FTIR spectroscopy study of CO and NO adsorption and co-adsorption on Pt/TiO$_2$

Elena Ivanova [a,b,*], Mihail Mihaylov [a], Frédéric Thibault-Starzyk [b],
Marco Daturi [b], Konstantin Hadjiivanov [a]

[a] *Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria*
[b] *Laboratoire Catalyse et Spectrochimie, CNRS-ISMRA, Université de Caen, 6 bd. Maréchal Juin, 14050 Caen Cedex, France*

Abstract

A Pt/TiO$_2$ sample has been studied by adsorption and co-adsorption of CO and NO. It has been found that platinum is present in different oxidation states on the surface of the activated sample. Pt^{4+} ions are coordinatively saturated and form complexes neither with CO nor with NO. Pt^{3+} ions form, after CO adsorption, linear Pt^{3+}–CO species stable up to 373 K and characterized by a band at 2183 cm^{-1}. However, the Pt^{3+} cations are not able to coordinate NO because of the unwillingness of the latter to form electrostatic bond. Pt^{2+} cations form both carbonyl and nitrosyl complexes. The Pt^{2+}–CO species are stable up to 623 K and display a band at 2134 cm^{-1}. NO appears to be more sensitive probe for the state of the Pt^{2+} cations and the Pt^{2+}–NO species are detected in the 1950–1900 cm^{-1} region. No evidence of Pt$^+$ cations is found. The linear carbonyls of metallic platinum (2095–2070 cm^{-1}) are less stable than the Pt^{2+}–CO species. On the contrary, the most stable nitrosyls are those of Pt^0 (linear species at 1850–1780 cm^{-1} and bent species around 1620 cm^{-1}). It is found that CO slowly reduces cationic platinum ultimately to metal. On the contrary, NO, even at ambient temperature oxidizes metallic platinum. The results obtained are compared with the results on carbonyls formed with platinum in zeolites.

1. Introduction

Platinum is one of the most used and most studied metals in the field of catalysis. However, the efforts have been, as a rule, concentrated on characterization of metal platinum particles [1–10]. Recently, some authors [11,12] indicated that in several cases (mainly oxidation reactions) the catalytically active sites could be platinum cations or Pt^{n+}/Pt^0 redox couples which could operate in the processes. For that reason, the characterization of different surface cationic sites, underestimated so far, is of great importance for understanding the mechanism of the redox catalytic reactions involving platinum catalysts.

IR spectroscopy of probe molecules is one of the most powerful techniques for characterization of catalyst surfaces [13–15]. The most frequently used IR probe is CO [13]. It can provide information on the oxidation and coordination state of the cations and their Lewis acidities. Nitrogen monoxide as an IR probe molecule could not only verify the results obtained, but could also provide additional information. In addition, investigations on NO adsorption is important for understanding the mechanism of NO$_x$ conversion reactions.

It is generally accepted that surface carbonyls of cationic platinum are observed above 2100 cm^{-1}, but there is no consensus on the oxidation state of the adsorption center. The carbonyl bands have been often simply assigned to Pt^{n+}–CO species [16–22]. As a probe molecule for characterization of cationic platinum sites NO is even less developed than CO.

Recently, we studied platinum cations in zeolites and observed formation of different non-classical (poly)carbonyls of platinum cations in different oxidation states. The aims of this work are (i) to study the carbonyl species formed after

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* Corresponding author at: Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria. Tel.: +359 2 979 6312; fax: +359 2 870 5024.

E-mail address: eivanova@svr.igic.bas.bg (E. Ivanova).

CO adsorption on oxide-supported platinum cations, namely Pt^{n+}/TiO_2 and (ii) by comparison with the spectra of adsorbed CO, to contribute in developing NO as a probe molecule for testing cationic platinum sites.

2. Experimental

Commercially available titania (Degussa P-25, 75% anatase and 25% rutile) was used as a support. To prepare a Pt/TiO_2 sample, platinum was deposited by anion-exchange as described elsewhere [23]. The starting material was a 1 wt.% Pt solution prepared from $PtCl_4$ (pH 2.1). Titania powder was suspended in this solution for 1 h, then the sample was filtered and again put in contact with the starting solution. After 20 h the precipitate was filtered, washed well with water, and dried at 353 K. According to the chemical analysis it contained 0.73 wt.% Pt.

The IR spectra were recorded on Nicolet Magna IR 550 spectrometer accumulating 64 scans at a spectral resolution of $4 \, cm^{-1}$. Self-supporting pellets (ca. $15 \, mg \, cm^{-2}$) were prepared from the sample powder and treated directly in a purpose-made IR cell. The latter was connected to a vacuum-adsorption apparatus with a residual pressure below $10^{-3} \, Pa$. Prior to the adsorption measurements, the sample was activated by heating for 1 h in oxygen (13.3 kPa) at 673 K and 1 h evacuation at the same temperature. To obtain a reduced sample, the pellet was treated for 1 h at 473 K in hydrogen (13.3 kPa) and then evacuated at the same temperature.

Carbon monoxide (>99.997% pure) and nitrogen monoxide (>99.9% pure) were supplied by Air Liquide, France. Before adsorption, carbon monoxide and oxygen were passed through liquid nitrogen trap while NO was additionally purified by fraction distillation. All adsorption experiments were performed at ambient temperature.

3. Results and discussion

3.1. Adsorption of CO on activated Pt/TiO_2

The IR spectrum of the Pt/TiO_2 sample heated at 673 K in oxygen (13.3 kPa) and then evacuated at the same temperature contains, in the OH region, two bands at 3730 and $3660 \, cm^{-1}$, which are due to isolated Ti–OH groups [24].

Adsorption of CO on the sample leads to the appearance of series of bands, at 2208, 2188, 2134, 2088 and 2073 (sh) cm^{-1} (Fig. 1, spectrum a). A very weak band at $1850 \, cm^{-1}$ (not shown) is also discernible. Upon evacuation the band at $2208 \, cm^{-1}$ disappears, and the band at $2188 \, cm^{-1}$ decreases in intensity (Fig. 1, spectrum b). Simultaneously, its maximum is shifted to $2183 \, cm^{-1}$. The lower frequency bands slightly develop. According to the literature [24–26], CO adsorption on the support is reversible, and the bands at 2208 and $2188 \, cm^{-1}$ are assigned to carbonyls formed with two kinds of c.u.s. Ti^{4+} cations on the surface. Hence, the bands resisting to the evacuation (at 2183, 2134 and $2088 \, cm^{-1}$) are due to different platinum carbonyls. The band at 2088 together with its shoulder at $2073 \, cm^{-1}$ can be attributed to linear carbonyls of metallic platinum, and the weak band at $1850 \, cm^{-1}$ to bridged Pt^0–CO–Pt^0
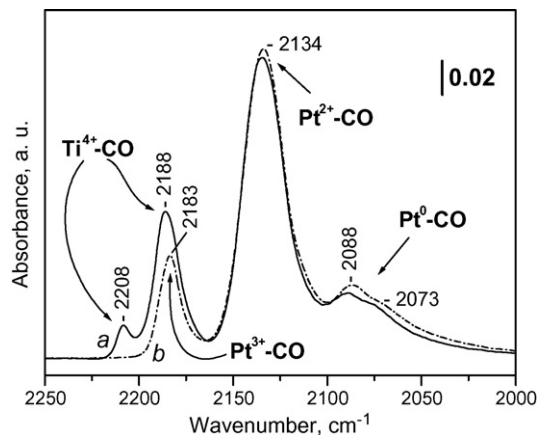

Fig. 1. FTIR spectra of CO adsorbed on activated Pt/TiO_2. Equilibrium CO pressure of 665 Pa (a) and after evacuation at 293 K (b). The spectra are background corrected and the CO gas phase subtracted.

species [1]. The band at $2134 \, cm^{-1}$ is assigned to Pt^{2+}–CO species, since the carbonyls of Pt^+ are expected at lower frequencies [27–29]. Obviously, the band at $2183 \, cm^{-1}$ characterizes more oxidized platinum sites than does the band at $2134 \, cm^{-1}$. The similarity to the stretching frequency of $[Pt(CO)Cl_5]^-$ ($2191 \, cm^{-1}$) suggests this band to be due to Pt^{4+}–CO carbonyls, as proposed earlier [27]. However, the following experiment favors its assignment to Pt^{3+}–CO species.

The sample was treated for 1 h at 673 K in a $NO + O_2$ mixture (4.5 kPa NO and 8.8 kPa O_2 initial pressures) and then evacuated at the same temperature. It is known that the $NO + O_2$ mixture is a stronger oxidizing agent than oxygen itself [30]. The spectrum of CO adsorbed on the sample thus treated displays bands similar to those observed with the normally-activated sample (Fig. 2, spectra a and b). However, in the latter case, they appear with reduced intensities and the Pt^0–CO bands are hardly observable. Subsequent outgassing and introduction of CO result in enhanced intensity of all carbonyl bands (Fig. 2, spectrum c).
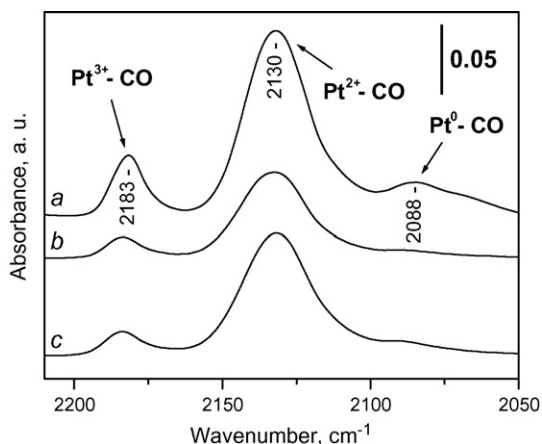

Fig. 2. FTIR spectra of CO (1070 Pa equilibrium pressure, followed by evacuation) adsorbed on Pt/TiO_2 after different pretreatments: sample activated in oxygen at 673 K and evacuated at the same temperature (a), sample treated in a $NO + O_2$ mixture at 673 K and evacuated at the same temperature (b), subsequent CO adsorption and evacuation (c). The spectra are background corrected.
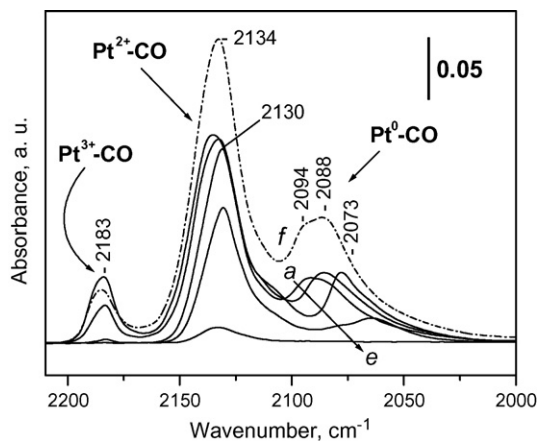
Fig. 3. FTIR spectra of CO adsorbed on activated Pt/TiO$_2$. Equilibrium CO pressure of 665 Pa, followed by evacuation at 293 (a) 373 (b), 473 (c), 523 (d) and 573 K (e) and after subsequent introduction of CO (665 Pa equilibrium pressure) and evacuation at 293 K (f). The spectra are background corrected.
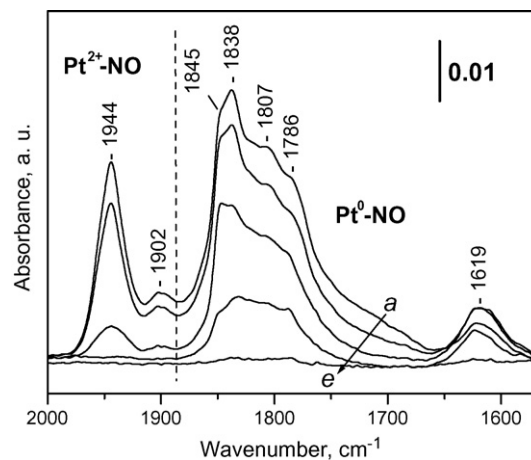

Fig. 4. FTIR spectra of NO adsorbed on activated Pt/TiO$_2$. Equilibrium NO pressure of 70 Pa (a) and after evacuation at 293 (b) 373 (c), 423 (d) and 473 K (e). The spectra are background corrected and the NO gas phase subtracted.

These results indicate the existence of some 'invisible' sources of platinum sites. We are of the opinion that the Pt^{4+} cations are coordinatively saturated and cannot adsorb CO. Indeed, many cations in their highest oxidation state (V^{5+}, Cr^{6+}, Mo^{6+}) are coordinatively saturated and not able to form carbonyl species [13,15]. However, these platinum sites can interact with carbon monoxide producing Pt^{3+}, Pt^{2+} and even Pt^0 species. Therefore the assignment of the band at 2183 cm^{-1} to Pt^{3+}–CO carbonyls appears plausible.

To verify the assignment of the different bands we have studied the stability of the carbonyls. Short evacuation at 373 K led to a strong decrease in intensity of the band at 2183 cm^{-1} while the band at 2134 cm^{-1} remained almost unaffected (Fig. 3, spectrum b). The Pt^0–CO feature slightly shifted to lower frequencies and even gained some intensity. This phenomenon is, however, most probably due to some reduction of cationic platinum to metal during the CO desorption. The band at 2183 cm^{-1} practically disappeared after short evacuation at 473 K (Fig. 3, spectrum c) and the band at 2134 cm^{-1} was eroded from its high-frequency side. The Pt^0–CO band was additionally red shifted which is typical of CO adsorbed on metal surfaces. It practically disappeared from the spectrum after evacuation at 573 K while the band at 2130 cm^{-1} was still observable (Fig. 3, spectrum e). To verify that some reduction of the sample had occurred during the experiments, we adsorbed CO again. Indeed, in this case, the Pt^{3+}–CO band (2183 cm^{-1}) appeared with a reduced intensity while the bands due to Pt^{2+}–CO (2134 cm^{-1}) and Pt^0–CO (ca. 2090 cm^{-1}) species were more intense than in the first set of experiments (Fig. 3, spectrum f).

The results showed that the most stable carbonyls were those of Pt^{2+} cations. This is due to the synergy between σ- and π-components of the Pt–CO bond [13]. As expected, Pt^{3+} cations form predominantly an electrostatic/σ-bond with CO and, as a result, the CO stretching modes are blue shifted with respect to gaseous CO (2143 cm^{-1}). On the contrary, the π-bonding predominates when CO is bound to Pt^0 atoms, and the respective CO modes are red shifted.

3.2. Adsorption of CO on reduced Pt/TiO$_2$

Finally, we studied CO adsorption on a reduced sample. Three bands, at 2091, 1863 and 1676 cm^{-1} were found (spectra not shown). The bands at 2091 and 1863 cm^{-1} were already assigned to Pt^0–CO and Pt^0–CO–Pt^0 species, respectively. The band at 1676 cm^{-1} is assigned to tilted Pt^0–CO–Ti^{4+} species [13].

3.3. Adsorption of NO on activated Pt/TiO$_2$

Adsorption of NO (ca. 70 Pa equilibrium pressure) on a freshly activated Pt/TiO$_2$ sample provoked the appearance of a series of bands in the nitrosyl stretching region, namely at 1944, 1902, 1845, 1838, 1807, 1786 (tailed) and 1619 cm^{-1} (Fig. 4, spectrum a). We used a low NO pressure, because at high pressures NO could disproportionate, thus providing strong oxidizing agents which could change the platinum speciation. Evacuation at elevated temperatures led to a gradual decrease in intensity of all bands above 1700 cm^{-1}, while the band at 1619 cm^{-1} initially gained some intensity and then started to decrease (Fig. 4, spectra b–d). The bands at 1944 and 1902 cm^{-1} disappeared after evacuation at 423 K (Fig. 4, spectrum d), while the bands at ca. 1838 and 1619 cm^{-1} vanished at 473 K (Fig. 4, spectrum e). Adsorption of NO on a reduced sample (see below) showed that the bands below 1880 cm^{-1} were due to nitrosyls of metallic platinum. According to data from the literature [31–34], the bands at 1845, 1838, 1807 and 1786 cm^{-1} are attributed to different linear Pt^0–NO nitrosyls. However, the bands at 1845 and 1838 cm^{-1} are at relatively high frequencies and could characterize nitrosyls on positively charged platinum atoms. The band at 1619 cm^{-1} could be due to bent nitrosyls of metallic platinum and/or nitrates. The bands above 1880 cm^{-1} were assigned to Pt^{n+}–NO species. Note that, although adsorption of NO often leads to formation of dinitrosyls [37], no evidence of any geminal species was found in our case.

Subsequent introduction of a larger amount of NO (665 Pa equilibrium pressure) to the sample resulted in spectrum similar
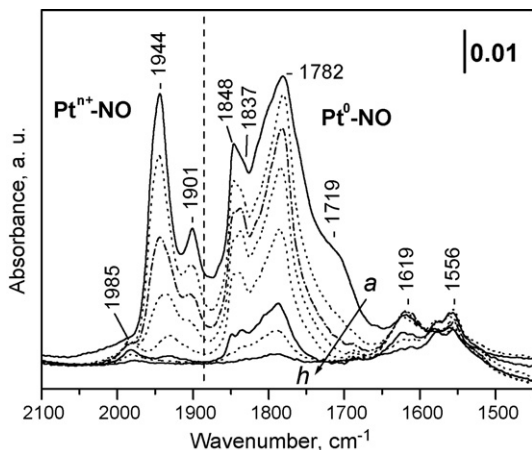
Fig. 5. FTIR spectra of NO adsorbed on activated Pt/TiO$_2$. Equilibrium NO pressure of 655 Pa (a) after evacuation at 293 (b), and after short evacuations at 473 K (c–h). The spectra are background corrected and the NO gas phase subtracted.
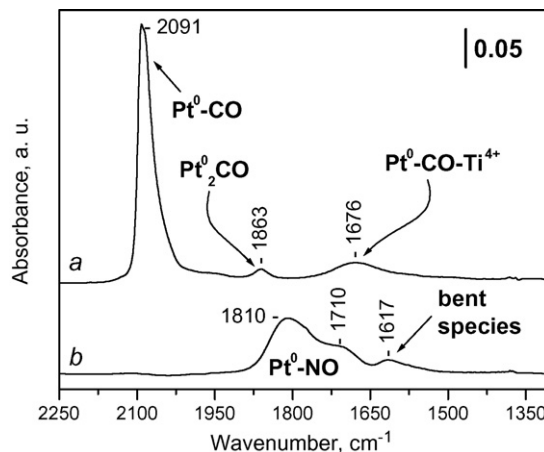

Fig. 6. FTIR spectra of NO and CO adsorbed on reduced Pt/TiO$_2$. Adsorption of CO (655 Pa equilibrium pressure, followed by evacuation at 293 K) (a) and subsequent introduction of NO (70 Pa equilibrium pressure) (b). The spectra are background corrected.

to that obtained during the previous experiment (Fig. 5, spectrum a). However, the bands at 1944, 1901 and 1782 cm^{-1} were more intense and an additional band at 1556 cm^{-1} was detected. The latter can be assigned to nitrate species [30].

Successive short evacuations at 473 K showed again that the bands at 1944 and 1901 cm^{-1} represented the less stable species, the band at 1944 cm^{-1} being slightly more resistant to evacuation (Fig. 5, spectra c–h). This behavior is consistent with the hypothesis that both bands characterize nitrosyls of platinum cations in the same oxidation state, but differing in acidity. We assign these bands to two types of Pt^{2+}–NO complexes. In addition, one new band at 1985 cm^{-1} became visible during the experiment, developed and then vanished. It should be noted that this band was observed simultaneously with the formation of nitrates. Therefore, this band may be assigned to nitrosyls of Pt^{2+} (or Pt^{3+}) cations with enhanced acidity as a result of the inductive effect of nearby nitrates.

Finally, we studied NO adsorption on a reduced sample. Preliminary CO adsorption proved the existence of only metallic platinum on the sample (Fig. 6, spectrum a). To prevent re-oxidation of metallic platinum, we introduced the gas into the cell through a liquid nitrogen trap, which purified it from NO$_2$ and ensured ca. 0.5 Torr equilibrium pressure over the sample. As a result, three bands at 1810, 1710 and 1617 cm^{-1} appeared immediately (Fig. 6, spectrum b). The bands at 1810 and 1710 cm^{-1} are due to linear Pt^0–NO nitrosyls, while the band at 1617 cm^{-1} is attributed to bent species.

Introduction of NO at higher pressures provokes the appearance of new bands in the nitrosyl stretching region, namely at 1948, 1934 and 1902 cm^{-1} (Fig. 7, spectrum b). These bands were already assigned to Pt^{2+}–NO species. At the same time, in the lower frequency area, bands of nitrates (1622 and 1575 cm^{-1}) developed. The experiment demonstrated oxidation of platinum particles by NO even at ambient temperature. This phenomenon was confirmed by subsequent CO adsorption (before that the sample was evacuated at 573 K). In addition to the strong Pt^0–CO band at 2091 cm^{-1}, bands due to Pt^{2+}–CO

(2130 cm^{-1}) and Pt^{3+}–CO (2187 cm^{-1}) species were detected (Fig. 7, spectrum c).

The above results provoke a question: why are Pt^{3+} cations detected by CO but not by NO? In fact, there are some observations in line with this phenomenon. A typical example is the support used in this work, TiO$_2$. As already mentioned, adsorption of CO on TiO$_2$ results in the formation of two kinds of Ti^{4+}–CO species. However, no Ti^{4+}–NO adducts are formed after NO adsorption [35]. In fact, CO is mainly bonded to Ti^{4+} ions by electrostatic forces. Since the polarizability of the NO molecule is lower, NO is a weaker electrostatic base than is CO. As a result, no nitrosyls with highly charged cations are typical.

3.4. Co-adsorption of NO and CO on activated Pt/TiO$_2$

In order to prove the proposed assignments, we studied co-adsorption of CO and NO. Adsorption of CO on an activated
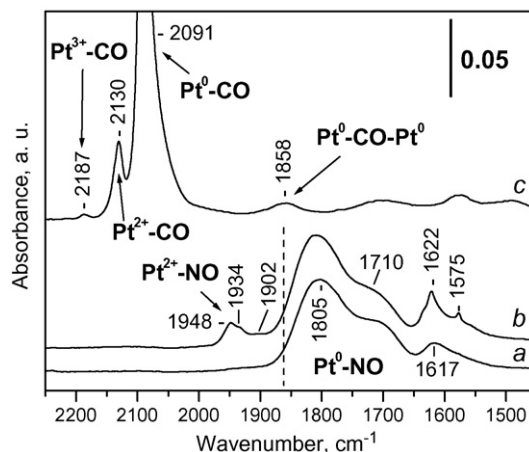

Fig. 7. FTIR spectra of NO and CO adsorbed on reduced Pt/TiO$_2$. Equilibrium NO pressure of 70 Pa (a), 470 Pa and evacuation at 293 K (b), subsequent evacuation at 573 K and introduction of CO (655 Pa equilibrium pressure) followed by evacuation at 293 K (c). The spectra are background corrected and the NO gas phase subtracted.
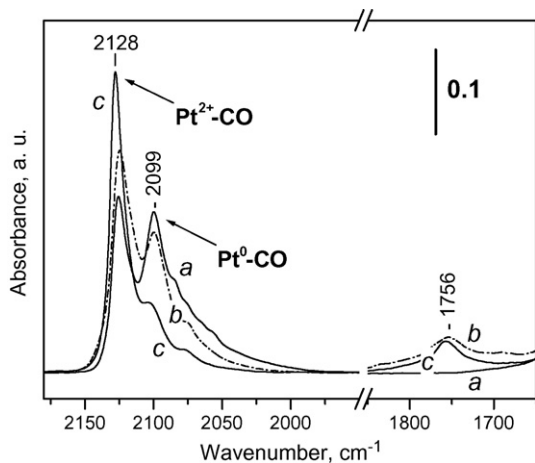
Fig. 8. FTIR spectra of CO and NO co-adsorbed on activated Pt/TiO$_2$. Adsorption of CO (655 Pa equilibrium pressure, followed by evacuation at 373 K) (a). Introduction of NO (1070 Pa equilibrium pressure) (b) and after a short heating of the sample at 673 K in the presence of NO (c). The spectra are background corrected and the NO gas phase subtracted.

sample led (as already described) to formation of carbonyls of Pt^{3+}, Pt^{2+} and Pt^0 (bands at 2183, 2128 and 2099 cm^{-1}, respectively). After evacuation at 373 K, the Pt^{3+} sites were liberated and bands at 2128 and 2099 cm^{-1} remained in the spectrum (Fig. 8, spectrum a). Then NO (1.33 kPa) was introduced to the system. Only a very weak Pt^0–NO band at 1756 cm^{-1} was formed. In addition development of the Pt^{2+}–CO band (2128 cm^{-1}) at the expense of the band of Pt^0–CO (2099 cm^{-1}) was observed (Fig. 8, spectrum b). This effect was even more pronounced after short heating of the pellet at 673 K in the NO atmosphere (Fig. 8, spectrum c). This proves that Pt^{3+} cations do not form nitrosyl species.

In another set of experiments NO (ca. 70 Pa equilibrium pressure) was initially adsorbed on activated Pt/TiO$_2$. Bands at 1953, 1823, 1773 and 1710 (sh) cm^{-1} were detected (Fig. 9, spectrum a). Then the sample was evacuated and small doses of CO
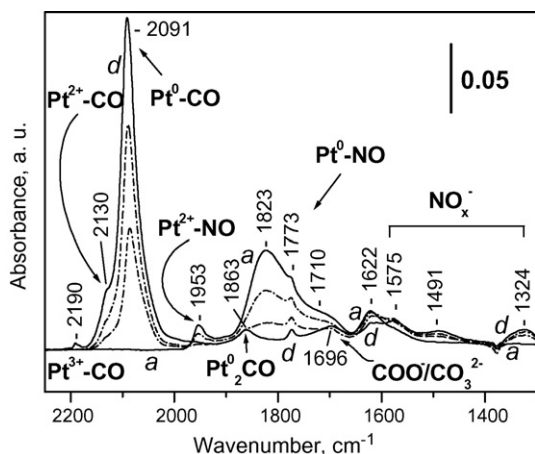

Fig. 9. FTIR spectra of NO and CO co-adsorbed on activated Pt/TiO$_2$. Adsorption of NO (ca. 70 Pa equilibrium pressure, followed by evacuation at 293 K) (a) and subsequent introduction of progressively increasing amounts of CO into the cell (b and c), equilibrium pressure of 40 Pa CO, followed by evacuation (d). The spectra are background corrected.

were successfully added to the system up to a CO equilibrium pressure of 40 Pa. With the first CO dose a Pt^0–CO band at 2091 cm^{-1} with a shoulder at 2130 cm^{-1} (Pt^{2+}–CO) developed (Fig. 9, spectrum b). Simultaneously, the bands at 1823 and 1773 cm^{-1} decreased in intensity. These changes were more pronounced when the second CO dose was introduced to the system (Fig. 9, spectrum c). When some CO equilibrium pressure was maintained and CO then evacuated, all nitrosyl bands disappeared, the described carbonyl bands rose additionally and a weak band at 2190 cm^{-1} was detected (Fig. 9, spectrum d). The latter is assigned to Pt^{3+}–CO species probably affected by nitrates. All these results indicate that the band at 1953 cm^{-1} for NO adsorbed species corresponds to the band at 2130 cm^{-1} after CO adsorption and, hence, characterizes nitrosyls of Pt^{2+}.

Finally, we shall compare the results obtained here with our previous results on platinum carbonyls in zeolites. With Pt-H-ZSM-5 and Pt-Na-MOR, we had detected Pt$^+$ cations. However, no such cations were found in this work. Evidently, the latter are somewhat stabilized by the zeolite matrix. In fact, Co$^+$ and Ni$^+$ cations can also be produced in zeolites [36–38], but not with the most oxide systems. Another principal difference from the results obtained with the zeolitic systems is that in the latter case polycarbonyls of Pt^{3+} and Pt^{2+} have been observed. However, with Pt/TiO$_2$ only linear species are detected. This confirms a series of previous observations, pointing out that cations in zeolites are, as a rule, characterized by a high number of effective coordinative vacancies and can thus coordinate up to four small molecules [38,39].

4. Conclusion

Adsorption of CO on a non-reduced Pt/TiO$_2$ sample reveals the existence of Pt^{3+} and Pt^{2+} cations as well as some amount of metallic platinum. However, Pt^{4+} species are also present on the sample but, being coordinatively saturated, cannot adsorb CO.

NO forms nitrosyl species with bare Pt^{2+} and Pt^0 sites, but is not coordinated to Pt^{3+} ions. It appears that NO is a more sensitive probe than CO is to test the state of Pt^{2+} cations.

Adsorbed CO slowly reduces the platinum cations. On the contrary, NO oxidizes metallic platinum even at ambient temperature.

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