

# Chromium nitrosyl complexes in Cr-ZSM-5: An FTIR spectroscopic study

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## Abstract

The species formed after adsorption of NO on a Cr-ZSM-5 sample pre-subjected to different red-ox treatments have been studied by FTIR spectroscopy. Only NO<sup>+</sup>, occupying cationic positions in the zeolite, is formed on a non-reduced sample. Adsorption of NO on samples reduced by hydrogen at temperatures between 473 and 773 K leads mainly to formation of different mononitrosyl (1890 and 1815 cm<sup>-1</sup>) and dinitrosyl species (1910 + 1780 cm<sup>-1</sup>). The latter are decomposed without producing a measurable fraction of the corresponding mononitrosyls. The dinitrosyl complexes are likely produced with the participation of Cr<sup>3+</sup> cations. Some Cr<sup>2+</sup> sites are created after reduction of the sample with hydrogen at 873 K or with CO at 773 K. These sites form another kind of dinitrosyl species (bands at 1902 and 1768 cm<sup>-1</sup>) which are converted during evacuation to mononitrosyls (band at 1782 cm<sup>-1</sup>). The assignments of the different bands are supported by <sup>14</sup>NO–<sup>15</sup>NO co-adsorption experiments. © 2006 Elsevier B.V. All rights reserved.

**Keywords:** Adsorption; FTIR spectroscopy; Nitrogen monoxide; <sup>15</sup>NO; Cr-ZSM-5

## 1. Introduction

Chromium-containing catalysts are widely used in industry, e.g. the famous Phillips catalysts (Cr/SiO<sub>2</sub>) are applied to the polymerization of ethylene at relatively low pressures to produce high-density polyethylene (HDPE) [1,2]. Other important reactions with chromium-based catalysts are hydrogenation–dehydrogenation (e.g. production of debutadiene from *n*-butane, methanol synthesis, WGS reaction), oxidation, isomerization, aromatization and selective catalytic reduction (SCR) of nitrogen oxides with hydrocarbons [1,2]. In particular Cr-ZSM-5 has been reported to be a promising catalyst for SCR with hydrocarbons [3], dehydrogenation of propane to propylene [4], oxidative dehydrogenation of ethane to ethylene with CO<sub>2</sub> [5], selective photocatalytic partial oxidation of propane to acetone [6], toluene disproportionation [7], neutralization of VOCs [8,9] and chlorinated VOCs [10,11], etc.

One of the most informative techniques for characterization of catalytic surfaces is IR spectroscopy of probe molecules [12–14]. There are many IR studies devoted to the establish-

ment of the oxidation and coordination state of surface-situated chromium cations [15–25]. The most used IR probe molecule is CO [14]. However, many recent data show that CO is not appropriate for testing some cations, such as W<sup>n+</sup>, V<sup>n+</sup> and Cr<sup>n+</sup> [16,26–28]. In these cases NO gives more information. For instance, it has recently been shown that NO is a more sensitive probe than CO for testing Cr/TiO<sub>2</sub> and Cr/ZrO<sub>2</sub> samples [16]. The aim of this study is the detailed characterization of Cr-ZSM-5 subjected to different red-ox pre-treatments, by means of analysis of the IR spectra of adsorbed NO.

## 2. Experimental

The starting H-ZSM-5 material was supplied by Degussa and had a Si/Al ratio of 26.8. The Cr-ZSM-5 sample was prepared by the conventional ion exchange technique: H-ZSM-5 was suspended in excess of 0.05 M solution of Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, and the mixture was stirred for 24 h at room temperature. The procedure was repeated with 0.1 M solution of Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O. Then the precipitate was filtered, washed thoroughly with deionized water, dried at 383 K, and calcined for 1 h at 723 K.

The IR spectra were recorded on a Nicolet Avatar 360 apparatus at a spectral resolution of 2 cm<sup>-1</sup> accumulating 64–128 scans. Prior to the experiments, the sample powder was pressed

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to a self-supporting wafer (density  $12 \text{ mg cm}^{-2}$ ) under a pressure of  $10^6$  to  $10^7$  Pa. Both the pre-treatment and the experiments were performed in situ using a purpose-made IR cell connected to a vacuum-adsorption apparatus with a residual pressure lower than  $10^{-3}$  Pa. Before the experiments the sample was activated by successive 1 h thermooxidative ( $13.3 \text{ kPa O}_2$ ) and thermovacuum treatments, both at  $723 \text{ K}$ . Reduction was performed by heating the sample in hydrogen ( $13.3 \text{ kPa}$ ) or CO ( $13.3 \text{ kPa}$ ) atmosphere for 1 h, followed by evacuation at  $673 \text{ K}$  for 1 h (for the samples reduced at  $T > 673 \text{ K}$  the evacuation was performed at the reduction temperature). Nitrogen monoxide (99.0) was supplied by Aldrich Chemical Company Inc., while  $^{15}\text{NO}$  was purchased from ONIA and had an isotopic purity of 98.5 at. %.

### 3. Results and discussion

#### 3.1. Background spectrum of the sample

The IR spectrum of the activated sample is similar to the spectrum of the parent H-ZSM-5 material. There are three peaks at  $1998$ ,  $1876$  and  $1637 \text{ cm}^{-1}$  due to the overtones and harmonics of the skeletal vibrations [29]. In the OH stretching region there are three bands at  $3744$ ,  $3662$  and  $3610 \text{ cm}^{-1}$ . The band at  $3744 \text{ cm}^{-1}$  is due to silanol groups and the band at  $3610 \text{ cm}^{-1}$ , to the zeolite acidic hydroxyls [30]. The latter band is less intense than in the case of H-ZSM-5, which indicates that some of these hydroxyls have been exchanged by chromium cations. The band at  $3662 \text{ cm}^{-1}$  could be due to Cr–OH type hydroxyls or to small amounts of water adsorbed on the sample. No substantial changes of the background spectrum have been noticed after the reduction of the sample.

#### 3.2. Adsorption of NO on activated Cr-ZSM-5

Introduction of a small amount of NO to the activated sample hardly affects the spectrum. Only a low-intensity band at  $2138 \text{ cm}^{-1}$  and a weak negative feature at  $1787 \text{ cm}^{-1}$  are seen (Fig. 1, spectrum a). The increase in amount of the NO introduced to the IR cell up to  $530 \text{ Pa}$  equilibrium pressure results in the appearance of bands at  $2880$ ,  $2455$ ,  $2267$ ,  $2249$  and  $1636 \text{ cm}^{-1}$  and a strong increase in intensity of the band at  $2138 \text{ cm}^{-1}$  (Fig. 1, spectrum b). The two bands, at  $2267$  and  $2249 \text{ cm}^{-1}$ , are attributed to adsorbed  $\text{N}_2\text{O}$  [15]. The  $2138 \text{ cm}^{-1}$  band is assigned to  $\text{NO}^+$  occupying cationic positions in the zeolite. It is produced according to the reaction [30]:



Since  $\text{NO}^+$  is not formed after adsorption of pure NO on H-ZSM-5, the results suggest some oxidation of NO by the chromium in the sample. The band at  $1636 \text{ cm}^{-1}$  is due to  $\text{H}_2\text{O}$  bending modes, the water being evolved according to the reaction (1). The bands at  $2880$  and  $2455 \text{ cm}^{-1}$  arise from the A and B components of the ABC structure of  $\text{H}_2\text{O}$  bonded to the acidic hydroxyls [30]. The negative band at  $1787 \text{ cm}^{-1}$  coincides in position with a zeolite own band and is thus assigned to changes in the background spectrum. In particular, the results

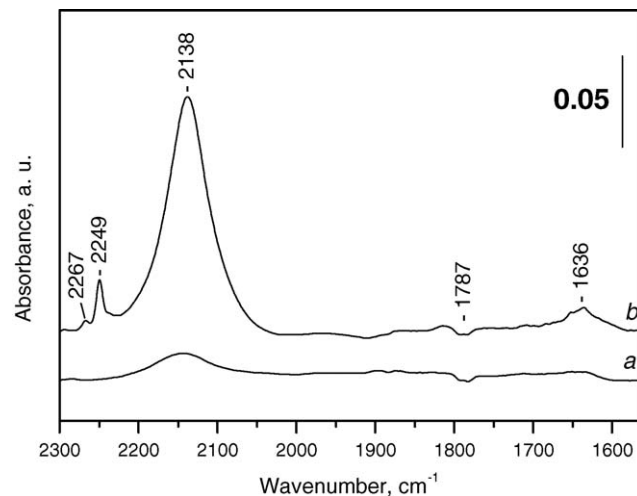


Fig. 1. FTIR spectra of NO adsorbed on a Cr-ZSM-5 sample activated at  $723 \text{ K}$ . Introduction of  $1.2 \mu\text{mol}$  NO (a) and equilibrium pressure of  $530 \text{ Pa}$  NO (b). The spectra are corrected with respect to the background and gaseous phase.

show that no nitrosyl species are formed on the activated sample. This suggests coordinative saturation and a high oxidation state of chromium, most probably  $6+$ . Evidently, the activation procedure has led to oxidation of the exchanged chromium cations. The fact that no nitrosyl bands are formed in parallel with the development of the  $\text{NO}^+$  band (associated with reduction of chromium cations) implies that the  $\text{Cr}^{5+}$  or/and  $\text{Cr}^{4+}$  species formed are not able to form dinitrosyl species.

#### 3.3. Adsorption of NO on a sample reduced with hydrogen at $473 \text{ K}$

Introduction of a small amount of NO to the  $473 \text{ K}$  reduced Cr-ZSM-5 sample leads to the appearance of three bands in the nitrosyl stretching region: at  $1911$ ,  $1891$  and  $1789 \text{ cm}^{-1}$  (Fig. 2, spectrum a). Two shoulders, at  $1769$  and  $1755 \text{ cm}^{-1}$ , are also visible. When NO equilibrium pressure is maintained,

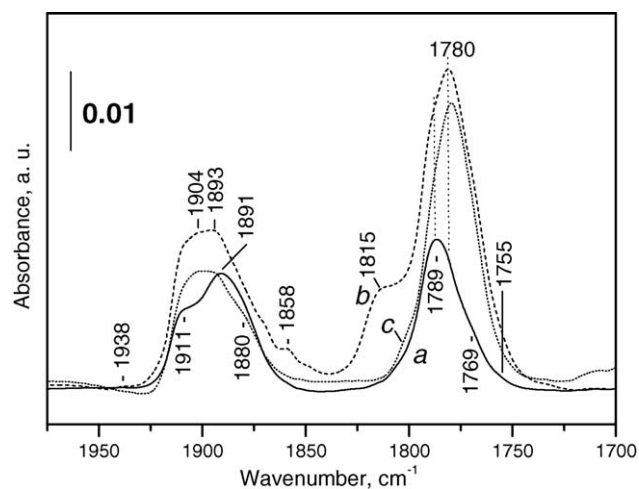


Fig. 2. FTIR spectra of NO adsorbed on a Cr-ZSM-5 sample reduced with hydrogen at  $473 \text{ K}$ . Introduction of  $1.2 \mu\text{mol}$  NO (a), equilibrium pressure of  $530 \text{ Pa}$  NO (b) and after evacuation (c). The spectra are corrected with respect to the background and gaseous phase.

Table 1  
Assignment of the bands observed after NO adsorption on Cr-ZSM-5

Band(s) (cm <sup>-1</sup> )	Assignment	Notes
1910 and 1782	$\nu_s$ and $\nu_{as}$ , respectively of Cr <sup>3+</sup> (NO) <sub>2</sub>	Dominant with samples reduced with H <sub>2</sub> at 473–773 K; resistant towards evacuation; <i>complex-specified</i> species
1902 and 1768	$\nu_s$ and $\nu_{as}$ , respectively of Cr <sup>2+</sup> (NO) <sub>2</sub>	Dominant with samples reduced with H <sub>2</sub> at 873 K or with CO at 773 K; lose one NO ligand during evacuation; <i>site-specified</i> species
ca. 1900 and 1790	$\nu_s$ and $\nu_{as}$ , respectively of Cr <sup>3+</sup> (NO) <sub>2</sub>	Only on samples reduced with H <sub>2</sub> at $T \leq 673$ K
1890	Cr <sup>n+</sup> -NO ( $n = 3$ or 4)	Stable at 373 K
1815	Cr <sup>n+</sup> -NO ( $n = 2$ or 3)	Produced in the presence of gas phase NO only
1782	Cr <sup>2+</sup> -NO	Produced during the decomposition of Cr <sup>2+</sup> (NO) <sub>2</sub> species (1902 + 1768 cm <sup>-1</sup> )

the intensity of all bands increases (Fig. 2, spectrum b). A broad feature with an ill defined maximum around 1900 cm<sup>-1</sup> is registered in the 1950–1850 cm<sup>-1</sup> region. A band at 1780 cm<sup>-1</sup> becomes the most intense one and two more new bands, at 1858 and 1815 cm<sup>-1</sup>, emerge. The latter two bands disappear after evacuation while the other bands decrease in intensity (Fig. 2, spectrum c).

Since the spectra obtained are rather complex, the assignment of different bands will be proposed below. Here we shall only note that the bands at 1858 and 1815 cm<sup>-1</sup> are produced in the presence of NO gas phase only and demonstrate an independent behavior (see also what follows). Thus they are assigned to two kinds of Cr<sup>n+</sup>-NO mononitrosyl species [15].

### 3.4. Adsorption of NO on a sample reduced with hydrogen at 573–773 K

For convenience and comparison purposes, selected spectra of NO adsorbed on activated sample and samples reduced at different temperatures are presented in Fig. 3. The observed frequencies and the assignments of the bands are summarized in Table 1.

The spectra of NO adsorbed on a sample reduced at 573 K (Fig. 3, spectra c and c') are very similar to the spectra of NO adsorbed on the 473 K reduced sample. No essential differences in the observed bands were noticed after NO adsorption on the sample reduced at 673 K (Fig. 3, spectra d and d'). Similar spectra were obtained with the 773 K reduced sample, but in this case the 1789 cm<sup>-1</sup> shoulder of the band at 1782 cm<sup>-1</sup> was absent (Fig. 3, spectra e and e'). Generally, the intensity of the bands continuously increased with the pre-reduction temperature.

The spectrum of NO (530 Pa equilibrium pressure) adsorbed on a sample reduced at 773 K is presented on Fig. 4, spectrum a. Bands at 1905, 1815 and 1780 cm<sup>-1</sup> are registered. Shoulders at 1894, 1877 and 1768 cm<sup>-1</sup> are also visible. Short evacuation provokes the disappearance of the 1815 cm<sup>-1</sup> band (Fig. 4, spectrum b). This is consistent with its assignment to mononitrosyl species. At the same time the broad feature around 1900 cm<sup>-1</sup> decreases in intensity. In the lower-frequency region it is the shoulder at 1768 cm<sup>-1</sup> that is more strongly affected by the evacuation, while the band at 1780 cm<sup>-1</sup> only slightly decreases.

A careful analysis of the difference spectra (see for example the inset in Fig. 4) shows that the shoulder at 1767 cm<sup>-1</sup> decreases in concert with a component at ca. 1902 cm<sup>-1</sup>, while the decrease of the band at 1782 cm<sup>-1</sup> is synchronous with the

decrease in a band around 1910 cm<sup>-1</sup>. These results suggest the existence of two families of dinitrosyl species: one with  $\nu_s$  and  $\nu_{as}$  at ca. 1910 and 1780 cm<sup>-1</sup>, respectively, and another with  $\nu_s$  at 1902 cm<sup>-1</sup> and  $\nu_{as}$  at ca. 1770 cm<sup>-1</sup> [15].

Short evacuation at 373 K leaves only one nitrosyl band at 1890 cm<sup>-1</sup> in the spectrum (Fig. 4, spectrum d). It decreases in intensity after additional evacuation at the same temperature (Fig. 4, spectrum e). This band can unambiguously be assigned to mononitrosyl species. Since it is not developed at the expense of any dinitrosyl bands, we can stress that it is produced with the participation of a definite fraction of reduced chromium sites.

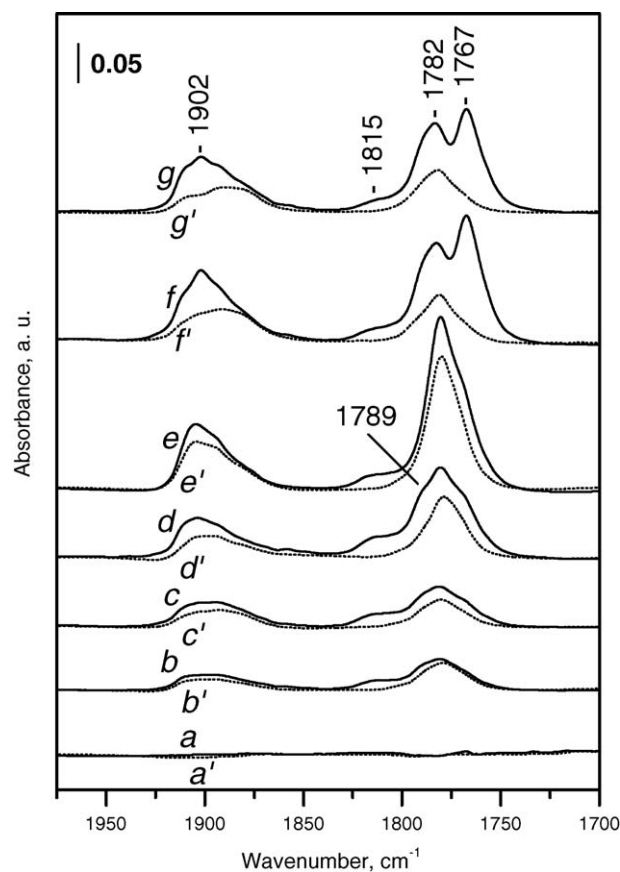


Fig. 3. FTIR spectra of NO (530 Pa equilibrium pressure) adsorbed on a Cr-ZSM-5 sample pre-subjected to different treatments. Activated sample (a), sample reduced with hydrogen at 473 K (b), 573 K (c), 673 K (d), 773 K (e) and 873 K (f) and sample reduced with CO at 773 K (g). The spectra shown with primed letters refer to the same conditions, but after evacuation of NO. The spectra are corrected with respect to the background and gaseous phase.

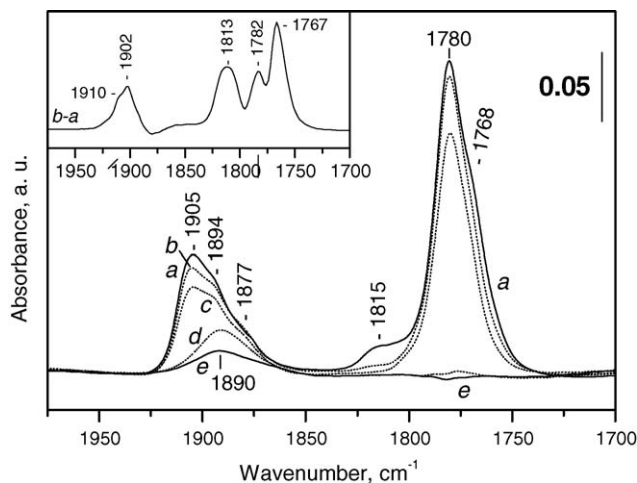


Fig. 4. FTIR spectra of NO adsorbed on a Cr-ZSM-5 sample reduced with hydrogen at 773 K. Equilibrium NO pressure of 530 Pa (a), after 1 (b) and 10 min evacuation at ambient temperature (c) and after 1 (d) and 10 min evacuation at 373 K (e). The spectra are corrected with respect to the background and gaseous phase. The difference spectrum “a – b” is presented in the inset.

### 3.5. Adsorption of NO on a sample reduced with hydrogen at 873 K

The picture obtained after NO adsorption on a sample reduced at 873 K differs from the spectra obtained with the samples reduced at lower temperatures (Fig. 3, spectra f and f'). In this case a set of bands at 1902 and 1768  $\text{cm}^{-1}$  dominate, while the band at ca. 1780  $\text{cm}^{-1}$  has a lower relative intensity. After evacuation the bands at 1902 and 1768  $\text{cm}^{-1}$  disappear and the bands resistant towards evacuation are less pronounced than is the case of the 773 K reduced sample. The spectrum resembles that obtained with the 673 K reduced sample, however, with the 873 K reduced sample the band around 1890  $\text{cm}^{-1}$  (mononitrosyl species) is more pronounced. Note that the amount of irreversibly adsorbed species decreases with the rise of the reduction temperature from 773 to 873 K.

In order to obtain more information on the state of chromium cations in the 873 K reduced sample, we studied the successive adsorption of small doses of NO. The first dose provoked the appearance of bands at 1910, 1902, 1892, 1879, 1790, 1780 and 1768  $\text{cm}^{-1}$  (Fig. 5, spectrum a). With the increase in amount of introduced NO, mainly the bands at 1902 and 1768  $\text{cm}^{-1}$  developed and two new bands, at 1858 and 1815  $\text{cm}^{-1}$ , emerged (Fig. 5, spectra b–e). The band at 1790  $\text{cm}^{-1}$  slightly decreased in intensity.

Evacuation of NO provokes (i) a fast disappearance of the bands at 1858 and 1815  $\text{cm}^{-1}$  and (ii) a progressive decrease in intensity mainly of the bands at 1902 and 1768  $\text{cm}^{-1}$  (Fig. 6, spectra b and c). At the same time bands at 1790 and 1783  $\text{cm}^{-1}$  develop. Additional evacuation provokes mainly a decrease in intensity of the bands at 1790 and 1783  $\text{cm}^{-1}$ , the changes in the 1950–1850  $\text{cm}^{-1}$  region being negligible (Fig. 6, spectra d and e). The principal bands remaining in the spectrum after evacuation at 373 K are at 1892 and 1880  $\text{cm}^{-1}$  (Fig. 6, spectrum f).

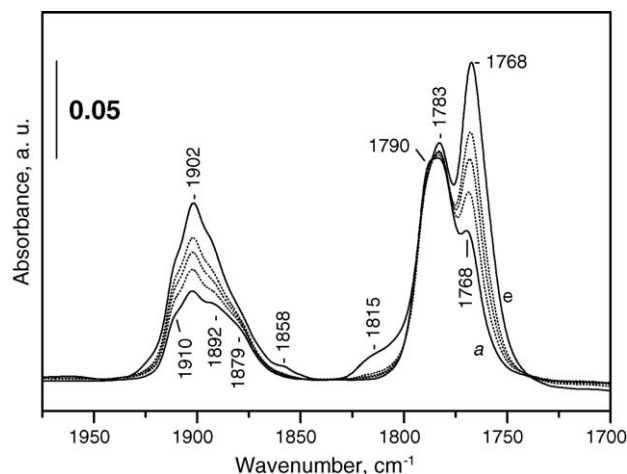


Fig. 5. FTIR spectra of NO adsorbed on a Cr-ZSM-5 sample reduced with hydrogen at 873 K. Successive adsorption of 1 (a), 2 (b) 4 (c) and 8 small doses of 1.2  $\mu\text{mol}$  NO each (d) and under NO equilibrium pressure of 530 Pa (e). The spectra are corrected with respect to the background.

The results obtained show that the species characterized by bands at 1902 and 1768  $\text{cm}^{-1}$  are unstable and destroyed via species displaying bands at 1790 and 1783  $\text{cm}^{-1}$  that are also decomposed during evacuation. However, the species displaying bands at 1790 and 1910  $\text{cm}^{-1}$  were suggested to characterize dinitrosyls. That is why, an alternative explanation of our results is that trinitrosyl species are stepwise decomposed. To choose between both hypotheses, we have studied  $^{14}\text{NO}$ – $^{15}\text{NO}$  co-adsorption (see below).

### 3.6. Adsorption of NO on a sample reduced with CO at 773 K

There is a widespread opinion that reduction of Cr/SiO<sub>2</sub> catalysts by H<sub>2</sub> leads to production of Cr<sup>3+</sup> ions while reduction with CO leads exclusively to formation of Cr<sup>2+</sup> cations [31]. Although

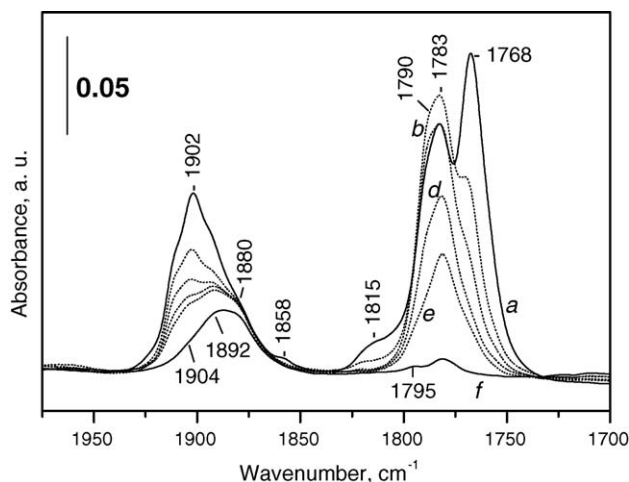


Fig. 6. FTIR spectra of NO adsorbed on a Cr-ZSM-5 sample reduced with hydrogen at 873 K. Equilibrium NO pressure of 270 Pa (a) and development of the spectra under progressive evacuation at ambient temperature (b–e) and after 1 min evacuation at 373 K (f). The spectra are corrected with respect to the background and gaseous phase.



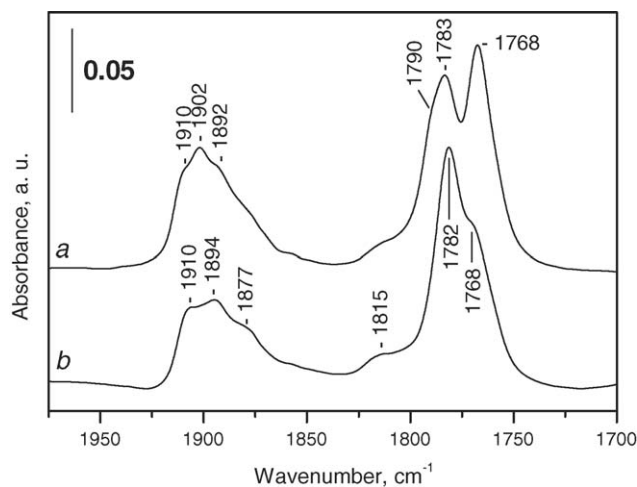


Fig. 7. FTIR spectra of NO adsorbed on a Cr-ZSM-5 sample reduced with CO at 773 K. Equilibrium NO pressure of 500 Pa (a), evacuation of the sample and subsequent introduction of NO (500 Pa equilibrium pressure) (b). The spectra are corrected with respect to the background and gaseous phase.

this rule is not valid for all chromium-containing systems, we studied a sample reduced with CO at 773 K. Spectra g and g' in Fig. 3 show that the results are very similar to those obtained with the sample reduced with hydrogen at 873 K (see spectra f and f' in Fig. 3). This indicates that the band at  $1780\text{ cm}^{-1}$  (registered mainly with samples reduced at lower temperatures) is associated with  $\text{Cr}^{3+}$  sites, while the band at  $1768\text{ cm}^{-1}$ , is connected with  $\text{Cr}^{2+}$  sites.

It is well known that nitrogen monoxide is an oxidizing agent [32]. Reactions with NO often occur during its evacuation. To prove the stability of the oxidation state of the surface sites, we initially adsorbed NO on the sample. The main resulting bands in the spectrum were at 1902, 1783 and  $1768\text{ cm}^{-1}$  (Fig. 7, spectrum a). Then the sample was evacuated and NO adsorbed again (Fig. 7, spectrum b). It is evident that the concentration of the sites producing dinitrosyls with bands at 1902 and  $1768\text{ cm}^{-1}$  has decreased, while the concentration of the sites, at which the dinitrosyls with bands at ca. 1910 and  $1782\text{ cm}^{-1}$  are formed, has augmented. This fact can be rationalized assuming oxidation of  $\text{Cr}^{2+}$  (nitrosyl bands at 1902 and  $1768\text{ cm}^{-1}$ ) to  $\text{Cr}^{3+}$  (bands at ca. 1910 and  $1782\text{ cm}^{-1}$ ) sites during the evacuation.

### 3.7. $^{14}\text{NO}$ – $^{15}\text{NO}$ co-adsorption experiments

The  $^{14}\text{NO}$ – $^{15}\text{NO}$  co-adsorption experiments were performed in order to prove/establish the mono-, di-, and eventual trin-nitrosyl structures. The first set of experiments was performed with a 773 K reduced sample since in this case the spectrum was simpler and the bands at 1902 and  $1768\text{ cm}^{-1}$  were with negligible intensity. Introduction of  $^{14}\text{NO}$  to the sample, followed by evacuation, led to the appearance of two main bands, at 1905 and  $1782\text{ cm}^{-1}$ , and some shoulders of the higher-frequency band at 1894 and  $1880\text{ cm}^{-1}$  (Fig. 8, spectrum a). The same spectrum was multiplied in the X-axis by the  $^{14}\text{NO}$ – $^{15}\text{NO}$  isotopic factor (0.98214) (Fig. 8, spectrum

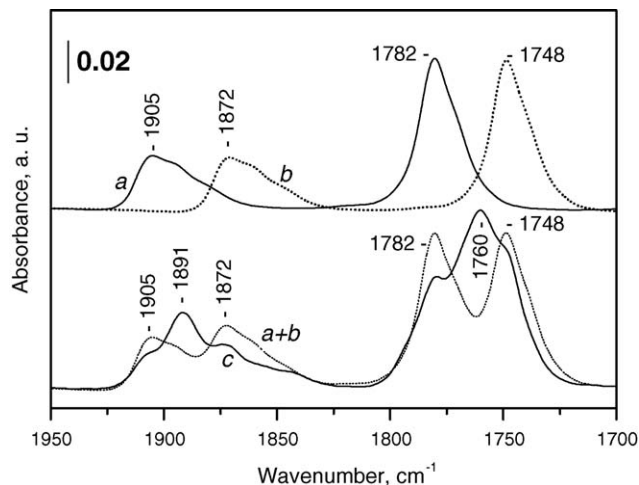


Fig. 8. FTIR spectra of adsorbed  $^{14}\text{NO}$  and co-adsorbed  $^{14}\text{NO}$  and  $^{15}\text{NO}$  on a Cr-ZSM-5 sample reduced with hydrogen at 773 K. Equilibrium NO pressure of 170 Pa, followed by evacuation (a); the same spectrum, shifted to lower frequencies by the  $^{14}\text{NO}$ – $^{15}\text{NO}$  isotopic factor (simulation of a spectrum expected after  $^{15}\text{NO}$  adsorption) (b); the sum of spectra a and b (simulation of a spectrum expected after  $^{14}\text{NO}$ – $^{15}\text{NO}$  adsorption supposing mononitrosyls only are formed) (a + b); equilibrium  $^{14}\text{NO}$  and  $^{15}\text{NO}$  pressure of 170 Pa, followed by evacuation (c). The spectra are corrected with respect to the background and gaseous phase.

b). In this way, the spectrum of adsorbed  $^{15}\text{NO}$  was simulated. The mathematical sum of both spectra (Fig. 8, spectrum “a + b”) corresponds to the spectrum expected after  $^{14}\text{NO}$ – $^{15}\text{NO}$  (1:1) co-adsorption in the case if only mononitrosyl species are produced (the small differences between the extinction coefficients are not taken into account). Formation of any dinitrosyl species should lead to a more complicated spectrum due to the appearance of the modes of mixed-ligand complexes,  $\text{Cr}^{3+}(\text{}^{14}\text{NO})(\text{}^{15}\text{NO})$ . Moreover, the equimolar isotopic ratio should lead to a  $\text{Cr}^{n+}(\text{}^{14}\text{NO})_2:\text{Cr}^{n+}(\text{}^{14}\text{NO})(\text{}^{15}\text{NO}):\text{Cr}^{n+}(\text{}^{15}\text{NO})_2$  ratio of 1:2:1. Hence, the bands of the mixed-ligand complexes should be more intense by a factor of two than will be the bands of the species with only  $^{14}\text{NO}$  or  $^{15}\text{NO}$  ligands.

Using the approximate force field model [33], we calculated the frequencies of the mixed  $\text{Cr}^{n+}(\text{}^{14}\text{NO})(\text{}^{15}\text{NO})$  complexes, supposing that the bands at 1910 and  $1782\text{ cm}^{-1}$  characterize dinitrosyl species. According to the calculation, the  $\nu(\text{}^{14}\text{N}-\text{O})$  and  $\nu(\text{}^{15}\text{N}-\text{O})$  modes are located at 1890 and  $1761\text{ cm}^{-1}$ , respectively. Spectrum c in Fig. 8 is the spectrum recorded after  $^{14}\text{NO}$ – $^{15}\text{NO}$  co-adsorption (molar ratio of ca. 1:1) under conditions analogical to the conditions of  $^{14}\text{NO}$  adsorption. Two bands, at 1891 and  $1760\text{ cm}^{-1}$ , dominate in the spectrum. The excellent coincidence of the experimental results with the calculated frequencies as well as with the expected intensity ratios prove the dinitrosyl structure of the species characterized by bands at 1910 and  $1782\text{ cm}^{-1}$ .

The next step of the co-adsorption experiments was designed with a view to obtaining information on the nature of the bands at 1902 and  $1768\text{ cm}^{-1}$ . For that purpose, we compared the spectra obtained with a sample reduced with hydrogen at 873 K and under NO equilibrium pressure (170 Pa). As in the previous case,

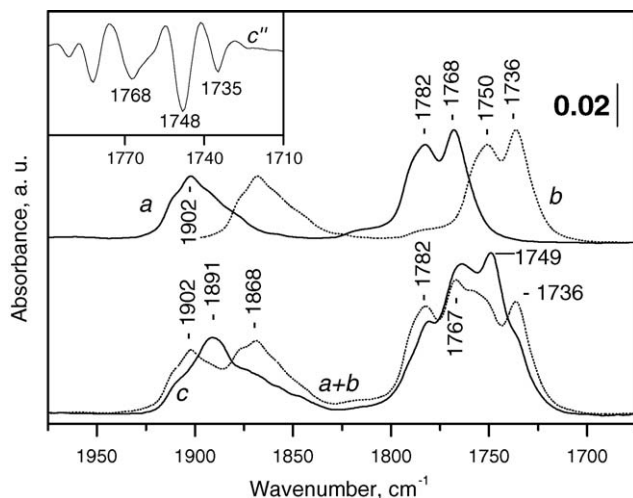


Fig. 9. FTIR spectra of adsorbed  $^{14}\text{NO}$  and co-adsorbed  $^{14}\text{NO}$  and  $^{15}\text{NO}$  on a Cr-ZSM-5 sample reduced with hydrogen at 873 K. Equilibrium NO pressure of 170 Pa (a); the same spectrum, shifted to lower frequencies by the  $^{14}\text{NO}$ – $^{15}\text{NO}$  isotopic factor (simulation of a spectrum expected after  $^{15}\text{NO}$  adsorption) (b); the sum of spectra a and b (simulation of a spectrum expected after  $^{14}\text{NO}$ – $^{15}\text{NO}$  adsorption supposing mononitrosyls only are formed) (a + b); equilibrium  $^{14}\text{NO}$  and  $^{15}\text{NO}$  pressure of 170 Pa (c). The spectra are corrected with respect to the background and gaseous phase. The second derivative of spectrum c is presented in the inset.

spectrum a from Fig. 9 corresponds to adsorbed  $^{14}\text{NO}$ , while spectrum b is the simulated spectrum of adsorbed  $^{15}\text{NO}$ .

Let us suppose that the bands at 1902 and 1768  $\text{cm}^{-1}$  characterize dinitrosyl species. The calculated frequencies for the corresponding  $\text{Cr}^{2+}(\text{NO})(^{15}\text{NO})$  complexes are at 1887 and 1750  $\text{cm}^{-1}$ . Spectrum c from Fig. 9 is obtained after co-adsorption of  $^{14}\text{NO}$  and  $^{15}\text{NO}$  under analogical conditions. Since the spectra are rather complicated, the exact maxima of the bands (especially in the lower-frequency region) have been determined by the second derivative (see the inset in Fig. 9). Intense bands at 1891 and 1749  $\text{cm}^{-1}$  are seen in the spectrum. Here again, a very good coincidence between the calculated frequencies and the experimental results has been found. In addition, the relative intensities of the bands are as expected for dinitrosyls.

Some experiments were designed to obtain information on the nature of the band at 1782  $\text{cm}^{-1}$  produced after the decomposition of the dinitrosyls displaying bands at 1902 and 1768  $\text{cm}^{-1}$  (mono- or dinitrosyls). For that purpose we analyzed some spectra obtained with the 873 K reduced sample after adsorption of NO (co-adsorption of  $^{14}\text{NO}$  and  $^{15}\text{NO}$ ) and short evacuation, i.e. under the conditions at which the 1782  $\text{cm}^{-1}$  band reaches the highest intensity. The results are presented in Fig. 10. If the band at 1782  $\text{cm}^{-1}$  was due to dinitrosyls, an intense band around 1760  $\text{cm}^{-1}$  should have appeared (as is the case of the dinitrosyls presented on Fig. 8). Analysis of the spectra (see the inset in Fig. 10) shows that such a band does exist, but its intensity is too weak. As already noted, an intensity two times higher than the intensities of the bands at 1782 and 1750  $\text{cm}^{-1}$  is expected. Therefore, the results prove the existence of mononitrosyls produced after the decomposition of the dinitrosyls characterized by bands at 1902 and 1768  $\text{cm}^{-1}$ .

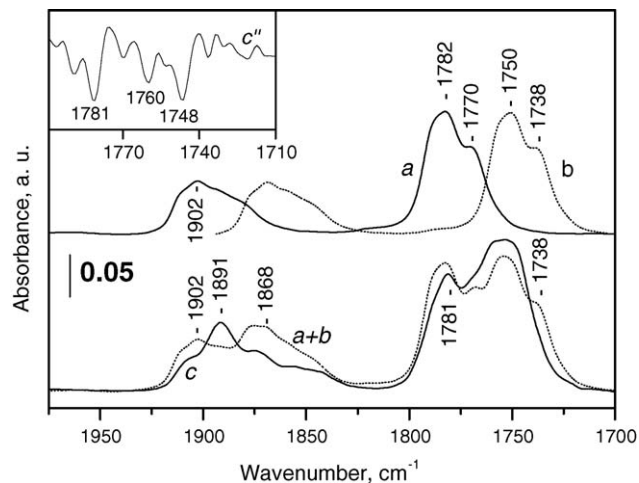


Fig. 10. FTIR spectra of adsorbed  $^{14}\text{NO}$  and co-adsorbed  $^{14}\text{NO}$  and  $^{15}\text{NO}$  on a Cr-ZSM-5 sample reduced with hydrogen 873 K. Equilibrium NO pressure of 170 Pa, followed by evacuation (a); the same spectrum, shifted to lower frequencies by the  $^{14}\text{NO}$ – $^{15}\text{NO}$  isotopic factor (simulation of a spectrum expected after  $^{15}\text{NO}$  adsorption) (b); the sum of spectra a and b (simulation of a spectrum expected after  $^{14}\text{NO}$ – $^{15}\text{NO}$  adsorption supposing mononitrosyls only are formed) (a + b); equilibrium  $^{14}\text{NO}$  and  $^{15}\text{NO}$  pressure of 170 Pa, followed by evacuation (c). The spectra are corrected with respect to the background and gaseous phase. The second derivative of spectrum c is presented in the inset.

### 3.8. Differences between the chromium dinitrosyl species

Let us denote the two principal dinitrosyl species observed in this study as A- and B-species. The A-species (bands at ca. 1910 and 1782  $\text{cm}^{-1}$ ) prevail with the samples reduced by hydrogen at temperatures between 473 and 773 K. Therefore, they are most probably  $\text{Cr}^{3+}(\text{NO})_2$  dinitrosyls. These complexes are relatively stable towards evacuation at ambient temperature and are destroyed without producing a measurable fraction of respective mononitrosyls, i.e. they are *complex-specified* [34]. In fact, most of the surface dinitrosyl species known so far are of this type. A typical example are the  $\text{Co}^{2+}(\text{NO})_2$  complexes that are always produced after NO adsorption on  $\text{Co}^{2+}$  containing surfaces and are normally decomposed without producing mononitrosyls [35].

The B-species are characterized by bands at 1902 and 1768  $\text{cm}^{-1}$ . They are evidently formed with the participation of more deeply reduced chromium sites and are thus assigned to  $\text{Cr}^{2+}(\text{NO})_2$  complexes. In contrast to the A-species, the B-species are easily destroyed during evacuation. We have found two routes of their decomposition: (i) loss of one NO ligand and formation of mononitrosyls (1783  $\text{cm}^{-1}$ ) that are also destroyed during further evacuation and (ii) destruction by oxidation of  $\text{Cr}^{2+}$  to  $\text{Cr}^{3+}$ . Thus, the B-species can be classified as *site-specified* geminal complexes [35] or “true” dinitrosyls [13]. Only a few cases of “true” surface dinitrosyls (*site-specified* species) are known, a typical example being the  $\text{Cu}^+(\text{NO})_2$  complexes formed during low-temperature NO adsorption on  $\text{Cu}^+$ -ZSM-5 [32]. In a series of works [34,36,37] we have stressed that a necessary condition for the formation of *site-specified* geminal complexes is the low coordination of the metal cation. Indeed, such species are mainly produced with cations exchanged in

zeolites. Especially with  $M^{n+}$ -ZSM-5 samples geminal dicarbonyls have been described for  $Cu^+$ -ZSM-5 [32],  $Ca^{2+}$ -ZSM-5 [34] and  $Mn^{2+}$ -ZSM-5 [36]. Therefore, we can conclude that the formation of the B-dinitrosyls is caused by the low coordinative saturation of the  $Cr^{2+}$  ions in a ZSM-5 matrix and is not determined by the nature (the oxidation state) of the cation. Note that the possibility of simultaneous coordination of two molecules to one site can be very important for the proceeding of some catalytic reactions, e.g. ethene polymerization.

An interesting phenomenon that should be discussed is the stability of the species. Generally, it is believed that the lower the oxidation state of the cation, the higher the stability of the corresponding nitrosyls because of the increasing probability of back  $\pi$ -donation. A possible explanation of the results obtained is that the enhanced stability of the A-species arises from the fact that they are *complex-specified*. It is believed that complex-specified species are additionally stabilized by reaching a stable electron configuration. A typical example are the well known rhodium gem-dicarbonyls,  $Rh^+(CO)_2$ . It is assumed that they are formed because of reaching a stable 16- or 18-electron configuration [38,39]. However, these considerations do not explain why the mononitrosyl species observed at  $1890\text{ cm}^{-1}$  are more stable than the mononitrosyls observed at lower frequencies, namely at  $1815$  and  $1783\text{ cm}^{-1}$ . Evidently, in the case of chromium nitrosyls the back  $\pi$ -donation is not important and the stability of the species is mainly determined by the strength of the  $\sigma$ -bond. This accounts for the fact that generally, the higher the frequency, the higher the stability of the different chromium dinitrosyls.

#### 4. Conclusions

- Chromium in activated Cr-ZSM-5 is encountered as  $Cr^{6+}$  and is not able to form nitrosyl species.
- Reduction of Cr-ZSM-5 with hydrogen at  $473\text{--}773\text{ K}$  leads to formation of  $Cr^{3+}$  ions forming relatively stable dinitrosyls ( $1910$  and  $1782\text{ cm}^{-1}$ ). These species are decomposed without producing mononitrosyls.  $Cr^{n+}$  ions ( $n = 3$  or  $4$ ) that form mononitrosyls only ( $1890\text{ cm}^{-1}$ ) are also produced.
- Reduction of Cr-ZSM-5 with hydrogen at  $873\text{ K}$  or with CO at  $773\text{ K}$  leads to formation of  $Cr^{2+}$  ions. The latter are low-coordinated and can accept up to two NO molecules. The dinitrosyls formed ( $1902$  and  $1768\text{ cm}^{-1}$ ) are, however, site specified and successively lose their NO ligands.

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