

Formation of Surface Carbonyl and Nitrosyl Complexes on Titania- and Zirconia-Supported Chromia

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The state of the chromium ions on Cr/ZrO₂ and Cr/TiO₂ samples has been tested by the IR spectra of adsorbed CO and NO. CO adsorption on activated samples leads mainly to formation of carbonyls related to the support. At low temperature, CO is also bonded to Crⁿ⁺–OH groups that are present in low concentration. When NO is adsorbed on these samples, it forms Crⁿ⁺–NO (*n* > 3) species and is slowly oxidized to NO⁺, NO₂[–], and NO₃[–]. Small amounts of Cr³⁺(NO)₂ species are also detected, which evidences the existence of a limited fraction of Cr³⁺ cations. Reduction of both samples leads to conversion of all chromium into Cr³⁺ cations. With CO, they form relatively stable linear carbonyls whereas dinitrosyls are mainly formed after NO adsorption. In addition, a fraction of Cr³⁺–OH groups with a very weak acidity is formed by reduction. CO–NO coadsorption experiments have revealed that NO is selectively adsorbed on Cr³⁺ sites, whereas CO is preferentially located on Zr⁴⁺ or Ti⁴⁺ cations. The possibility of selective detection of chromium sites on supported chromia catalysts is discussed.

Introduction

IR spectroscopy of probe molecules is a powerful technique for determination of the properties of coordinatively unsaturated (cus) cations.^{1–5} In particular, this method has been widely applied to investigate chromium-containing systems.^{1–29} When chromia is supported on silica, there are no problems with the detection of chromium cations.^{6–9} However, the use of some molecules, especially CO, to probe the state of chromium cations supported on many other oxides is accompanied by many difficulties. They arise from the fact that the C–O stretching frequencies of chromium carbonyls are usually observed in the same spectral region in which the carbonyls of the support are detected.² Moreover, the stability of the carbonyls is similar, which additionally complicates the interpretation of the spectra. Typical examples are titania- and zirconia-supported chromia.

Analysis of literature data^{30–32} shows that a similar situation is also encountered with other cations. Thus, CO is not an appropriate probe molecule for detection of V⁴⁺ or V³⁺ cations on reduced vanadia–titania catalysts. However, the application of NO in this case can be advantageous.^{30,31}

Adsorption of CO on zirconia has been studied by many authors.^{33–43} Generally, the surface acidity of zirconia is affected by its crystal modification and dehydroxylation degree. CO adsorption of monoclinic zirconia leads to the appearance of carbonyl bands located at 2210–2200 and 2195–2185 cm^{–1} suggesting the existence of two families of cus Zr⁴⁺ sites.^{33–36} The latter band has not been reported^{37,38} by all authors. When CO adsorption is performed at low temperature, at least one more type of weakly acidic Zr⁴⁺ sites is indicated by a CO band at 2170–2160 cm^{–1}.³⁹ All these bands are blue shifted with

decreasing coverage. In addition, at low temperature a band at 2156 cm^{–1} corresponding to CO H-bonded to Zr⁴⁺–OH groups is detected.⁴⁰ Some authors believe that after reduction at high temperatures, Zr³⁺ sites are created and detected by a carbonyl band at 2125–2101 cm^{–1}.^{41,42} Low-temperature adsorption of CO on tetragonal zirconia reveals two kinds of sites characterized by carbonyl bands at 2195–2185 cm^{–1} and 2175–2170 cm^{–1}.⁴³

Adsorption of CO on titania is also affected by the crystal structure. Two kinds of sites are detected on anatase by CO at room temperature (ca. 2208 and 2185 cm^{–1}).^{44,45} At low temperature, the 2185 cm^{–1} band is shifted to 2179 cm^{–1} and a band characterizing a third kind of weakly acidic sites is formed (2165 cm^{–1}).⁴⁵ Low-temperature CO adsorption on rutile reveals the existence of one kind of Ti⁴⁺ sites that are characterized by a carbonyl band at ca. 2190 cm^{–1}. Here again, it is believed that Ti³⁺ sites exist on reduced samples and are responsible for a carbonyl band at ca. 2115 cm^{–1}.⁴⁴

According to recent investigations, NO adsorption on both pure titania and zirconia does not lead to formation of nitrosyl species.^{47–49} However, nitrates are produced with time. They affect the acidity of the cations being located in close proximity, and, as a result, (NO₃[–])–Ti⁴⁺–NO (ca. 1880 cm^{–1}) or (NO₃[–])–Zr⁴⁺–NO (1926–1906 cm^{–1}) species are produced.

The chemistry of surface chromium carbonyls has been the subject of great interest^{6,7,10–20} because of the wide application of chromium-containing materials in catalysis. Because of coordinative saturation and high covalency of the Cr–O bond, Cr⁶⁺ species do not form carbonyls.^{1,10} Some authors suggest that bands in the 2206–2170 cm^{–1} region characterize Crⁿ⁺–CO (*n* = 4 or 5) species.^{11–14} The most commonly observed Cr³⁺ cations are detected by CO at 2206–2162 cm^{–1}.^{2,10–20} When chromium-containing samples are deeply reduced, usually by CO, Cr²⁺ cations are created. Their properties are strongly affected by the support. Because of the formation of a π -back-

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bond, the CO stretching modes of the monocarbonyls are shifted to lower frequencies, namely, 2130,^{6,7,12,15,17,20} 2101,¹⁰ or 2082–2070 cm^{-1} .^{15,20} These species are definitely more stable than the Cr^{3+} –CO species and are resistant toward evacuation at room temperature. The formation of polycarbonyls and bridged species (at low temperature) is also reported for Cr^{2+} .^{5,11,15,17}

According to summarized literature data, NO forms complexes with both Cr^{3+} and Cr^{2+} cations.³ Different mononitrosyls have been detected in a wide spectral region, namely, 1905–1685 cm^{-1} .^{8,9} However, the formation of dinitrosyl species is more typical. The symmetric and antisymmetric modes of the $\text{Cr}^{3+}(\text{NO})_2$ species have been proposed at 1940–1859 and 1820–1725 cm^{-1} , respectively.^{17,21–24} These modes have been found at 1893–1848 and 1768–1737 cm^{-1} , respectively, for the $\text{Cr}^{2+}(\text{NO})_2$ species.^{8,9,22,25,26} Although the assignments cannot be correct in several cases, the general trend is that the stretching frequencies are higher for the $\text{Cr}^{3+}(\text{NO})_2$ than for the $\text{Cr}^{2+}(\text{NO})_2$ complexes.

The aim of this work was to investigate CO and NO adsorption and coadsorption on Cr/ZrO₂ and Cr/TiO₂ samples which were subjected to different reduction/oxidation treatments and to test the applicability of these probe molecules to selective determination of Cr^{n+} and Ti^{4+} (Zr^{4+}) sites.

Experimental Section

The ZrO₂ and TiO₂ used for the experiments were commercial Degussa samples. Zirconia had a monoclinic structure and its specific surface area was 53 $\text{m}^2 \text{g}^{-1}$. Titania consisted of 75% anatase and 25% rutile and had a similar specific surface area, namely, 54 $\text{m}^2 \text{g}^{-1}$.

The Cr/ZrO₂ and Cr/TiO₂ samples were prepared by incipient wetness impregnation of the supports with a 0.02 M solution of ammonium dichromate. After the impregnation, the samples were dried at 378 K and then calcined at 673 K for 1 h. The nominal chromium concentration in both samples was 5 wt. % Cr. The specific surface areas of the calcined materials were similar to those of the pure supports, that is, 51 and 55 $\text{m}^2 \text{g}^{-1}$ for the Cr/ZrO₂ and Cr/TiO₂ samples, respectively. Using these data, the average surface concentrations of chromium were calculated to be 11.3 Cr nm^{-2} on Cr/ZrO₂ and 10.5 Cr nm^{-2} on Cr/TiO₂. This exceeds a monolayer coverage. For comparison, the concentration of Ti^{4+} sites on the surface of anatase is about 5 $\text{Ti}^{4+} \text{nm}^{-2}$.

The IR spectra were recorded on Nicolet Avatar 360 and Bruker IF 66 spectrometers at a spectral resolution of 2–4 cm^{-1} accumulating 64–128 scans. Prior to the experiments, the sample powders were pressed into self-supporting wafers (density of ca. 11 mg cm^{-2}) under a pressure of 10^6 – 10^7 Pa. The similar densities of the pellets allowed direct comparison between the intensities of the IR bands observed with the two samples. Both the pretreatment and the experiments were performed in situ using purpose-made IR cells connected to a vacuum-adsorption apparatus with a residual pressure lower than 10^{-3} Pa. The design of the cells permitted IR measurements in the range between 85 K and room temperature. Before the experiments, the samples were activated by successive thermooxidative and thermovacuum treatments (both at 673 K). To obtain reduced samples, the pellets were reduced by hydrogen (1 h, 573 K, in 50 kPa H₂) and evacuated for 1 h at 673 K.

Carbon monoxide (>99.997) was supplied by Merck and nitrogen monoxide (99.0) by Aldrich Chemical Co. Inc.

The TPR experiments were performed with 10 vol % hydrogen in argon (25 mL min^{-1}) at a heating rate of 7.5 K min^{-1} , the hydrogen consumption being measured by a catharo-

metric detector. The TPR profiles were normalized for the same catalyst mass. Before the experiments, the samples were calcined for 1 h under air flow (25 mL min^{-1}) at 773 K. The XPS spectra were taken by an ESCALAB Mk II (VG Scientific) apparatus with a magnesium anode ($h\nu = 1254.6 \text{ eV}$). The binding energy values were corrected using the C 1s level (284.8 eV) of the carbon contaminants on the surface. The electron paramagnetic resonance (EPR) measurements at 9.23 GHz (X-band) were carried out with an ERS 220/Q spectrometer in the temperature range 85–410 K. The *g*-factors were established with respect to a $\text{Mn}^{2+}/\text{ZnS}$ standard.

Results

Initial Characterization of the Samples. The samples were initially characterized by XPS, EPR, and TPR. XPS is a widely used technique for distinguishing between different oxidation states of supported chromium.^{11,50} Generally, Cr^{6+} ions are characterized by a $2p_{3/2}$ peak at about 580 eV. This signal shifts to lower binding energies with the decrease of the chromium oxidation state and is detected at ca. 579, 577, and 576 eV for Cr^{5+} , Cr^{3+} , and Cr^{2+} , respectively. The photoelectron spectrum of our Cr/ZrO₂ sample (not shown) contains a complex band with a distinguished maximum at 579.8 eV and a pronounced shoulder at 577.7 eV. According to literature data,^{11,50} the main peak at 579.8 eV is assigned to Cr^{6+} species. The lower-energy shoulder is typical of Cr^{3+} ions. Thus, the results indicate that the principal part of chromium in the sample is highly oxidized, but some of the chromium is encountered as Cr^{3+} . The results do not exclude the existence of a restricted fraction of Cr^{5+} species, the eventual peak being masked by the strong signal of Cr^{6+} .

The XP spectrum of the Cr/TiO₂ sample contains the same two peaks (detected at 579.9 and 577.5 eV, respectively). In this case, however, the $\text{Cr}^{6+}/\text{Cr}^{3+}$ ratio is slightly changed in favor of the Cr^{3+} species. Hence, chromium is less oxidized on the Cr/TiO₂ than on the Cr/ZrO₂ sample.

The Cr:Zr ratio, calculated on the basis of the XPS spectra, was 1:2.9, while the Cr:Ti ratio was 1:6.2. At first sight, these results suggest a better dispersion of chromia on titania. However, we propose another explanation of this phenomenon (see Discussion).

Characterization of supported chromium species by EPR is supplementary to XPS. EPR is “blind” to the even oxidation states of chromium but can provide more detailed information on the state of the Cr^{3+} and Cr^{5+} cations.^{9,50,51} Thus, a signal with a *g*-factor around 2 and width (ΔH) of 40–60 G is typical of isolated Cr^{5+} cations. Isolated Cr^{3+} cations in disordered octahedral coordination are characterized by a broad signal with a *g*-value of 2.2–4.3. Clusters of Cr_2O_3 are responsible for an EPR line with ΔH between ca. 800 and 1800 G and a *g*-factor of 1.9–2.4. However, Cr_2O_3 ($\Delta H = 500 \text{ G}$, *g* = 1.98) is antiferromagnetic and has a Néel temperature of 307 K. This means that α -chromia cannot be detected below this temperature.

To obtain information on the existence of a separate chromia phase on our samples, we have measured the EPR spectra at different temperatures. The spectrum of the Cr/ZrO₂ sample taken at 373 K contains a broad signal with a *g*-factor of 2.00 and $\Delta H = 550 \text{ G}$ (Figure 1A, spectrum a). A careful inspection of the spectrum also shows a weak narrow line with *g* around 1.97 which will be discussed below. The spectra taken at 293 and 113 K contain the same main signal. However, its intensity decreases with temperature (Figure 1A, spectra b, c). On the contrary, the weak narrow signal (*g* = 1.97, $\Delta H = 40 \text{ G}$) gains intensity. The above results can be rationalized assuming the

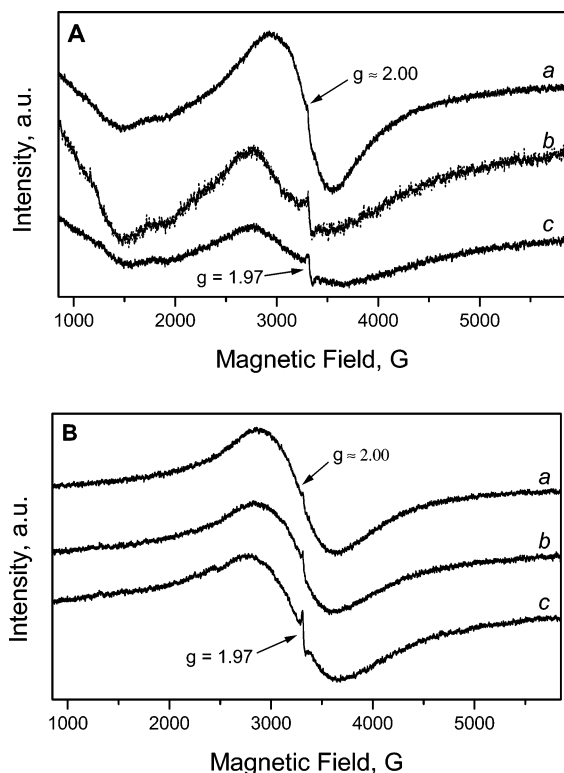


Figure 1. (A) EPR spectra of Cr/ZrO₂. The spectra are registered at 373 (a), 293 (b), and 113 K (c). (B) EPR spectra of Cr/TiO₂. The spectra are registered at 373 (a), 293 (b), and 113 K (c).

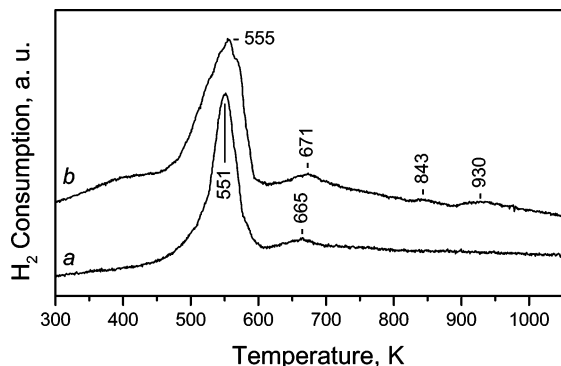


Figure 2. TPR patterns of Cr/ZrO₂ (a) and Cr/TiO₂ (b).

simultaneous existence of Cr³⁺ and small fraction of Cr⁵⁺ cations. Indeed, the narrow signal is typical of Cr⁵⁺ and is expected to increase with lowering temperature.⁵⁰ The broad signal is characteristic of Cr₂O₃ clusters. The decrease in intensity of this signal indicates some magnetic correlation which suggests the existence of a separate chromia phase.

The EPR spectra of Cr/TiO₂ are shown in Figure 1B. Similarly to the case of the Cr/ZrO₂ sample, a broad Lorentzian signal ($g = 2.00$, $\Delta H = 753$ G) and a weak line ($g = 1.97$, $\Delta H = 39$ G) are detected. In this case, however, the broad signal is not temperature dependent which suggests that the chromia clusters are smaller than is the case of Cr/ZrO₂. Thus, this is consistent with the higher line width. As for the small fraction assigned to Cr⁵⁺ cations, they seem to be identical with those found on Cr/ZrO₂.

The TPR pattern of the calcined Cr/ZrO₂ sample contains one main peak at 551 K and a weaker component at 665 K (Figure 2, pattern a). These two peaks are observed at almost the same temperatures in the spectra of the Cr/TiO₂ sample (at 555 and 671 K, respectively). In addition, a low-temperature

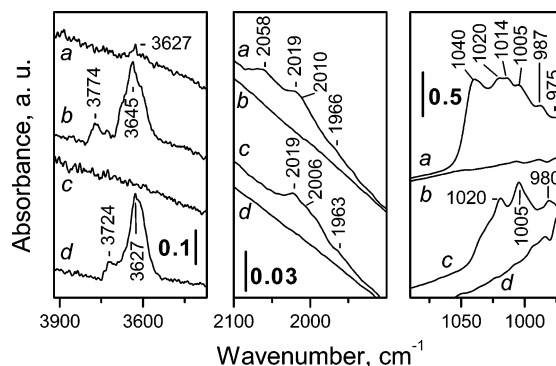


Figure 3. Background spectra of activated (a) and reduced Cr/ZrO₂ (b) and activated (c) and reduced Cr/TiO₂ (d).

feature around 400 K and a series of low-intensity peaks at higher temperatures are detected (Figure 2, pattern b). The main peaks at about 550 and 670 K can be attributed to reduction of oxidized chromium species to Cr³⁺.⁵² However, it is not excluded for the peaks around 670 K to be due to reduction of some Cr³⁺ ions to Cr²⁺.⁵³ The high-temperature peaks observed with Cr/TiO₂ could be due to a deeper reduction of chromium or reduction of the support.

Background IR Spectra of the Samples. The IR spectrum of the activated Cr/ZrO₂ sample contained several intense bands at 1040, 1020, 1014, 1005, 987, and 975 cm⁻¹ (Figure 3, spectrum a). Bands at 1020 cm⁻¹ (with a high-frequency shoulder), 1005, and 980 cm⁻¹ were recorded with the Cr/TiO₂ sample (Figure 3, spectrum c). Similar bands were observed with bulk chromia (1015, 995, and 980 cm⁻¹) and assigned to Crⁿ⁺=O ($n = 5$ or 6) stretching modes.^{1,10,27,28} Thus, the appearance of these bands on our samples evidences the existence of oxidized chromium sites on their surfaces. The slight difference between the bands observed on Cr/TiO₂ and bulk chromia is attributed to the effect of the support. Some complementary bands were observed with Cr/ZrO₂ suggesting existence of oxidized chromium species differing from those found with chromia. These bands were attributed to surface chromate species.⁵⁰

Some weak bands in the 2100–1950 cm⁻¹ region were also observed and assigned to the first overtones of the fundamental Cr=O bands (Figure 3, spectra a, c). Analysis of this region could be very helpful for two reasons: (i) the higher resolution of the bands and (ii) the absence of influence of the support self-absorbance. The higher intensity of the Crⁿ⁺=O bands and the respective overtones on the Cr/ZrO₂ sample, compared to Cr/TiO₂, are consistent with the XPS observation that the chromium species are more oxidized on zirconia.

One weak band at 3627 cm⁻¹ was observed with the activated Cr/ZrO₂ sample in the OH stretching region (Figure 3, spectrum a). This band has not been detected with the pure support which indicates that it characterizes Crⁿ⁺–OH species. No hydroxyl bands were detectable with the activated Cr/TiO₂ sample, (Figure 3, spectrum c), which suggests that during the impregnation chromium-containing species have replaced the OH groups typical of the supports. This is consistent with the fact that the OH groups on zirconia and titania possess a basic rather than acidic character.^{41,45}

Reduction of the samples results in disappearance of the bands because of Cr=O modes and those of the respective overtones (Figure 3, spectra b, d). In the OH region, new bands appear. With the Cr/ZrO₂ sample, their maxima are at 3774 and 3645 cm⁻¹ (Figure 3, spectrum b). Separate experiments showed that the OH bands of our pure zirconia support are observed at 3770

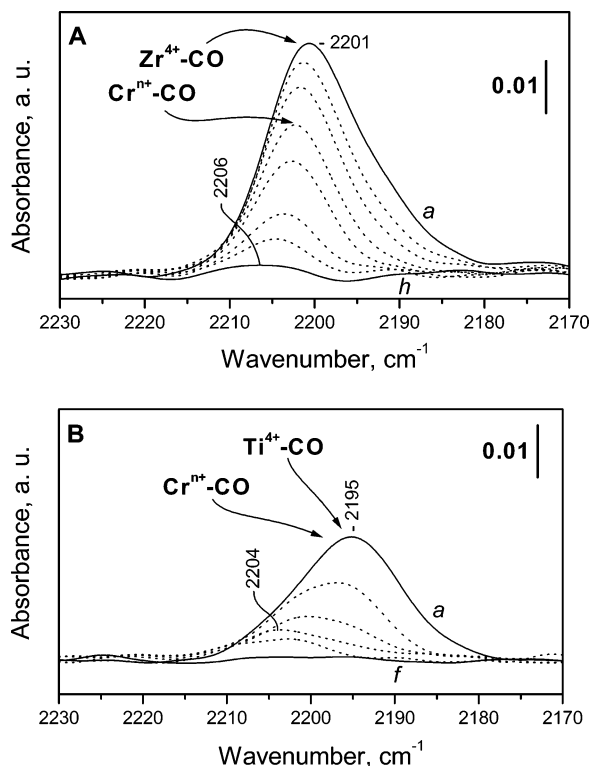


Figure 4. (A) FTIR spectra of CO adsorbed at room temperature on oxidized Cr/ZrO₂. Equilibrium pressure: 3 200 (a), 690 (b), 150 (c), 30 (d), and 7 Pa (e) and after short (f, g) and prolonged evacuation (h). (B) FTIR spectra of CO adsorbed at room temperature on oxidized Cr/TiO₂. Equilibrium pressure: 3 200 (a), 690 (b), 150 (c), 30 (d), and 7 Pa (e) and after evacuation (f).

and 3680 cm⁻¹. This suggests that the weak band at 3774 cm⁻¹ is due to Zr–OH species generated during the reduction. The other band is not typical of zirconia and is, therefore, attributed to Cr–OH species. The new OH bands on the reduced Cr/TiO₂ sample are located at 3724 and 3627 cm⁻¹ (Figure 3, spectrum d). The band at 3724 cm⁻¹ is typical of the support and is attributed to Ti–OH hydroxyls.⁴⁵ By analogy with the Cr/ZrO₂ sample, the band at 3627 cm⁻¹ is assigned to Cr–OH groups.

A subsequent oxidation/activation procedure resulted in oxidation of the samples, that is, restoration of their initial states.

Adsorption of CO on the Oxidized Samples at Room Temperature. Adsorption of CO (3200 Pa equilibrium pressure) on the activated (oxidized) Cr/ZrO₂ sample results in the appearance of one low-intensity band with a maximum at 2201 cm⁻¹ (Figure 4A, spectrum a). The band has a low-frequency shoulder. Decrease of the equilibrium pressure and evacuation lead to a gradual intensity decrease of the 2201 cm⁻¹ band and a blue shift of its maximum to 2206 cm⁻¹ (Figure 4A, spectra b–h). The band was only removed after an extended period of evacuation.

The spectra obtained after CO adsorption on the activated Cr/TiO₂ sample were very similar (Figure 4B). The carbonyl band produced under a CO equilibrium pressure of 3200 Pa was less intense and located at 2195 cm⁻¹ (Figure 4B, spectrum a). It also decreased in intensity with decreasing equilibrium pressure and disappeared after a prolonged evacuation (Figure 4B, spectra b–f).

As already discussed above, the band at 2206–2195 cm⁻¹ may be assigned to both Crⁿ⁺–CO and M⁴⁺–CO (M = Ti, Zr) species. The somewhat higher resistance of the band toward evacuation, as compared to the cases of the pure supports,

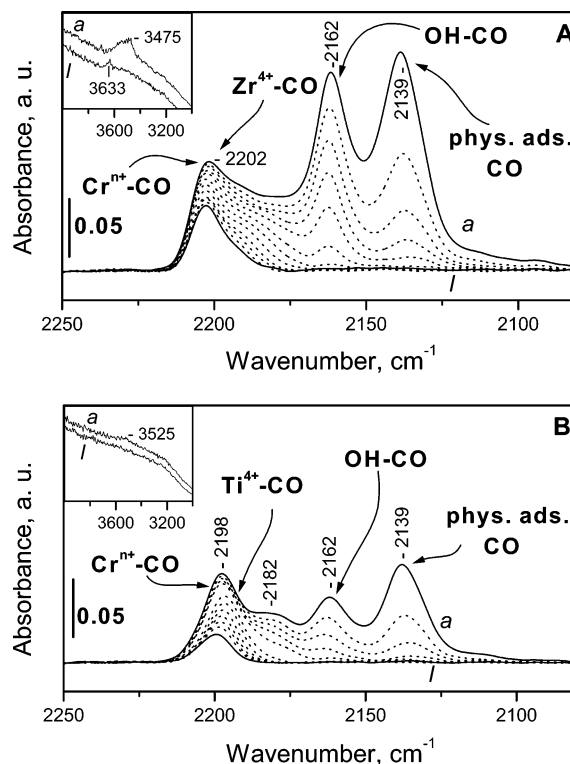


Figure 5. (A) FTIR spectra of CO adsorbed at 85 K on oxidized Cr/ZrO₂. Equilibrium pressure: 100 (a), 25 (b), 6 (c), and 2 Pa (d) and after short (e, f) and prolonged evacuation (g–i). (B) FTIR spectra of CO adsorbed at 85 K on oxidized Cr/TiO₂. Equilibrium pressure: 100 (a), 25 (b), 6 (c), and 2 Pa (d) and after short (e) and prolonged evacuation (f–i).

suggests that it is partly due to some chromium carbonyls. However, no detailed analysis is possible.

Adsorption of CO on the Oxidized Samples at Low Temperature. To detect all cationic sites, we have investigated the adsorption of CO at low temperature. Introduction of CO (100 Pa equilibrium pressure) at 85 K to the Cr/ZrO₂ sample results in the appearance of three principal bands with maxima at 2202, 2162, and 2139 cm⁻¹ (Figure 5A, spectrum a). Some features (ca. 2190 and 2180 cm⁻¹) can also be seen between the bands at 2202 and 2162 cm⁻¹. In addition, the weak OH band at 3633 cm⁻¹ disappears and a new, broader, and much more intense band centered at 3475 cm⁻¹ emerges instead (see inset in Figure 5A). Decrease of the equilibrium CO pressure and evacuation lead to a fast intensity drop of the 2139 cm⁻¹ band, followed by the band at 2162 cm⁻¹ (Figure 5A, spectra b–i). Then, the features around 2190 and 2180 cm⁻¹ also disappear and the band at 2202 cm⁻¹ (with a low-frequency shoulder) is the only one that resists evacuation at 85 K. The spectrum in the OH region is restored.

The band at 2139 cm⁻¹ is unambiguously assigned to physically adsorbed CO.² The band at 2162 cm⁻¹ changes in concert with the red shift of the Cr–OH band at 3633 cm⁻¹. Therefore, it is attributed to CO H-bonded to Cr–OH type surface hydroxyl groups. Indeed, the red shift of 160 cm⁻¹ is too high for Zr⁴⁺–OH hydroxyls and is similar to that found with oxidized chromia.²⁷ The band at 2202 cm⁻¹ has been observed at ambient temperature and we have already speculated (vide supra) that it arises from both Zr⁴⁺–CO and (a small amount of) Crⁿ⁺–CO species.

Adsorption of CO (100 Pa equilibrium pressure) at 85 K on the activated Cr/TiO₂ sample leads again to the formation of three principal CO bands at 2198, 2162, and 2139 cm⁻¹ (Figure

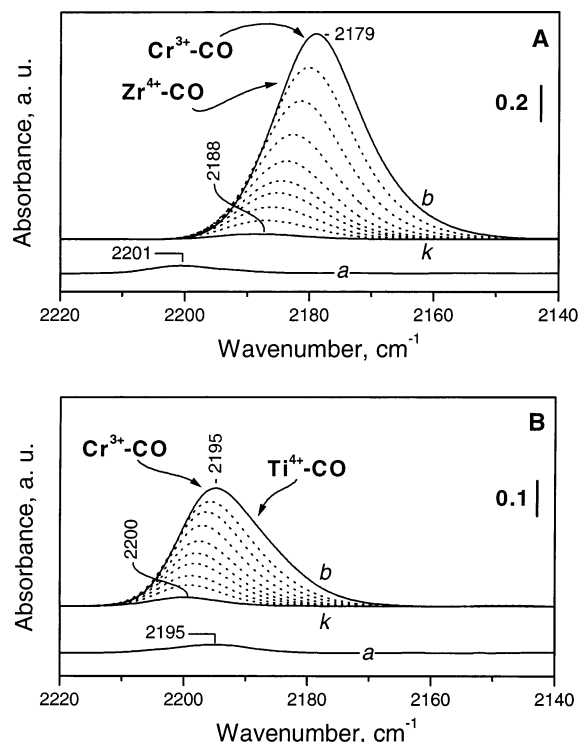


Figure 6. (A) FTIR spectra of CO adsorbed at room temperature on oxidized (a) and reduced Cr/ZrO₂ sample (b–k). Equilibrium pressure: 3 200 (a, b), 690 (c), 150 (d), 30 (e), 7 (f), 1 (g), and 0.3 Pa (h) and after short (i) and prolonged evacuation (j, k). (B) FTIR spectra of CO adsorbed at room temperature on oxidized (a) and reduced Cr/TiO₂ sample (b–k). Equilibrium pressure: 3 200 (a, b), 690 (c), 150 (d), 30 (e), 7 (f), and 1 (g) and after short (h) and prolonged evacuation (i–k).

5B, spectrum a). The band at 2139 cm⁻¹ arises from physically adsorbed CO. The band at 2162 cm⁻¹ is definitely less intense than is the case of Cr/ZrO₂. A broad OH band at 3525 cm⁻¹ has also been detected. Again, the 2162 cm⁻¹ band can be assigned to CrOH–CO species. Evidently, the intensity of the original Cr–OH band is too low to be detected. The band at 2198 cm⁻¹, that is most resistant toward evacuation, has a well discernible lower frequency shoulder at 2182 cm⁻¹. As above, the bands in the 2200–2180 cm⁻¹ region are assigned to Crⁿ⁺–CO or Ti⁴⁺–CO species.

A significant part of the carbonyl band in the 2200–2180 cm⁻¹ region is easily removed by evacuation, which suggests that it is due to Ti⁴⁺–CO species. This indicates a more pronounced exposure of a bare support surface as compared to the Cr/ZrO₂ sample.

Adsorption of CO on the Reduced Samples at Room Temperature. Introduction of CO (3 200 Pa equilibrium pressure) at room temperature to the reduced Cr/ZrO₂ sample leads to the appearance of one band at 2179 cm⁻¹ (Figure 6A, spectrum b). This band is much more intense (ca. 24 times) than the carbonyl band observed for the nonreduced sample (Figure 6A, spectrum a). This implies that the band is mainly due to carbonyls of reduced chromium sites. Decrease of the CO pressure leads to a gradual decrease in band intensity and a gradual shift of the band maximum to 2185 cm⁻¹ (Figure 6A, spectra c–h). The band strongly decreases in intensity after a prolonged evacuation and its maximum at low coverage is settled at 2188 cm⁻¹ (Figure 6A, spectrum k). Two very weak bands at 2132 and 2082 cm⁻¹ (not shown) are also observed and, according to literature data,¹¹ assigned to carbonyls of Cr²⁺ cations.

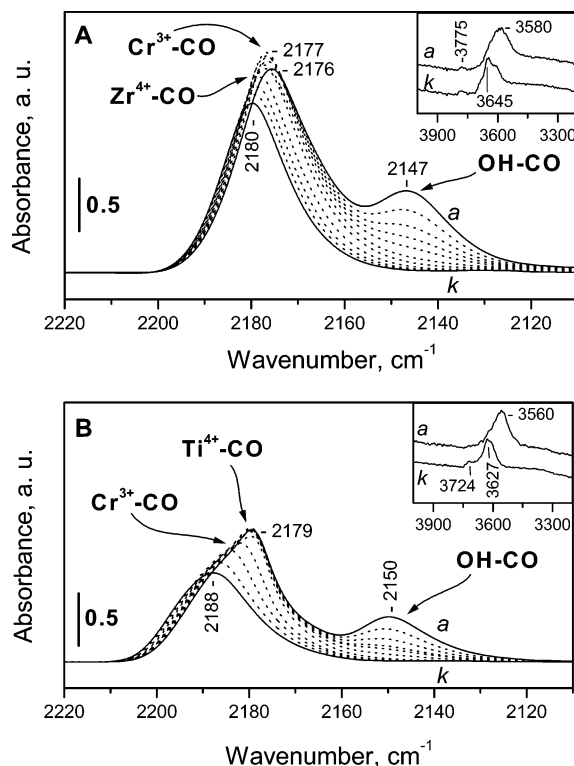


Figure 7. (A) FTIR spectra of CO adsorbed at 85 K on reduced Cr/ZrO₂. Equilibrium pressure: 400 (a), 100 (b), 25 (c), and 6 Pa (d) and after short (e, f) and prolonged evacuation (g–k). (B) FTIR spectra of CO adsorbed at 85 K on reduced Cr/TiO₂. Equilibrium pressure: 400 (a), 100 (b), 25 (c), 6 (d), and 2 Pa (e) and after short (f) and prolonged evacuation (g–k).

Adsorption of CO (3 200 Pa equilibrium pressure) on the reduced Cr/TiO₂ sample leads to the formation of an intense band at 2195 cm⁻¹ (Figure 6B, spectrum b). In this case, again the band is assigned mainly to chromium carbonyls since it is much more intense than the band detected with the nonreduced sample (Figure 6B, spectrum a). Note, however, that the increase of the band intensity after reduction (ca. 15 times) is not so pronounced as in the Cr/ZrO₂ sample. This is consistent with the XPS results showing a more reduced state of the chromium species when supported on titania.

Another effect of CO adsorption on Cr/TiO₂ at room temperature is the appearance of a set of bands at 1608, 1423, 1352, 1322, and 1223 cm⁻¹ (not shown). The bands at 1608, 1423, and 1223 cm⁻¹ are assigned to hydrogen carbonates.⁵⁴ The bands at 1352 and 1322 cm⁻¹ are due to formates or monodentate carbonates, the higher frequency component being masked by the strong band at 1608 cm⁻¹.⁵⁴ It thus appears that CO reacts more easily with a reduced Cr/TiO₂ sample. A similar phenomenon, observed with bulk chromia,^{1,10,27} has not found an adequate explanation. Note, however, that no such reduction was found with the Cr/ZrO₂ sample.

Adsorption of CO on the Reduced Samples at Low Temperature. When CO (400 Pa equilibrium pressure) was admitted at 85 K to the reduced Cr/ZrO₂ sample, two bands were recorded in the carbonyl region, their maxima being located at 2176 and 2147 cm⁻¹ (Figure 7A, spectrum a). Simultaneously, in the hydroxyl region the 3645 cm⁻¹ band disappeared and a new band at 3580 cm⁻¹ emerged (see the inset in Figure 7A). This small shift of 65 cm⁻¹ suggests a very weak acidity of the OH groups. Hence, the CO band in this case should be observed below 2162 cm⁻¹ (the OH–CO band recorded with the oxidized sample). The only candidate in this respect can be the band at

2147 cm^{-1} . This assignment is supported by the results on the Cr/TiO₂ sample (see below). A weak component of the 2147 cm^{-1} band (around 2143 cm^{-1}) should be due to physically adsorbed CO.

To the best of our knowledge, the lowest carbonyl frequency proved for OH–CO surface species is at 2148 cm^{-1} and has been found with ZnO.⁵⁵ The H-bonded CO on ZrO₂ is detected at 2158 cm^{-1} .⁴⁰ All this confirms that the OH groups in the present case are of Cr–OH type. The acidity of the hydroxyls decreases with the polarizing power of the metal cation to which they are bonded. Hence, the weak acidity of the OH groups on our reduced samples indicates a low oxidation state of chromium, which is consistent with the sample pretreatment.

The decrease of the CO equilibrium pressure leads to a decrease of the 2147 cm^{-1} band intensity. The band at 2176 cm^{-1} is slightly blue shifted and, interestingly, slightly increased in intensity (Figure 7A, spectra b, c). There are two possibilities to explain this phenomenon. First, it is possible that at high CO pressures partial conversion of chromium mono- to dicarbonyls might occur. The latter species should be characterized by symmetric vibrations below 2177 cm^{-1} and a more intense antisymmetric mode coinciding with the OH–CO band at 2147 cm^{-1} . However, we prefer the second possibility, that is, initially CO is not statistically distributed on the sample surface but a layer at the external macroscopic surface of the pellet is saturated. This explains the somewhat lower frequency of the carbonyl band in the first spectrum: although the total coverage is lower, the density of the CO molecules on the occupied surface is higher, which is reflected in a more pronounced static shift. Evacuation at 85 K only results in a decrease in intensity of the band at 2177 cm^{-1} and a slight blue shift of its maximum position. These changes are analogous to those observed at ambient temperature. Also, the maximum intensity of the band around 2180 cm^{-1} is almost the same at ambient and at low temperature which implies a relatively strong adsorption.

Adsorption of CO (400 Pa equilibrium pressure) was performed at 85 K on the reduced Cr/TiO₂ sample and two principal IR bands, at 2179 and 2150 cm^{-1} , were recorded in the carbonyl region (Figure 7B, spectrum a). The former band had a pronounced high-frequency shoulder. In the OH region, the band at 3627 cm^{-1} disappeared and a new band at 3560 cm^{-1} emerged instead. The band at 3724 cm^{-1} decreased in intensity.

A decrease of the CO pressure and evacuation cause the disappearance of the bands at 2179 and 2150 cm^{-1} and a more symmetric band at 2188 cm^{-1} remains in the spectrum (Figure 7B, spectra b–k).

The band at 2150 cm^{-1} is assigned to CO H-bonded to Cr–OH groups. Indeed, the disappearance of the band is accompanied by gradual restoration of the initial spectrum in the hydroxyl stretching region. The band at 2179 cm^{-1} is typical of the support and is assigned to CO attached to Ti⁴⁺ sites. The band at 2188 cm^{-1} is assigned to carbonyls of chromium and Ti⁴⁺ cations.

Adsorption of NO on Oxidized Samples. Adsorption of NO (1 000 Pa equilibrium pressure) on the oxidized Cr/ZrO₂ sample results in the appearance of a strong band at 1932 cm^{-1} with a broad high-frequency shoulder (Figure 8A, spectrum a). In the lower-frequency region, three bands, at 1560, 1206, and 1139 cm^{-1} , also emerge. In addition, weak bands at 1621 and 1275 cm^{-1} are visible. The intensities of the bands at 1560 and 1206 cm^{-1} rise synchronously with time, whereas with the band at 1621 cm^{-1} this growth is faster (Figure 8A, spectrum b). A decrease of the NO pressure results in a gradual decrease in intensity and disappearance of the bands at 1932, 1275, and

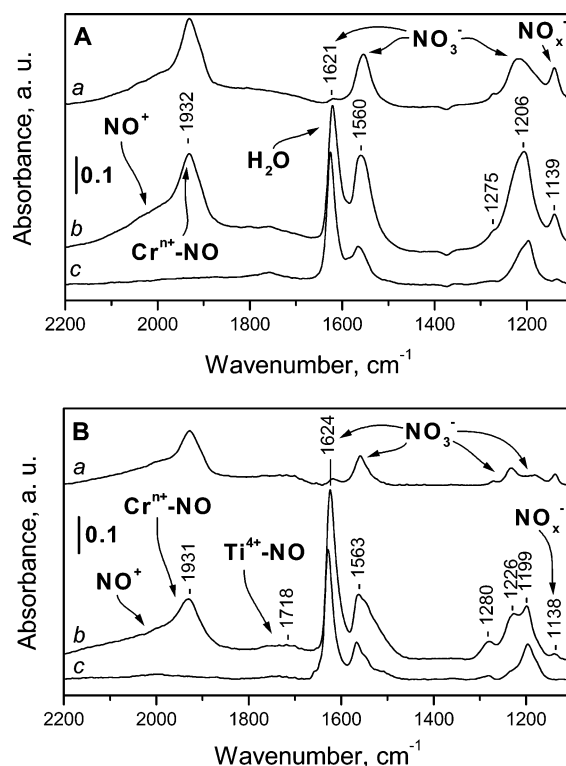


Figure 8. FTIR spectra of NO adsorbed on oxidized Cr/ZrO₂ (A) and Cr/TiO₂ (B). Equilibrium NO pressure of 1000 Pa (a), after time (b), and evacuation (c).

1139 cm^{-1} . The bands at 1560 and 1206 cm^{-1} also decrease in intensity, the latter being red shifted. The band at 1621 cm^{-1} remains almost unaffected. After evacuation, only the bands at 1621, 1560, and 1206 cm^{-1} remain in the spectrum (Figure 8A, spectrum c).

The broad high-frequency shoulder of the band at 1932 cm^{-1} can be assigned to NO⁺ species.³ Similar bands have already been detected after NO adsorption on various oxide surfaces.^{32,56} The band at 1932 cm^{-1} is typical of N–O stretching modes of mononitrosyl species. These could be nitrosyls of chromium cations or Zr⁴⁺–NO species affected by closely located nitrogen-oxo anions.^{48,49} Indeed, analysis of the spectra indicates that this band changes in synchrony with the band at 1139 cm^{-1} . The latter can be assigned to NO₂⁻ or NO⁻ entities.³ The set of bands at 1560 and 1206 cm^{-1} are assigned to surface nitrates, while the band at 1621 cm^{-1} is probably at least partly due to water evolved during the formation of nitrates. Indeed, a broad band centered at 3275 cm^{-1} , characterizing H-bonded hydroxyls, develops in parallel. However, most probably some nitrates also contribute to the band at 1621 cm^{-1} . It changes irrespective of the other bands, because there are different routes for production of nitrates and some of the water formed could dissociate on the surface. Finally, the band at 1275 cm^{-1} may characterize small amounts of adsorbed N₂O₃. The fact that some of the nitrates disappear after evacuation could be explained by their interaction with NO⁺ resulting in formation of NO₂.⁵⁷ Most probably some of the nitrates undergo a similar interaction with the 1138 cm^{-1} band species.

A careful inspection of the spectrum observed after evacuation shows the existence of two weak bands at 1882 and 1762 cm^{-1} which are assigned to chromium dinitrosyl species.³

The spectra obtained after NO adsorption on the Cr/TiO₂ sample are similar (Figure 8B). A nitrosyl band at 1931 cm^{-1} is recorded. This indicates that the band is rather due to nitrosyls of chromium cations. The other bands are slightly shifted. In

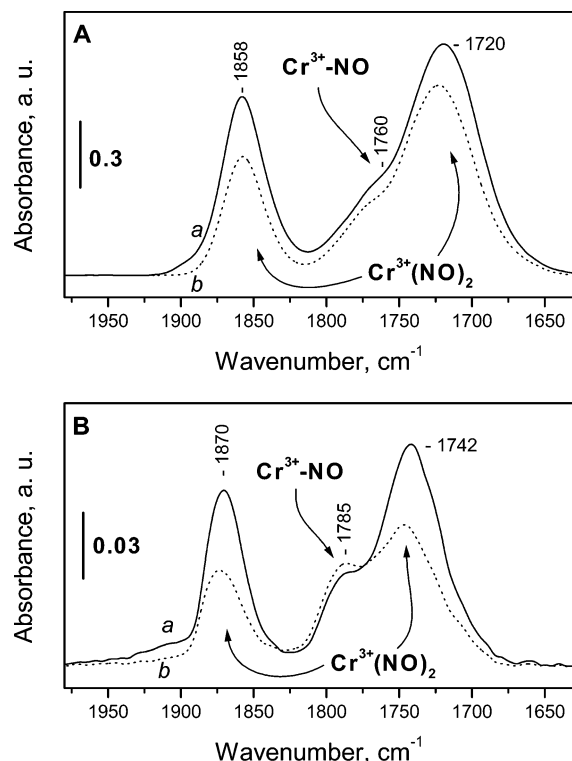


Figure 9. FTIR spectra of NO adsorbed on reduced Cr/ZrO₂ (A) and Cr/TiO₂ (B). Equilibrium NO pressure of 1000 Pa (a) and after evacuation (b).

particular, a band at 1280 cm⁻¹ is assigned to nitrates formed on bare titania⁴⁷ which is consistent with the results on the more pronounced exposure of the support surface with this sample. A weak band at 1718 cm⁻¹ is due to nitrosyls formed on the support.⁴⁷ As with the Cr/ZrO₂ sample, evacuation leads to disappearance of the nitrosyl and NO⁺ bands and decrease in intensity of the nitrate bands. Here again, the 1931 cm⁻¹ band changes in concert with the band at 1139 cm⁻¹.

Adsorption of NO on Reduced Samples. Introduction of NO (1000 Pa equilibrium pressure) onto the reduced Cr/ZrO₂ sample results in the appearance of two principal bands with maxima at 1858 and 1720 cm⁻¹ (Figure 9A, spectrum a). A shoulder of the latter band is visible at 1760 cm⁻¹. A band at 1190 cm⁻¹ (not shown) also emerges. The two principal nitrosyl bands slightly increase in intensity with time. Evacuation leads to the reverse effect, that is, these bands slightly decrease in intensity (Figure 9A, spectrum b). The band at 1760 cm⁻¹ also decreases but to a smaller extent.

The bands at 1858 and 1720 cm⁻¹ are assigned to the symmetric and antisymmetric modes, respectively, of dinitrosyl species of Cr²⁺(NO)₂ or Cr³⁺(NO)₂ type.^{8,9,17,21–26} The band at 1760 cm⁻¹ is most probably due to mononitrosyls.^{8,9} The band at 1190 cm⁻¹, found after NO adsorption on pure zirconia, has been assigned to NO⁻ species.⁴⁹

When NO was adsorbed on the reduced Cr/TiO₂ sample, mono and dinitrosyl species were produced again; however, all bands were observed at higher frequencies (Figure 9B, spectrum a). The mononitrosyls were characterized by an IR band at 1785 cm⁻¹. The two bands due to dinitrosyls were recorded at 1870 and 1742 cm⁻¹. A weak band at 1910 cm⁻¹ was seen in the presence of NO only. The bands due to dinitrosyls slightly decreased in intensity after evacuation while the mononitrosyl band even gained some intensity (Figure 9B, spectrum b).

Coadsorption of CO and NO on the Oxidized Samples. At first, CO (3200 Pa equilibrium pressure) was adsorbed on

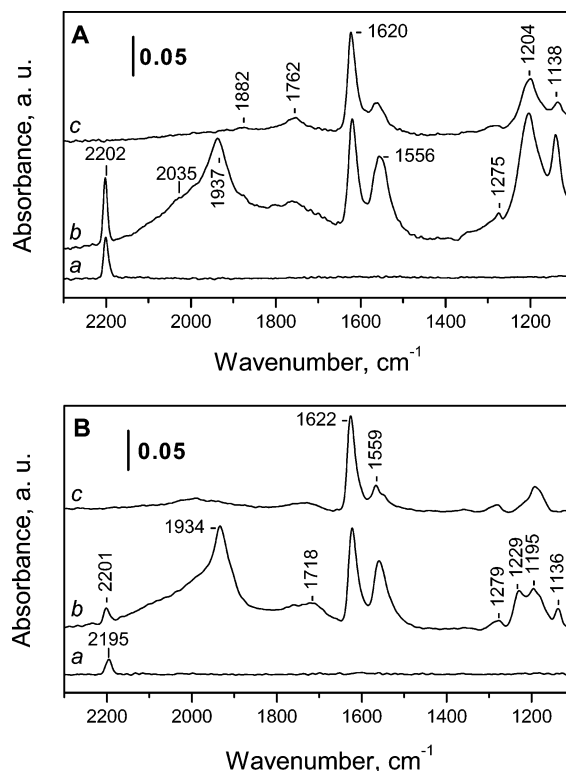


Figure 10. FTIR spectra of CO and NO coadsorbed on oxidized Cr/ZrO₂ (A) and Cr/TiO₂ (B). Adsorption of CO (3200 Pa equilibrium pressure) (a), admission of 450 Pa NO (b), and after evacuation (c).

the oxidized Cr/ZrO₂ sample and a carbonyl band at 2202 cm⁻¹ was registered (Figure 10A, spectrum a). Then, NO (450 Pa) was added to the system. The same bands as those observed after NO adsorption were produced (Figure 10A, spectra b, c). The carbonyl band even slightly increased in intensity and then started to decrease. This effect was attributed to initial compression of CO and increase of its partial pressure around the sample. However, liberation of some Zr⁴⁺ sites after formation of chromium nitrates cannot be excluded. Evacuation leads to a fast disappearance of the carbonyl band (indicating that it is due exclusively to Zr⁴⁺-CO species) and of the bands around 1940 cm⁻¹. Two weak bands due to dinitrosyl species (1882 and 1762 cm⁻¹) remain in the spectrum. The other changes are similar to those already described for NO adsorption experiments.

Carbon monoxide (3200 Pa equilibrium pressure) was adsorbed on the activated Cr/TiO₂ sample and a carbonyl band at 2195 cm⁻¹ was produced (Figure 10B). Then, NO (450 Pa) was introduced into the system. The changes were similar to those observed after NO adsorption on the oxidized sample (see Figure 8B); however, the bands due to nitrates were less intense. The carbonyl band slightly decreased in intensity and was shifted to 2201 cm⁻¹.

Coadsorption of CO and NO on the Reduced Samples. When CO (3200 Pa equilibrium pressure) was adsorbed on the reduced Cr/ZrO₂ sample, a carbonyl band at 2179 cm⁻¹ was detected (Figure 11A, spectrum a). Introduction of NO to the system led to a decline of the carbonyl band and development of bands due to dinitrosyl (1863 and 1718 cm⁻¹) and mononitrosyl (1754 cm⁻¹). In addition, bands at 1619, 1560, 1432, 1317, and 1223 cm⁻¹ (the latter with a pronounced low-frequency shoulder) appeared when the amount of NO was increased. The bands at 1560 and 1206 cm⁻¹ (the latter observed as a shoulder) were already assigned to nitrate species. The set of bands at 1619, 1432, and 1223 cm⁻¹ are most probably due

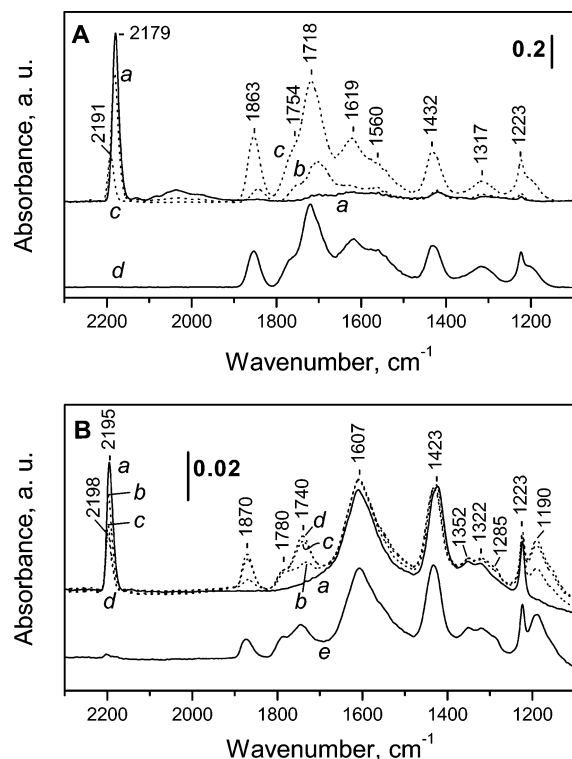


Figure 11. FTIR spectra of CO and NO coadsorbed on reduced Cr/ZrO₂ (A) and Cr/TiO₂ (B). (A) Adsorption of CO (3 200 Pa equilibrium pressure) (a), admission of 450 (b) and 1400 Pa NO (c), and after evacuation (d). (B) Adsorption of CO (3 200 Pa equilibrium pressure) (a), admission of 450 (b, c) and 1050 Pa NO (d), and after evacuation (e).

to hydrogen carbonates and the band at 1317 cm⁻¹ was assigned to nitrospecies formed on the support.⁴⁸ These results imply that CO is replaced by NO on the reduced chromium sites.

A carbonyl band at 2195 cm⁻¹ was recorded when CO (3200 Pa equilibrium pressure) was adsorbed on the reduced Cr/TiO₂ sample (Figure 11B). In addition, bands due to bicarbonates (1607, 1423, and 1223 cm⁻¹) and carbonates (1352 and 1322 cm⁻¹) appeared. Then, NO was added to the system. As a result, the carbonyl band gradually decreased in intensity and was slightly blue shifted, and bands due to (di)nitrosyl species developed at its expense. Bands at 1285 and 1190 cm⁻¹ also developed. Here again, the results show that NO replaces CO from the reduced chromium sites.

Discussion

Oxidized Samples. Activation of the samples in vacuo is not sufficient to reduce the chromia phase supported on ZrO₂ or TiO₂. The major part of the chromium ions in both samples are encountered as Cr⁶⁺. However, both samples contain a considerable amount of Cr³⁺ cations. The results of IR spectroscopy of probe molecules show that these Cr³⁺ cations are (in general) not surface located. Only a negligible fraction of the chromium species are reduced to Cr³⁺ after activation of the samples. This was proved in the NO and CO adsorption experiments.

The results obtained can be rationalized assuming the existence of Cr₂O₃ clusters containing Cr³⁺ in the bulk and Cr⁶⁺ on the surface. This is not surprising because a similar situation is reported with α -chromia.^{6,10,13,27–29} Comparison of the results obtained by different techniques allows us to conclude that part of the chromium species are well dispersed on zirconia as surface chromates and the other part are included in relatively

big Cr₂O₃ clusters. On the contrary, the Cr₂O₃ clusters on titania are smaller but the fraction of well-dispersed chromium species is more restricted. Indeed, the spectra presented in Figure 3 show that the Cr=O stretching bands, recorded with the Cr/TiO₂ sample, are less intense and are more similar to the bands observed with Cr₂O₃ than is the case of the Cr/ZrO₂ sample. This model also explains the higher Cr:Ti ratio calculated on the basis of the XP spectra. The small Cr₂O₃ clusters on titania screen the Ti⁴⁺ cation while this screening is restricted with both highly dispersed chromium ions and relatively big chromia clusters.

A small amount of Cr⁵⁺ species were also detected by EPR. Comparison with the IR results indicates that, in this case again, these cations are not surface situated. This inference is supported by the absence of Lewis acidity that could be related to the existence of Cr⁵⁺ cations.

Generally, no Brønsted acidity is typical of oxidized Cr/ZrO₂ and Cr/TiO₂ samples. However, a small fraction of Crⁿ⁺–OH groups were detected on Cr/ZrO₂. The acid strength of these groups, as measured by the shift of their stretching modes after low temperature CO adsorption (160 cm⁻¹), was relatively high. The most acidic surface OH groups presently known are the bridged hydroxyls in some zeolites, such as H-ZSM-5. In these cases, the shift of the OH stretching modes can exceed 300 cm⁻¹.^{1,2} However, the acid strength of the hydroxyls on different oxides is definitely lower. Thus, the shift of the Si–OH groups is typically 90 cm⁻¹.^{1,2} The various OH groups on alumina are characterized by different acidities,⁵⁸ and the most acidic of them (bands at 3735–3670 cm⁻¹) are red shifted, after CO adsorption, by 90–145 cm⁻¹.^{58,59} These considerations confirm a strong acidity of the Cr–OH groups and imply that the respective chromium cations are in a high oxidation state.

It is not possible to draw any conclusions about the extinction coefficient of the OH groups on the basis of their stretching frequency. Many data in the literature suggest a small extinction coefficient of the hydroxyls on oxidized chromia. Thus, these groups have not been detected in the IR spectra but their existence has been unambiguously proven by adsorption of ammonia and formation of NH₄⁺.²⁹ However, the concentration of these groups can be roughly estimated by the intensity of the band because of CO H-bonded to them. Indeed, the extinction coefficient of CO is almost independent of the stretching frequency when no π -back-bond is formed.² In fact, the low extinction coefficient of the Cr–OH groups was the most probable reason for the failure to detect any hydroxyls on the Cr/TiO₂ sample. Evidently, their intensities were within the noise level. However, after low-temperature CO adsorption, these groups were monitored. In addition, the H-bonding enhanced the extinction coefficient of the hydroxyls and, as a result, the bands of the perturbed Cr–OH groups were found on both Cr/ZrO₂ and Cr/TiO₂ samples.

Reduced Samples. Reduction of the samples resulted in disappearance of all Cr=O modes and the respective overtones. This proved that the reduction was complete. In principle, reduction could lead to creation of Cr²⁺ and Cr³⁺ sites. We exclude formation of Cr²⁺ on our samples for several reasons:

(1) It is generally accepted that reduction of supported chromium species with hydrogen leads to formation of Cr³⁺ cations.⁵²

(2) The carbonyls produced with participation of Cr²⁺ cations are characterized by frequencies lower than those we have observed. In particular, this has been reported for Cr²⁺–CO species detected on deeply reduced Cr/ZrO₂.⁹

(3) The dinitrosyls of Cr^{2+} are also expected at lower frequencies.³

(4) Similar carbonyl bands have been observed by Trunschke et al.¹¹ Independent XPS measurements have shown the oxidation state of chromium on their samples to be 3+.

In line with the above discussion, we can speculate that the TPR peaks around 670 K observed with both samples are due to formation of Cr^{3+} species probably created during reduction of some oxidized chromium cations from the catalyst bulk.

Inspection of the carbonyl spectra recorded with the reduced Cr/ZrO_2 and Cr/TiO_2 samples reveals that the support also affects the state of the supported chromia after reduction. The CO band observed at room temperature on reduced Cr/TiO_2 is similar to the bands recorded with bulk chromia. However, the carbonyl band on Cr/ZrO_2 is found at lower frequencies, which is evidently due to the influence of the support. These results are consistent with the above conclusion that chromia on titania is present as small Cr_2O_3 clusters whereas on zirconia the major part of chromium species are highly dispersed (probably forming a monolayer), the other part forming relatively big Cr_2O_3 clusters.

Analysis of summarized literature data^{2,3} shows that there is no correlation between the strengths of CO and NO adsorption when bonded to different cations. Many authors report that NO is not adsorbed at ambient temperature on cations with a d^0 configuration.³ However, when the positive charge is great enough (as is the case of Ti^{4+} and Zr^{4+} cations), CO is adsorbed on them, although not very strongly. In contrast, NO forms stable dinitrosyls with some cations, for example, V^{4+} and V^{3+} , but CO is adsorbed on them very weakly, often at low temperatures only.² Turning to our present results, it is evident that NO is more strongly adsorbed on the Cr^{3+} cations than is CO, while CO is adsorbed on Cr^{3+} , Ti^{4+} , and Zr^{4+} sites and the carbonyls have a similar stability and are observed in the same spectral region. Thus, it appears that CO is not appropriate for detecting reduced chromium sites on Cr/TiO_2 and Cr/ZrO_2 samples. The same situation is expected with other chromium-containing systems, for example, $\text{Cr/Al}_2\text{O}_3$. However, the Cr^{3+} sites (the same should also be valid for Cr^{2+}) can easily be detected using NO as a probe. In this case, the formation of nitrates as a result of NO oxidation by Cr^{6+} sites could complicate the spectra and hinder the adequate conclusions. However, the process is strongly suppressed with the reduced samples, which makes NO suitable for probing reduced surfaces. Co-adsorption of CO and NO could be used for simultaneous and selective detection of Cr^{3+} and M^{4+} ($\text{M} = \text{Ti, Zr}$) cations on the surface.

Conclusions

(1) Cr/ZrO_2 and Cr/TiO_2 samples activated in vacuo are characterized by a small amount of Lewis acid sites which are mainly due to the exposure of bare support surfaces. A negligible fraction of strong Brønsted acid centers is also found.

(2) Part of the chromium species on zirconia are highly dispersed as surface chromates and the rest form relatively big Cr_2O_3 clusters. Chromia on titania forms small Cr_2O_3 clusters. In both cases, the surface-situated cations are Cr^{6+} , whereas the Cr^{3+} cations are in the bulk of the clusters.

(3) Treatment with hydrogen at 573 K leads to reduction of chromium to Cr^{3+} . These cations form carbonyl complexes and more stable dinitrosyl species. Consequently, NO replaces preadsorbed CO. Reduction also creates Cr^{3+}OH groups which are characterized by a very low acid strength.

(4) CO is not an appropriate probe for selective detection of Cr^{3+} and M^{4+} ($\text{M} = \text{Ti, Zr}$) sites on Cr/ZrO_2 and Cr/TiO_2 samples. NO can be used for detection of Cr^{3+} , while Cr^{3+} and M^{4+} ($\text{M} = \text{Ti, Zr}$) can be simultaneously and selectively monitored by co-adsorption of CO and NO.

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