

# IR study of CO and H<sub>2</sub>O coadsorption on Pt<sup>n+</sup>/TiO<sub>2</sub> and Pt/TiO<sub>2</sub> samples†

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The adsorption of CO on a Pt/TiO<sub>2</sub> sample has been studied by IR spectroscopy. On the unreduced sample, CO is adsorbed reversibly on Ti<sup>4+</sup> cations (bands at 2188 and 2206 cm<sup>-1</sup>) and irreversibly on Pt<sup>4+</sup> and Pt<sup>2+</sup> sites (bands at 2186 and 2138 cm<sup>-1</sup>, respectively). Water replaces CO adsorbed on Pt<sup>4+</sup> sites and interacts with the Pt<sup>2+</sup>—CO carbonyls producing a doublet with maxima at 2114 and 2088 cm<sup>-1</sup>. The 2114 cm<sup>-1</sup> band is assigned to Pt<sup>2+</sup>—CO carbonyls interacting with water adsorbed on the support, whereas the 2088 cm<sup>-1</sup> band is attributed to Pt<sup>2+</sup>(H<sub>2</sub>O)CO species. CO adsorption on reduced Pt/TiO<sub>2</sub> samples causes the appearance of bands due to Ti<sup>4+</sup>—CO complexes and to linear and bridged carbonyls of Pt<sup>0</sup> (bands at 2084 and 1860 cm<sup>-1</sup>, respectively). Subsequent water adsorption produces a tailed Pt<sup>0</sup>—CO carbonyl band. It is demonstrated that, as a result of the strong CO adsorption on both, Pt<sup>2+</sup> and Pt<sup>0</sup> sites, CO can be used as a probe molecule to test inactivated samples, thus providing information about the coexistence of oxidized and reduced platinum on the surface. The stability of the different carbonyls is discussed in terms of the  $\sigma$ - and  $\pi$ -components of Pt—CO bond.

## 1 Introduction

There have been many studies devoted to the adsorption of CO on supported platinum.<sup>1–20</sup> This interest is provoked by the wide application of platinum as catalysts in various reactions.<sup>21</sup> The IR spectra of CO adsorbed on metal platinum are well documented. It is established that linear Pt<sup>0</sup>—CO species are characterized by a band at about 2060 cm<sup>-1</sup>, whereas bridged carbonyls produce a band at about 1850 cm<sup>-1</sup>.<sup>1–7</sup>

Surprisingly, very little attention has been paid to Pt<sup>n+</sup>—CO species.<sup>7–18</sup> Moreover, as a rule, these studies are focused on the reduced metallic platinum sites.<sup>7–15</sup> In most cases the oxidation number of platinum is not specified and the adsorption sites are denoted as Pt <sup>$\delta$ +</sup> or Pt<sup>n+</sup>.<sup>10–16,18</sup> The knowledge of the spectral characteristics of CO adsorbed on platinum cations is important because it can help in the clarifying of the processes of (i) formation of supported metal platinum and (ii) reoxidation of the metal under different conditions.

The most detailed study on this problem is that of Solomennikov and Davydov.<sup>17</sup> These authors reported that CO adsorption on oxidized Pt/Al<sub>2</sub>O<sub>3</sub> samples produced two bands: higher frequency (HF) at 2180 cm<sup>-1</sup>, and lower frequency (LF) at 2135 cm<sup>-1</sup>. The HF band was detected only with samples oxidized at temperatures higher than 300 °C. In a CO atmosphere this band was slowly converted into the LF band. The latter, on its behalf, was transformed into a band at 2080 cm<sup>-1</sup>, typical of metallic platinum. The authors attributed the HF band to Pt<sup>2+</sup>—CO species and the LF band to Pt<sup>+</sup>—CO carbonyls. White and co-workers<sup>19,20</sup> are of the opinion that the 2130 cm<sup>-1</sup> band is due to Pt<sup>0</sup>—CO carbonyls with an oxygen atom attached to the metal site. Other authors, however, assign the bands at *ca.* 2130 cm<sup>-1</sup> to species of the Pt<sup>2+</sup>—CO type.<sup>8,9</sup> The observations supporting such an interpretation can be summarized as follows. (i) XPS results have shown that oxidation of supported platinum at 100 °C results in formation of Pt<sup>2+</sup> cations. CO adsorption on a sample, treated in the same manner, results in the appearance of a band at about 2130 cm<sup>-1</sup>.<sup>20</sup> (ii) CO adsorption on

unreduced Pt<sup>2+</sup>/TiO<sub>2</sub> catalysts causes the appearance of LF bands at 2130–2110 cm<sup>-1</sup>.<sup>18</sup> (iii) The adsorption of COCl<sub>2</sub> on supported platinum metal produces a band at 2135 cm<sup>-1</sup> assigned to Pt<sup>2+</sup>(Cl)<sub>2</sub>—CO species.<sup>7</sup>

In this work the CO adsorption on unreduced and reduced Pt/TiO<sub>2</sub> samples was investigated. In order to obtain more information about the  $\sigma$ - and the  $\pi$ -components of the Pt—CO bond, the coadsorption of CO and water was also studied. Finally, the possibility of using CO as a probe molecule for testing Pt-containing samples without preliminary activation was demonstrated.

## 2 Experimental

### 2.1 Preparation of the samples

Commercially available titania (Degussa P-25, 75% anatase and 25% rutile, 54 m<sup>2</sup> g<sup>-1</sup>) was used as a support. To prepare a Pt/TiO<sub>2</sub> sample, platinum was deposited by anion-exchange as described elsewhere.<sup>18</sup> The starting material was a 1 wt.% Pt solution prepared from PtCl<sub>4</sub>. Titania powder was suspended in this solution for 1 h, and after that the sample was filtered and again put in contact (1 h) with the starting solution in order to ensure equilibrium with the initial solution composition. Then the precipitate was filtered, washed well with water, and dried at 80 °C. The Pt concentration in the sample was 0.73 wt.% Pt.

Another sample was prepared by double ion-exchange.<sup>18</sup> According to this technique, a sample of Pt/TiO<sub>2</sub> reduced with hydrogen at 100 °C was used instead of TiO<sub>2</sub> to perform the ion-exchange. All other procedures were exactly the same as those described for the preparation of Pt/TiO<sub>2</sub>. The sample synthesized by double ion-exchange is denoted 2Pt/TiO<sub>2</sub>, and contained 1.18 wt.% Pt.

### 2.2 Methods

IR spectroscopy studies were carried out with a Specord M-80 apparatus. Self-supporting pellets were prepared from the samples and heated directly in the IR cells. The latter were connected to a vacuum/adsorption apparatus with a residual pressure lower than 10<sup>-5</sup> Torr.

† This work is dedicated to the memory of Prof. A. Andreev.

Chemical analysis was performed by flame atomic absorption spectrophotometry using a PYE-UNICAM SP-1950 apparatus.

### 3 Results

The Pt/TiO<sub>2</sub> sample was activated by heating for 1 h under 100 Torr of oxygen at 400 °C and evacuation for 1 h at the same temperature. Adsorption of CO (10 Torr equilibrium pressure) on the sample thus treated leads to the appearance in the IR spectrum of two intense bands with maxima at 2188 and 2138 cm<sup>-1</sup> and a weak band at 2208 cm<sup>-1</sup> (Fig. 1). Evacuation results in a negligible decrease in intensity of the 2138 cm<sup>-1</sup> band and then a shoulder at 2090 cm<sup>-1</sup> can be detected. In addition, the band at 2208 cm<sup>-1</sup> disappears, whereas the 2188 cm<sup>-1</sup> band strongly decreases in intensity and its maximum is shifted to 2186 cm<sup>-1</sup>. In agreement with data from the literature,<sup>7-18</sup> the 2138 cm<sup>-1</sup> band is assigned to Pt<sup>n+</sup>-CO species. The bands at 2208 and 2188 cm<sup>-1</sup> are typical of Ti<sup>4+</sup> carbonyls on a bare titania surface. Many authors<sup>22-25</sup> have documented these two bands and have established that they are unstable upon evacuation and shift towards higher frequencies with decreasing coverage. This implies that the 2188 cm<sup>-1</sup> band is due to two different adsorption forms. The first characterizing reversibly bound species, arises from Ti<sup>4+</sup>-CO carbonyls. The irreversible part cannot be attributed to CO on Ti<sup>4+</sup> sites somewhat affected by chlorine ions since no irreversible CO adsorption is reported for Cl<sup>-</sup>-containing titania samples.<sup>23</sup> Evidently, it characterizes some kind of Pt<sup>m+</sup>-CO species. The shoulder at 2090 cm<sup>-1</sup> indicates the existence of small amounts of metallic platinum.

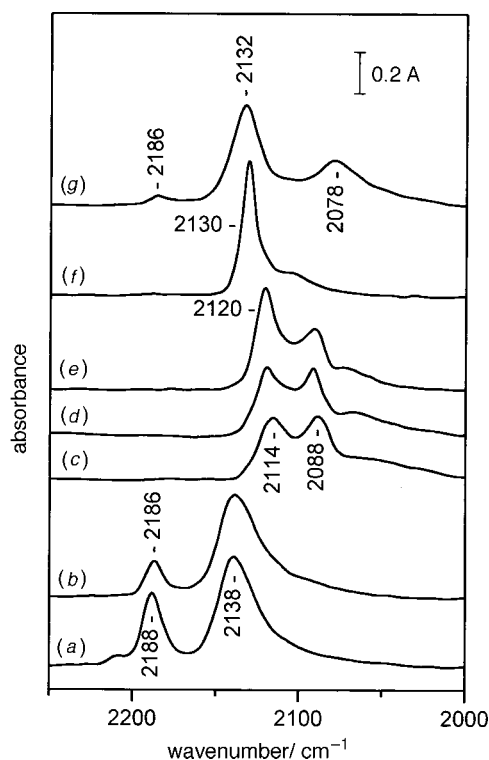
Adsorption of water vapor (3 Torr equilibrium pressure) on the CO pre-covered sample leads to drastic changes in the IR spectrum. In this case, two bands with maxima at 2114 and 2088 cm<sup>-1</sup> dominate the spectrum, while a shoulder at *ca.*

2070 cm<sup>-1</sup> is also visible. Simultaneously, a δ(H<sub>2</sub>O) band at 1625 cm<sup>-1</sup>, indicating the existence of molecularly adsorbed water is detected. Evacuation at elevated temperatures leads to a decrease in intensity of the 1625 cm<sup>-1</sup> band and an increase in intensity of the 2114 cm<sup>-1</sup> band at the expense of the band at 2088 cm<sup>-1</sup>. With sample dehydroxylation, the 2114 cm<sup>-1</sup> band is shifted towards higher frequencies and after evacuation at 200 °C one main band at 2130 cm<sup>-1</sup> is detected, the water δ(H<sub>2</sub>O) band is no longer visible. It should be noted that the overall intensity of the 2114 and 2088 cm<sup>-1</sup> bands increases in the series of spectra (c)–(e) which implies an increase of the average CO coefficient of molar absorptivity. All CO bands are removed from the spectrum after evacuation at 300 °C.

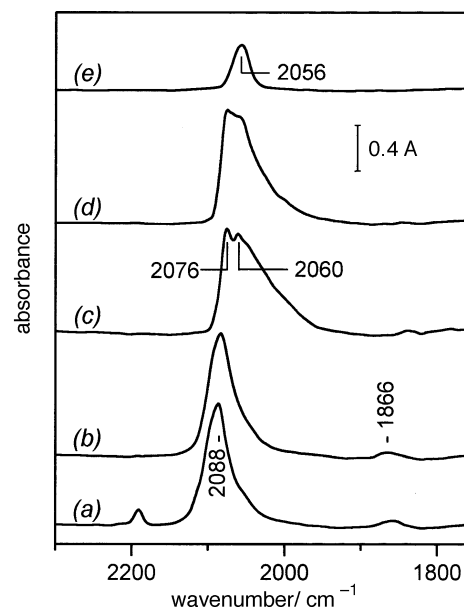
Three different types of platinum sites are well monitored on the sample surface by subsequent CO adsorption (10 Torr, followed by evacuation): Pt<sup>m+</sup>-CO (2186 cm<sup>-1</sup>), Pt<sup>n+</sup>-CO (2132 cm<sup>-1</sup>) and Pt<sup>0</sup>-CO (2078 cm<sup>-1</sup>). The coexistence of these three different platinum carbonyls can be explained by the assumption that reduction of some Pt<sup>n+</sup> to Pt<sup>0</sup> has occurred during the destruction of the Pt<sup>m+</sup>-CO complexes, whereas the Pt<sup>m+</sup> cations, where CO has been replaced by water, have not been affected by the CO desorption. In this case the Ti<sup>4+</sup>-CO bands are not visible because the respective carbonyls are destroyed during the evacuation.

The sample was reduced by hydrogen (1 h, 100 Torr H<sub>2</sub>, 200 °C). Separate TPR experiments have proved that this temperature is high enough to ensure a full reduction of platinum. On the other hand, no reduction of Ti<sup>4+</sup> occurs, which excludes transformation of our catalyst in a strong metal support interaction (SMSI) state.<sup>26,27</sup> Adsorption of CO (10 Torr equilibrium pressure) on the reduced sample leads to the appearance of two bands due to Ti<sup>4+</sup>-CO complexes (at 2208 and 2189 cm<sup>-1</sup>) and two bands assigned to linear and bridged Pt<sup>0</sup> carbonyls (2088 and 1860 cm<sup>-1</sup>, respectively). The intensity of the 2189 cm<sup>-1</sup> band is lower than for the oxidized sample, which confirms the proposed assignments of part of the band at this position to Pt<sup>m+</sup>-CO species. Evacuation causes disappearance of the Ti<sup>4+</sup>-CO bands, whereas the other two bands are only little changed: their maxima are now observed at 2084 and 1866 cm<sup>-1</sup> (Fig. 2).

After introduction of water vapor (3 Torr) into the cell, the band at 2084 cm<sup>-1</sup> undergoes a red shift to 2076 cm<sup>-1</sup> and



**Fig. 1** IR spectra of CO adsorbed on a Pt/TiO<sub>2</sub> sample. Equilibrium pressure of 10 Torr CO (a) and after 10 min evacuation (b); subsequent introduction of 3 Torr water vapor in the cell (c) and 10 min evacuation at ambient temperature (d); at 100 (e) and 200 °C (f); evacuation at 300 °C, followed by introduction of 10 Torr CO and subsequent evacuation (g).



**Fig. 2** IR spectra of CO adsorbed on a reduced Pt/TiO<sub>2</sub> sample. Introduction of 10 Torr CO (a), followed by 10 min evacuation (b), in the presence of 3 Torr of water vapor (c); after 10 min evacuation at 100 (d) and 200 °C (e).

decreases in intensity. At the same time a new tailed band at  $2060\text{ cm}^{-1}$  emerges. The existence of molecularly adsorbed water was evidenced by a band at  $1625\text{ cm}^{-1}$ . The spectrum is practically unaffected by evacuation at ambient temperature. Evacuation at  $100^\circ\text{C}$  results in a change of the shape of the CO feature; it becomes more symmetric and narrow. A symmetric, low intensity band at  $2056\text{ cm}^{-1}$  is the only one detected after evacuation at  $200^\circ\text{C}$  [no  $\delta(\text{H}_2\text{O})$  band is visible in this case]. With the reduced Pt/TiO<sub>2</sub> sample the red shift of the Pt<sup>0</sup>—CO band after water treatment is accompanied by an increase of its total intensity, i.e., contrary to the case of Pt<sup>n+</sup>—CO species, coadsorbed water enhances the CO molar absorptivity coefficient.

The observation that H<sub>2</sub>O does not block the Pt<sup>0</sup> and Pt<sup>n+</sup> sites for CO adsorption suggests that platinum containing catalysts can be tested by CO without preliminary activation, since the water is the principal adspecies on inactivated samples.

A Pt/TiO<sub>2</sub> sample was only evacuated for 1 h at ambient temperature and CO at 10 Torr was introduced into the IR cell. As a result, a strong and asymmetric band at  $2124\text{ cm}^{-1}$  and a very weak feature at  $2186\text{ cm}^{-1}$  were observed (Fig. 3). The  $2124\text{ cm}^{-1}$  band is evidently due to formation of Pt<sup>n+</sup>—CO species slightly affected by water.

Another inactivated sample tested by CO was 2Pt/TiO<sub>2</sub>, prepared by the double ion-exchange technique. The principle of this technique is the following.<sup>18</sup> The metal is deposited by simple ion-exchange and then reduced. During the reduction the active sites for exchange are liberated which allows a subsequent exchange to be performed. The reduced metal, however, may be reoxidized during sample exposure to air which might lead to reblocking of the active sites. To obtain more information about the mechanism of the process, a simultaneous detection of reduced and oxidized platinum has to be performed. Conventional IR spectroscopy of probe molecules is not appropriate for this purpose, because the oxidative/reduction treatment during activation can affect the oxidation state of the supported metal.

CO adsorption (10 Torr) on the 2Pt/TiO<sub>2</sub> sample, evacuated for 1 h at ambient temperature, causes the appearance of two bands with maxima at  $2123$  and  $2081\text{ cm}^{-1}$ . These bands are evidently due to carbonyls formed on Pt<sup>n+</sup> and Pt<sup>0</sup>

sites, respectively. Using reported values for the molar absorptivity coefficients of the different CO bands,<sup>7</sup> we estimated the ratio between the surface Pt<sup>n+</sup> and Pt<sup>0</sup> sites to be 1.14. The total Pt<sup>n+</sup> and Pt<sup>0</sup> ratio, calculated on the basis of chemical analysis data was 0.62, i.e. definitely lower (it is assumed that all of the platinum, deposited during the first ion exchange, 0.73 wt.%, is in the Pt<sup>0</sup> state, whereas the platinum loaded during the second exchange, 0.45 wt.%, is in the oxidized form; thus, the ratio Pt<sup>n+</sup>/Pt<sup>0</sup> would be 0.62). This is evidently due, in part, to the fact that not all of the platinum atoms are situated on the surface, however, partial oxidation of platinum may also have occurred. In this case no Pt<sup>m+</sup> species were detected which is probably due to their interaction with metallic platinum resulting in formation of Pt<sup>n+</sup>.

## 4 Discussion

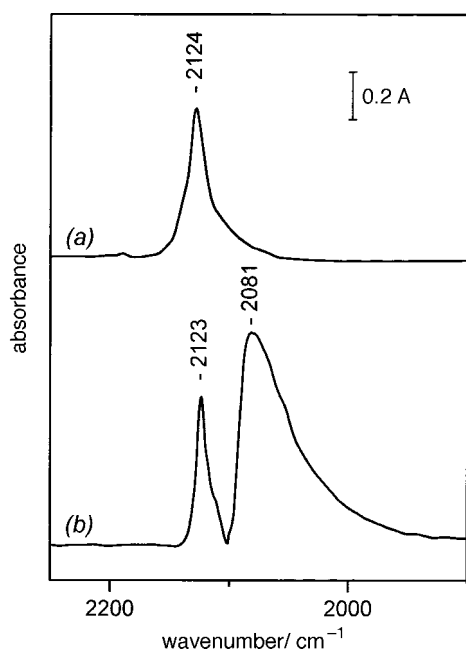
Platinum typically forms non-classical carbonyls. In a recent review Aubke and Wang<sup>28</sup> summarized the IR spectral data of Pt<sup>n+</sup> carbonyls. Owing to the high charge of Pt<sup>4+</sup> cations, CO is bound to them predominantly by  $\sigma$ -bonding. As a result, the CO stretching modes are observed at higher frequencies than for gaseous CO. For instance, [Pt(CO)Cl<sub>5</sub>]<sup>−</sup> shows band at  $2191\text{ cm}^{-1}$ . A back  $\pi$ -donation occurs to some extent for Pt<sup>2+</sup>—CO carbonyls. As a result, CO stretching modes may be observed over a wide spectral range, but are usually found at lower frequencies. Thus, the  $\nu(\text{CO})_{\text{av}}$  values for [Pt(CO)Cl<sub>3</sub>]<sup>−</sup> and [Pt<sub>2</sub>(CO)<sub>2</sub>Cl<sub>4</sub>] are observed at 2095 and  $2146\text{ cm}^{-1}$ , respectively.

When CO is coordinated to cations with a  $\sigma$ -bond only, the strength of the resulting carbonyls, reflected by the CO stretching frequency, is a measure of the adsorption site acidity. In these cases, strong bases, such as water and ammonia, suppress CO adsorption. By contrast, when back  $\pi$ -donation is predominant, a strong M—CO bond is formed. As a result, it may be expected that the heats of CO and H<sub>2</sub>O adsorption on such cations will be of the same order of magnitude and water (a strong Lewis base) will not fully suppress CO adsorption. Hence, a CO/H<sub>2</sub>O coadsorption experiment may provide valuable information for the  $\sigma$ - and  $\pi$ -components of the metal—CO bond.

The Pt<sup>n+</sup>—CO band at  $2186\text{ cm}^{-1}$  disappears in a water vapour atmosphere, which implies that it is due to  $\sigma$ -bonded carbonyls. Taking this into account, the fact that it characterizes more oxidized Pt sites than the band at  $2130\text{ cm}^{-1}$ , and the similarity with the stretching frequency of [Pt(CO)Cl<sub>5</sub>]<sup>−</sup> ( $2191\text{ cm}^{-1}$ ), we assign this band to Pt<sup>4+</sup>—CO carbonyls. Very weak Pt<sup>4+</sup>—CO bands were detected on water pre-covered and on non-activated Pt/TiO<sub>2</sub> samples. Its appearance may be due either to liberation of some Pt<sup>4+</sup> sites during evacuation, or to replacement of some water molecules in the CO atmosphere.

The band at *ca.*  $2130\text{ cm}^{-1}$ , in agreement with the view of other authors,<sup>7</sup> can be attributed to Pt<sup>2+</sup>—CO species. Two bands appear in its place in a water atmosphere, at  $2114$  and  $2088\text{ cm}^{-1}$ . The former band shifts to  $2130\text{ cm}^{-1}$  with sample dehydroxylation and may be attributed to Pt<sup>2+</sup>—CO carbonyls somewhat affected by water adsorbed on the support. However, the band at  $2088\text{ cm}^{-1}$  is converted into a higher-frequency band upon dehydroxylation and may be assigned to Pt<sup>2+</sup>(H<sub>2</sub>O)CO species. For the reduced sample, the shifted Pt<sup>0</sup>—CO bands may be due to indirect interaction between CO and water molecules adsorbed on the support.

Water is a strong Lewis base and transmits electrons to the site to which it is coordinated. This would result in an increase of the electron density and a decrease of the Lewis acidity of the site. Thus, two possibilities can be considered to explain the red shift of the CO stretching modes after coadsorption of water and CO on a Pt<sup>2+</sup> or Pt<sup>0</sup> site: increase in the back  $\pi$ -bonding or (ii) decrease of the  $\sigma$ -bond order



**Fig. 3** IR spectra of CO (10 Torr equilibrium pressure) adsorbed on inactivated Pt/TiO<sub>2</sub> samples prepared by ion-exchange (a) and double ion-exchange (b).

between  $\text{Pt}^{2+}$  and CO (and a simultaneous decrease in the  $\pi$ -bonding owing to synergism between both bonds). A reliable criterion for distinguishing between both effects is the CO molar absorptivity coefficient<sup>29</sup> which is strongly enhanced by the formation of a back  $\pi$ -bond but is practically independent of the strength of the  $\sigma$ -bond. The results imply that water coordination to  $\text{Pt}^{2+}$ —CO sites leads to some decrease in the back  $\pi$ -bonding which (due to the strong synergism between the  $\sigma$  and  $\pi$ -bonds) results in a substantial decrease in the order of the  $\sigma$ -bond between the cation and CO. By contrast for  $\text{Pt}^0$  sites, the opposite effect takes place, which is due to the weak  $\sigma$ -component of the  $\text{Pt}^0$ —CO bond.

Finally, it may be suggested that CO can be used as a probe molecule to test unactivated samples based on other metal cations forming a strong,  $\pi$ -stabilized bond with CO: *e.g.*  $\text{Ag}^+$ ,  $\text{Au}^+$ ,  $\text{Ru}^{n+}$ ,  $\text{Rh}^+$ ,  $\text{Pd}^{n+}$ ,  $\text{Os}^{n+}$  and  $\text{Ir}^+$ .

## 5 Conclusions

$\text{Pt}^{4+}$ —CO species formed after CO adsorption on oxidized Pt/TiO<sub>2</sub> samples show a band at  $2186\text{ cm}^{-1}$ . In these carbonyls CO is bonded *via* a  $\sigma$ -bond and as a result adsorbed CO is replaced by water.

$\text{Pt}^{2+}$ —CO species formed after CO adsorption on oxidized Pt/TiO<sub>2</sub> samples are characterized by a band at *ca.*  $2138\text{ cm}^{-1}$ . Here CO is bonded *via* both a  $\sigma$ -bond and back  $\pi$ -donation. Water molecules can be adsorbed on the same  $\text{Pt}^{2+}$  sites thus weakening the  $\sigma$ - and  $\pi$ -components of the  $\text{Pt}^{2+}$ —CO bond and shifting the CO band to  $2088\text{ cm}^{-1}$ .

$\text{Pt}^0$ —CO linear species produced after CO adsorption on a reduced Pt/TiO<sub>2</sub> sample absorb at *ca.*  $2080\text{ cm}^{-1}$ . Here a  $\pi$ -bond is predominantly formed. Water molecules can affect the adsorbed CO thus shifting the  $\text{Pt}^0$ —CO band to lower frequencies. In this case the shift is associated with an increase of the back  $\pi$ -donation of electrons.

CO can be used as a probe molecule to test inactivated Pt-containing samples, thus providing information about the coexistence of oxidized and reduced platinum on their surface.

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