d-electron density, forming a π-bond. That is why we believe that the band at 1855 cm^{-1} corresponds to Ni$^+$–NO species. This is in agreement with the results on CO adsorption which also evidence the presence of small amounts of Ni$^+$ on the sample surface. According to the works of Platero et al. [47], the band at 1932 cm^{-1} can be attributed to small amounts of Ni^{3+}–NO nitrosyls. We exclude the probability for it to characterize Ti^{4+}–NO-type nitrosyls since they have been observed with TiO$_2$ [21] (i) at lower frequencies (1913 and 1848 cm^{-1}) and (ii) only after the formation of surface nitrates. Thus, NO appears to be a better probe molecule than CO for detection of c.u.s. Ni^{3+} cations.

Subsequent introduction of a higher amount of NO (1.3 kPa equilibrium pressure) to the sample leads to the reappearance of the bands due to Ni^{3+}–NO (1931 cm^{-1}), Ni^{2+}–NO (1878 cm^{-1}), and NO$^+$ (2130 cm^{-1}) species (Fig. 4, spectrum a). Shoulders at 1897 and 1851 cm^{-1} are also detected. In addition, bands of N$_2$O (2265 and 2235 cm^{-1}) and low-intensity bands at 1616, 1580, 1552, 1324, and 1173 cm^{-1} are observed. Similar bands have also been established [21] after adsorption of NO on TiO$_2$ and have been assigned to nitrates (1616, 1580, and 1552 cm^{-1}), hyponitrites (1324 cm^{-1}), and NO$^-$ species (1173 cm^{-1}). All these compounds are formed in the presence of higher concentrations of NO in the gas phase, when NO disproportionates. The decrease in equilibrium pressure of the gas down to 400 Pa results in a simultaneous intensity decrease of the bands at 1897 and 1851 cm^{-1} (Fig. 4, spectrum b). At the same time, a slight increase in intensity of the band at 1878 cm^{-1} is observed. These results can be explained by conversion of Ni^{2+}(NO)$_2$ dinitrosyls (ν_s at 1897 cm^{-1} and ν_{as} at 1851 cm^{-1}) to Ni^{2+}–NO mononitrosyls (1878 cm^{-1}). After evacuation, the bands of linear Ni^{2+}–NO and Ni^{3+}–NO complexes as well as the bands below 1700 cm^{-1} remain in the spectrum (Fig. 4, spectrum d). It should be noted that in this case the band of the stable Ni$^+$–NO complexes at 1856 cm^{-1} is not observed. This can be explained by the fact that the Ni$^+$ cations on the surface are oxidized in the presence of a higher NO equilibrium pressure. Evacuations at higher temperatures (up to 473 K) result in an initial decrease (Fig. 4, spectra e and f) followed by a slight increase in intensity (evacuation at 573 K; Fig. 4, spectrum g) of the band due to Ni^{2+}–NO species. Simultaneously, a gradual disappearance of the bands for N$_2$O$_2$$^{2-}$ (at 373 K), NO$^-$ (at 473 K), and NO$_3$$^-$ compounds (at 573 K) occurs. Evidently, during evacuation at 573 K the decomposition of nitrates leads to the formation of a certain amount of nitrosyls. Evacuation at 673 and 723 K causes an intensity drop and disappearance of the band of Ni^{2+}–NO complexes, a low-intensity band at 1856 cm^{-1} appearing at its expense (Fig. 4, spectra h and i). This suggests that evacuation at high temperatures leads to generation of small amounts of Ni$^+$ sites.

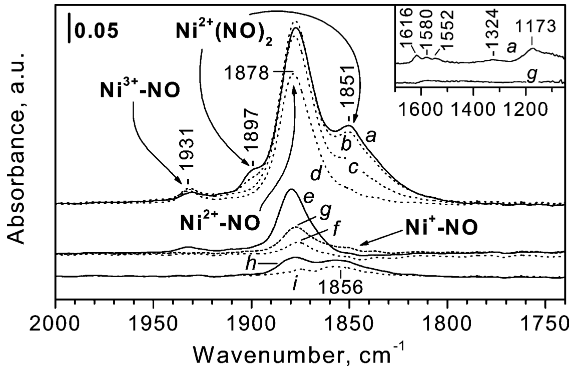

Fig. 4. FTIR spectra of NO adsorbed on Ni/TiO$_2$. Equilibrium pressure: 1300 (a) and 400 Pa (b), and after evacuation at room temperature (c, d), 373 (e), 473 (f), 573 (g), 623 (h), and 723 K (i).

3.2.3. ZrO$_2$

The results concerning NO adsorption on ZrO$_2$ are already reported [22]. Briefly, the adsorption does not lead initially to formation of nitrosyl complexes. After disproportionation of NO, formation of N$_2$O (2282, 2244, and 1233 cm^{-1}), small amounts of nitro compounds (1443 and 1423 cm^{-1}), nitrates (1558, 1189, and 1057 cm^{-1}), and HNO$_2$ (1621 and 1142 cm^{-1}) has been established. Bands due to nitrates (1646–1560, 1290–1220, and 1042–1004 cm^{-1}) develop with time. Similar to the case of TiO$_2$, the nitrates enhance the Lewis acidity of the neighboring Zr^{4+} cations. As a result, (NO$_3$$^-$)–Zr^{4+}–NO complexes (1926–1906 cm^{-1}) are formed.

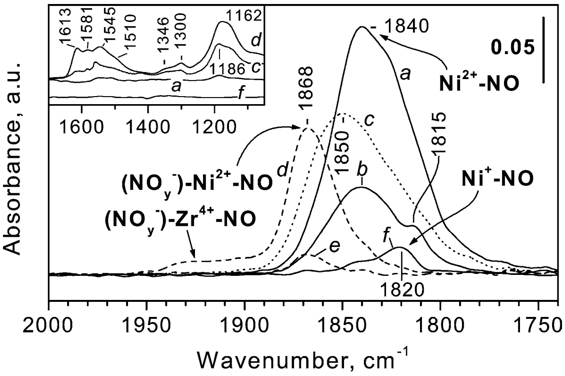

Fig. 5. FTIR spectra of NO adsorbed on Ni/ZrO$_2$. Equilibrium pressure of ca. 70 Pa (a) and after evacuation (b); subsequent adsorption of NO (1300 Pa equilibrium pressure) (c), after 10 min (d), and after evacuation at room temperature (e) and at 723 K (f).

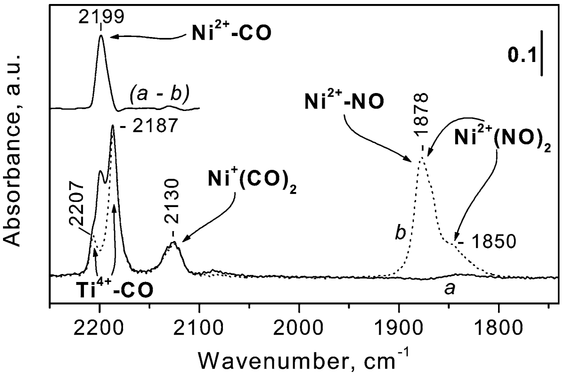

Fig. 6. FTIR spectra of CO and NO coadsorbed on Ni/TiO$_2$. Adsorption of CO (3300 Pa equilibrium pressure) (a) and admission of NO (400 Pa partial pressure).

3.2.4. *Ni/ZrO$_2$*

Adsorption of NO (ca 70 Pa equilibrium pressure) on Ni/ZrO$_2$ produces a band at 1840 cm^{-1} having a pronounced low-frequency shoulder (Fig. 5, spectrum a). After evacuation the band decreases in intensity and the shoulder is now well seen as a separate band at 1815 cm^{-1} (Fig. 5, spectrum b). The band at 1840 cm^{-1} can be attributed to Ni^{2+}–NO complexes [8,11,14,29,30,37,48–53]. The 1815 cm^{-1} band characterizes more stable complexes and is therefore assigned to Ni^{+}–NO species.

Subsequent introduction of a larger amount of NO (1.3 kPa equilibrium pressure) to the sample produces a low-intensity broader band with a maximum at 1850 cm^{-1} (Fig. 5, spectrum c). After 10 min the band becomes narrower and decreases in intensity and the maximum is shifted to 1868 cm^{-1} (Fig. 5, spectrum d). In addition, a low-intensity broad band at about 1925 cm^{-1} arises. It is worth noting that all these changes are accompanied by the appearance and gradual increase in intensity of a series of bands with maxima at 1615, 1587, 1541, 1510, 1425, 1348, 1298, 1246, 1186, and 1162 cm^{-1} (see the inset of Fig. 5). The latter bands are in general due to nitro and nitrato groups [11]. Thus, the higher frequency of the nitrosyl band observed after the second NO admission can be explained by an enhanced acidity of the nickel ions induced by nitrogen-oxo anions in the vicinity. The lower intensity of the nitrosyl band may be attributed to total blocking of some Ni^{2+} sites by NO_x^- anions. The band at about 1925 cm^{-1} has been observed [22] on pure ZrO$_2$ and ascribed to (NO_3^-)–Zr^{4+}–NO complexes. Finally, the band assigned to Ni^{+}–NO species has disappeared which suggests that (as in the case of the Ni/TiO$_2$ sample) oxidation of Ni^{+} ions to Ni^{2+} has occurred under NO atmosphere.

After evacuation at ambient temperature, the band at 1868 cm^{-1} significantly decreases in intensity, while the band at about 1925 cm^{-1} completely disappears (Fig. 5, spectrum e). Evacuation at 723 K produces a low-intensity band at 1820 cm^{-1} which has been attributed to Ni^{+}–NO species (Fig. 5, spectrum f). They are probably formed after decomposition of the NO_x^- compounds and partial reduction of the nickel on the surface.

3.3. *Coadsorption of CO and NO*

The results showed the carbonyls of supported nickel cations (Ni^{2+}) and those of the supports (Ti^{4+} or Zr^{4+}) to appear in the same spectral region, this making spectral interpretation difficult. Nitrogen oxide, on its part, is selectively bonded to Ni^{2+} ions. In order to study the possibility of detecting simultaneously nickel and support (Ti^{4+} or Zr^{4+}) cations, coadsorption of CO and NO was performed. It should be taken into consideration that in a NO atmosphere, formation of surface nitrate begins with time, as a result of which (NO_3^-)–Ti^{4+}–NO and (NO_3^-)–Zr^{4+}–NO nitrosyl species appear [21–23]. To prevent this, the experiments were carried out at low partial pressures of nitrogen monoxide.

3.3.1. *Ni/TiO$_2$*

At first CO (3.3 kPa equilibrium pressure) was adsorbed on Ni/TiO$_2$, which resulted in a spectrum similar to spectrum b in Fig. 1. Bands at 2207, 2199, 2187, and 2130 cm^{-1} were detected (see spectrum a in Fig. 6). Then, a reservoir with NO was opened and nitrogen monoxide was allowed to diffuse to the sample (maximum partial pressure of ca. 400 Pa). This led to an intensity decrease of the band at 2199 cm^{-1}, two distinct bands at 2207 and 2187 cm^{-1} becoming clearly visible in the spectrum (Fig. 6, spectrum b). Simultaneously, an intense band at 1878 cm^{-1} with a shoulder at 1850 cm^{-1} appeared in the nitrosyl-stretching region. Adsorption of CO on the pure support evidenced that the bands at 2207 and 2187 cm^{-1} were due to α- and β-Ti^{4+}–CO complexes; i.e., NO was not able to displace CO as a ligand of the Ti^{4+} cations.

The band at 1878 cm^{-1} is due to linear Ni^{2+}–NO species while the band at 1850 cm^{-1} corresponds to ν_{as} of Ni^{2+}(NO)$_2$ dinitrosyls (the band of ν_s vibration has a low intensity and is masked by the strong band of linear nitrosyls). In this case NO displaces CO as a ligand of the Ni^{2+}

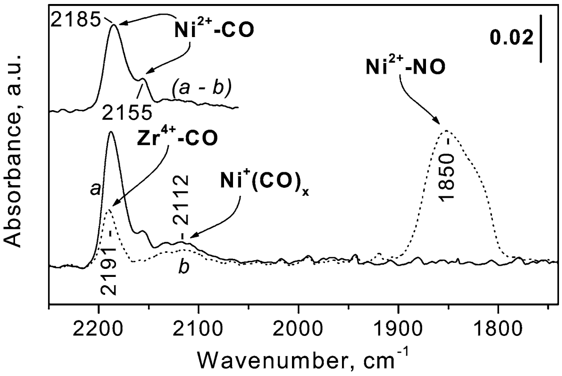

Fig. 7. FTIR spectra of CO and NO coadsorbed on Ni/ZrO$_2$. Adsorption of CO (1700 Pa equilibrium pressure) (a) and admission of NO (ca. 70 Pa partial pressure) (b).

sites, forming (di)nitrosyls. The difference spectrum (Fig. 6) confirms that the Ni^{2+}–CO carbonyls are characterized by a band at 2199 cm^{-1}, which is in agreement with the interpretation of the spectra registered after CO adsorption. It is to be noted that the Ni^{+} (di)carbonyl band (2130 cm^{-1}) practically does not change after introduction of NO, which shows that NO does not displace CO from the Ni^{+} sites. After evacuation, the Ti^{4+}–CO bands disappear while the Ni^{+}–CO band is resistant to evacuation. The nitrosyl bands at 1878 and 1850 cm^{-1} gradually lose intensity, which is more pronounced with the band at 1850 cm^{-1}. This is consistent with the already proposed assignments of the bands.

3.3.2. *Ni/ZrO$_2$*

Adsorption of CO on Ni/ZrO$_2$ (1.7 kPa equilibrium pressure) leads to the appearance of bands due to different carbonyl complexes (Fig. 7, spectrum a) and carbonate–carboxylate structures (vide supra). Addition of a small amount of nitrogen oxide was performed as described above. As a result, the intensity of the band at 2187 cm^{-1} gradually decreased, its maximum being slightly shifted to 2191 cm^{-1} (Fig. 7, spectrum b). The band at 2155 cm^{-1} disappeared completely. Simultaneously with the changes in the carbonyl-stretching region, an intense band of Ni^{2+}–NO complexes developed at about 1850 cm^{-1}. The higher frequency of the nitrosyl band as compared to the band observed after NO adsorption at low pressures on a freshly activated sample can be explained by the presence of carbonate–carboxylate species which (similarly to the nitrates) increase the acidity of surface Ni^{2+} ions. A band at 2191 cm^{-1}, which remains after the introduction of NO to the system, is evidently due to Zr^{4+}–CO complexes. The part of the initial band that disappears after NO adsorption is due to Ni^{2+}–CO carbonyls. The difference spectrum (Fig. 7) shows that the band of linear Ni^{2+}–CO carbonyls has a maximum at 2185 cm^{-1}; i.e., the Ni^{2+} cations on Ni/ZrO$_2$ have a lower acidity than Ni^{2+} on Ni/TiO$_2$ (band of Ni^{2+}–CO carbonyls at 2199 cm^{-1}). Analogous results were obtained with titania- and zirconia-supported chromium catalysts. The Cr^{3+} ions on Cr/TiO$_2$ showed a higher electrophilicity (respective carbonyl band at 2195 cm^{-1}) than Cr/ZrO$_2$ (Cr^{3+}–CO band at 2179 cm^{-1}) [20].

After evacuation at 723 K, a low-intensity band at 1820 cm^{-1} remains in the spectrum. As already noted, this band is probably due to very stable Ni^{+}–NO nitrosyls. Subsequent introduction of CO results in the disappearance of the band of Ni^{+}–NO and the appearance of carbonyl bands at 2187, 2155, and 2113 cm^{-1}. The result shows that CO displaces NO from the Ni^{+} sites.

4. Discussion

In agreement with data from the literature [67] and on the basis of our previous investigations [13,14,36,46], adsorption of Ni^{2+} from a nickel ammine complex solution is a technique ensuring a high dispersion of the supported phase. In the case of zirconia, however, there is some heterogeneity in the distribution of nickel. In addition to highly dispersed Ni^{2+} ions, a “NiO”-like phase is also registered on the surface. This has been confirmed by other techniques, e.g., TPR [14]. Similar results have been obtained on Cr/TiO$_2$ and Cr/ZrO$_2$ samples [20]. Here again, the titania-supported sample is characterized by a more homogeneous distribution of the active phase.

Adsorption of probe molecules (CO and NO) has shown the nature of the support to affect the electrophilicity of the Ni^{2+} ions. Ni^{2+} ions on Ni/TiO$_2$ have a higher acidity than those on Ni/ZrO$_2$: the respective carbonyl and nitrosyl complexes are observed at higher frequencies. As already noted, the same phenomenon has been reported for titania- and zirconia-supported chromium cations [20].

The activation of the samples under vacuum leads to the formation of negligible amounts of Ni^{+} sites on the surface. Obviously, only a restricted number of a definite type of nickel ions undergoes this reduction since attempts to increase their concentration by reduction with CO fail. For the sake of comparison we have established [35,36] that the reduction of Ni–H-ZSM-5 with CO leads to generation of Ni^{+} ions. The fraction of Ni^{+} ions on Ni/TiO$_2$ and Ni/ZrO$_2$, however, is more resistant to oxidation with NO. While the Ni^{+} ions in Ni–H-ZSM-5 are oxidized by NO even at low temperatures [68], in the cases under consideration the oxidation of Ni^{+} ions proceeds at room temperature and higher concentrations of NO when it disproportionates.

Analysis of literature data [8,10,11] shows that some c.u.s. cations form stronger bonds with CO, and others with NO. Thus, no nitrosyl species are formed with participation of Ti^{4+} and Zr^{4+} cations on bare titania (zirconia) surfaces at room temperature [21,22]. However, they can adsorb CO, although not very strongly. This fact has not been explained in the literature but is very important for the choice of an IR probe molecule. In what follows we shall try to give an explanation of the phenomenon.

The metal cations could be soft or hard acids thus preferring to form bonds with soft or hard ligands. Zhung [69] has quantified this point of view, dividing the metal ions into electrostatic and covalent acids depending on the nature of the bonds they form with ligands. Alkali-metal cations form electrostatic bonds, whereas the bond of Au^+ and Pd^{2+} with ligands is mainly covalent. According to this classification, the Ti^{4+} and Zr^{4+} cations are electrostatic acids. Our calculations aimed at estimating the electrostatic interaction of Ti^{4+} (Zr^{4+}) cations with CO and NO have shown that the energy of interaction with CO is higher than that in the case of NO [68]. This is due to the fact that the CO molecule is polarized more easily, although the free NO molecule is characterized by a somewhat higher dipole moment. Thus, the electrostatic field of the cation induces a larger dipole moment in the CO molecule as compared to the molecule of NO.

The Ni^{2+} ions are on the border line between covalent and electrostatic acids. Due to their relatively high charge, they form mainly σ-bonds with the ligands. Thus, the Ni^{2+} cations should form a stronger bond with NO, which is a stronger σ-base than CO.

However, cations with a higher d-electron density and a low charge (e.g., different univalent cations, such as Ni^+) should make stronger bonds with CO than is the case of NO [10,11,24,25]. The reason is that CO forms a π-backbond more easily than NO due to the presence of an electron of a $2\pi^*$ antibonding orbital in NO, i.e., CO is a stronger π-acid than NO.

The results of the present study demonstrate that CO is adsorbed on c.u.s. Ni^{2+}, Ti^{4+}, and Zr^{4+} sites and it is difficult to distinguish between the carbonyls formed. In contrast, the Ni^+ ions form carbonyl complexes that are found at lower frequencies and have a much higher stability. This means that Ni^+ ions can easily be monitored by CO but this probe molecule is not suitable for registering Ni^{2+} cations on the surfaces of Ni/TiO_2 and Ni/ZrO_2. A similar situation may be expected with other nickel-containing systems such as Ni/Al_2O_3.

However, selective detection of Ni^{3+} and Ni^{2+} cations on titania or zirconia is easy when using NO as a probe molecule. While Ni^{3+} and Ni^{2+} sites form (di)nitrosyl complexes, nitrogen monoxide is not adsorbed on pure titania or zirconia surfaces. In this case one should recommend performing the adsorption studies at low equilibrium pressures of NO. High NO pressures may lead to NO disproportionation and modification of the surface by NO_x^- compounds. This can provoke the following effects: (i) increase in Lewis acidity of the surface cations (due to an induction effect) and, as a result, formation of Ti^{4+} and Zr^{4+} nitrosyls and blue shift of the Ni^{2+}–NO band, and (ii) blocking of (part of) the Ni^{2+} sites. In addition, oxidation of Ni^+ can occur. All this should be taken into consideration when interpreting the spectra in the region of N–O vibrations.

Finally, a mixture of CO and NO (low equilibrium pressure of NO) can be used for both simultaneous and selective determination of Ni^{2+} and Ti^{4+} (Zr^{4+}) cations on Ni/TiO_2 and Ni/ZrO_2 samples as well as for speciation of the supported nickel ions (Ni^{2+} or Ni^+).

5. Conclusions

- A Ni/TiO_2 sample prepared by an equilibrium adsorption technique is characterized by isolated Ni^{2+} cations which form linear carbonyl (2199 cm^{-1}) and nitrosyl (1878 cm^{-1}) complexes. At equilibrium pressures of NO, part of the mononitrosyls are converted to dinitrosyls (ν_s at 1897 cm^{-1} and ν_{as} at 1851 cm^{-1}). The Ni^{2+} cations form stronger bonds with NO than CO due to which nitrogen monoxide displaces carbon monoxide from Ni^{2+} sites. Ni^{3+} sites can also be detected by NO (1932 cm^{-1}). Activation of the sample leads to formation of small amounts of Ni^+ ions characterized by stable linear carbonyl (2134 cm^{-1}) and nitrosyl (1855 cm^{-1}) complexes. At equilibrium pressures of CO, the monocarbonyls are converted to dicarbonyls (ν_s at 2130 cm^{-1} and ν_{as} at 2124 cm^{-1}). In this case the Ni^+ ions (in contrast to the Ni^{2+} ones) form stronger bonds with CO than with NO.
- A Ni/ZrO_2 sample prepared by an equilibrium adsorption technique is characterized by a certain heterogeneity in distribution of the Ni^{2+} cations: both isolated (band of the respective Ni^{2+}–CO species at 2185 cm^{-1}) and associated Ni^{2+} ions (a “NiO”-like phase characterized by a Ni^{2+}–CO band at 2155 cm^{-1}) are present on the surface. The lower frequencies of the carbonyl bands as compared to those with Ni/TiO_2 show that the Ni^{2+} ions are in this case less electrophilic. This is also confirmed by the results on NO adsorption: Ni^{2+}–NO complexes characterized by a band at 1840 cm^{-1} are observed. A small fraction of Ni^+ ions forming stable carbonyl (2134–2112 cm^{-1}) and nitrosyl (1820–1815 cm^{-1}) complexes also exists on Ni/ZrO_2.
- Coadsorption of CO and NO permits simultaneous and selective registration of (i) Ni^{2+} and Ti^{4+} (Zr^{4+}), and (ii) Ni^{2+} and Ni^+ surface cations. This is based on the fact that CO is adsorbed more strongly on Ti^{4+}, Zr^{4+}, and Ni^+ ions while NO forms a stronger bond with Ni^{2+} ions.

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