

Letter

# XPS observation of surface interaction between H<sub>2</sub> and CO<sub>2</sub> on platinum foil

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## Abstract

Using XPS linearly adsorbed CO species were observed on Pt foil, as a result of the surface reaction between H<sub>2</sub> and CO<sub>2</sub> at room temperature. A small amount of bridged CO species was also detected upon adsorption of pure CO<sub>2</sub> over Pt foil, which suggests partial decomposition of CO<sub>2</sub>. However, subsequent exposure to hydrogen removed the bridged CO species, while a small portion of additional linear CO species was formed.

## 1. Introduction

Adsorption of simple gases such as CO, O<sub>2</sub>, H<sub>2</sub> and CO<sub>2</sub> on platinum has been the subject of XPS studies [1–7] over a large domain of pressure and temperature. Investigations of interaction between these simple gases using the XPS technique are, however, mainly concerned with those involving CO [5–9]. On the other hand, an increasing number of investigations using other methods has been devoted to the catalytic transformation of CO<sub>2</sub> into more valuable compounds, such as carbon monoxide, methanol, formate and hydrocarbons [10–12]. For example, the formation of chemisorbed CO from the H<sub>2</sub> + CO<sub>2</sub> reaction is reported by Solymosi et al. [13,14] over Rh/SiO<sub>2</sub>. In the case of platinum, the yield of CO from the same reaction at –60°C over Pt–silica has been cited by Bond [15] as early as in 1960's. This reaction is also claimed by Nagy et al. [16] over platinum

metal, using mass spectrometric detection of isotopically marked molecules <sup>14</sup>CO<sub>2</sub> and C<sup>18</sup>O. Another recent paper [17] also reports this reaction under electrochemical conditions on platinum metal. A particular potential (–0.20 V) at which co-adsorbed hydrogen is present is however required. More recently [18] the occurrence of this reaction at room temperature over Silicalite-supported platinum was established by the direct IR observation of the chemisorbed CO formed. According to our knowledge, no XPS data about the interaction between H<sub>2</sub> and CO<sub>2</sub> over platinum have been reported. In the current work, the interaction between H<sub>2</sub> and CO<sub>2</sub> is investigated on pure polycrystalline Pt metal using XPS. Obviously, the direct observation on pure metal avoids the complexity due to the presence of a support, and it is then a necessary premise for the further study of supported Pt catalysts using the same technique.

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## 2. Experimental

The platinum foil was from Aldrich Inc. It was 0.025 mm thick with a purity of 99.99%. All the H<sub>2</sub>, CO<sub>2</sub>, CO and O<sub>2</sub> gases were obtained from Air Products Inc. Ultra-pure hydrogen (99.9999%) was employed in this work, while the purity of other gases was 99.9%.

A V.G. Scientific Escalab Mark II system with a hemispherical analyzer was employed in XPS experiments. A Mg K $\alpha$  X-ray source ( $h\nu = 1253.6$  eV) was operated at 20 mA and 15 kV. Spectra were recorded at room temperature or liquid nitrogen temperature (77 K). The pressure in the XPS analysis chamber was less than 10<sup>-9</sup> Torr. In XPS experiments the Pt foil was always first sputtered with Ar ions in situ. During the sputtering the holder was rotated by 90° every 15 min. The sputtering lasted for one hour using an Ar ion beam of 5 keV energy. The beam intensity was 30  $\mu$ A while its sectional area was 1 cm<sup>2</sup>. The platinum foil was usually exposed to various atmospheres at room temperature before XPS recording. The exposure was performed in a treatment chamber, which allows a pressure of one atmosphere for every kind of gas and also evacuation down to 10<sup>-3</sup> Torr. The details of the pretreatments are listed in Table 1.

## 3. Results and discussion

The clean platinum foil obtained after ion sputtering showed the typical Pt<sub>4f</sub> peak of platinum metal, located at 71.06 eV [19,20]. Meanwhile, there was no oxygen signal and only a minor C<sub>1s</sub> signal was detected around 284.4 eV (Fig. 1 and Fig. 2).

Further treatments in this work caused a very slight increase in Pt<sub>4f</sub> binding energy, while the FWHM also showed a small increase in most of the cases (Table 2). A similar phenomenon was observed by Legare et al. [4] for adsorption of oxygen on platinum, namely, no shift of the peak or change in its shape of the Pt<sub>4f</sub> signal could be detected upon exposure to oxygen, though chemisorbed oxygens were detected by O<sub>1s</sub> signals. Thus our conclusion is that the adsorption of O<sub>2</sub>, CO and CO<sub>2</sub> under our conditions is not able to cause any remarkable change in the Pt<sub>4f</sub> lines. This was an expected result since the adsorption of these simple gases would not result in a large charge transfer between adsorbate and adsorbent. In fact, the Pt<sub>4f7/2</sub> binding energy of platinum bearing adsorbed oxygen was located at 71.1 eV [21], which was close to that of platinum metal.

The O<sub>1s</sub> region yielded some significant information. A series of previous publications con-

Table 1  
XPS pretreatment and measurement conditions

Name of pretreatment	Pretreatment	Measurement temperature
(Initial state)	sputtering	RT
(CO)	sputtering; exposure to CO atmosphere for one min, evacuation	RT
(H <sub>2</sub> + CO)	sputtering; exposure to H <sub>2</sub> atmosphere for 5 min, evacuation; exposure to CO atmosphere for 1 min, evacuation	RT
(O <sub>2</sub> )	sputtering; exposure to O <sub>2</sub> atmosphere for 3 min, evacuation	RT
(O <sub>2</sub> + CO)	sputtering; exposure to O <sub>2</sub> atmosphere for 5 min, evacuation; exposure to CO atmosphere for 1 min, evacuation	RT
(H <sub>2</sub> )	sputtering; exposure to H <sub>2</sub> atmosphere for 5 min, evacuation	RT
(H <sub>2</sub> + CO <sub>2</sub> )	sputtering; exposure to H <sub>2</sub> atmosphere for 5 min, evacuation; exposure to CO <sub>2</sub> atmosphere for 4 h, evacuation	77 K
(H <sub>2</sub> + CO <sub>2</sub> )-RT	following above measurement, increase the temperature to RT	RT
(CO <sub>2</sub> )	sputtering; exposure to CO <sub>2</sub> atmosphere for 5 min, evacuation	77 K
(CO <sub>2</sub> + H <sub>2</sub> )	sputtering; exposure to CO <sub>2</sub> atmosphere for 5 min, evacuation; exposure to H <sub>2</sub> atmosphere for 5 min, evacuation	RT

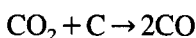
cluded that the  $O_{1s}$  binding energy of CO linearly chemisorbed (on-top) on platinum was located at 532.7 eV [1–3,22]. Fig. 1 shows that the binding energy after CO adsorption (532.6 eV) is in good agreement with the literature results. In the case of chemisorbed oxygen, early reports suggested a value of 530.2 eV [1] for the corresponding  $O_{1s}$  signal. However, a recent result observed on polycrystalline platinum revealed that an  $O_{1s}$  binding energy at 530.2 eV was from the presence of PtO species, while the  $O_{1s}$  binding energy of chemisorbed oxygen on platinum was located between 530.9 and 531.6 eV [22]. In this work the  $O_{1s}$  binding energy observed after adsorption of pure oxygen was found at 530.9 eV. When CO was adsorbed after the pre-adsorption of hydrogen (Fig. 1,  $H_2 + CO$ ), the  $O_{1s}$  binding energy was still located at 532.6 eV; however, the intensity of the peak was slightly increased. When CO was adsorbed after the pre-adsorption of oxygen (Fig. 1,  $O_2 + CO$ ), the  $O_{1s}$  line became broader and the apparent binding energy shifted to 531.8 eV. Obviously, this  $O_{1s}$  line was actually a combination of two different  $O_{1s}$  components: the chemisorbed CO and the chemisorbed oxygen. A computer deconvolution suggested that the atomic ratio between chemisorbed CO and chemisorbed oxygen species was around 0.75. The coexistence of two adsorbed species and also the weaker intensity (Fig. 1,  $O_2 + CO$ ) revealed that the CO was not replacing all of the pre-adsorbed oxygen on platinum. Vice versa, the pre-adsorbed oxygen prevented the adsorption of CO.

After hydrogen adsorption (Fig. 1,  $H_2$ ) a very weak fluctuation appeared in the  $O_{1s}$  region. It might be due to adsorption of a minor oxygen impurity of the hydrogen gas. It was, however, so weak that it could not be clearly distinguished from the base line. The subsequent exposure to  $CO_2$  at room temperature caused a dramatic change in the  $O_{1s}$  region (Fig. 1,  $H_2 + CO_2$ ). The binding energy in this case was clearly located at 532.6 eV, indicating the formation of a new adsorbed species, which possesses the same  $O_{1s}$  binding energy as that of chemisorbed CO. In addition to the 532.6 eV peak, a shoulder peak is

Table 2  
Binding energy and FWHM of  $Pt_{4f7/2}$  of platinum foil (eV)

Treatment	$Pt_{4f7/2}$	$Pt_{4f5/2}$	FWHM of $Pt_{4f7/2}$
(Initial state)	71.06	74.34	1.37
(CO)	71.11	74.37	1.43
( $H_2 + CO$ )	71.13	74.44	1.46
( $O_2$ )	71.14	74.43	1.50
( $O_2 + CO$ )	71.10	74.42	1.52
( $H_2$ )	71.05	74.32	1.36
( $H_2 + CO_2$ )	71.19	74.52	1.40
( $H_2 + CO_2$ )-RT	71.09	74.38	1.37
( $CO_2$ )	71.14	74.46	1.38
( $CO_2 + H_2$ )	71.16	74.51	1.35

also visible at 531.2 eV. Increasing the temperature (Fig. 1, ( $H_2 + CO_2$ )-RT) slightly reduced the intensity of the  $O_{1s}$  peak. The possible sources for the new adsorbed species have to be discussed before its assignment. First, it is not due to minor CO impurity contained in the  $H_2$  or  $CO_2$ . In the blank experiments there is no  $O_{1s}$  binding energy at this position (532.6 eV) observed after sole introduction of  $H_2$  or  $CO_2$  under the same operating conditions (Fig. 1  $H_2$  and Fig. 1  $CO_2$ ). Secondly, this species cannot be from the decomposition of  $CO_2$ . In fact, the  $O_{1s}$  binding energy after adsorption of pure  $CO_2$  was not located at 532.6 eV but at 531.2 eV, and subsequent exposure to hydrogen removed almost all the  $O_{1s}$  signal (Fig. 1,  $CO_2 + H_2$ ). In another experiment, even after exposure to  $CO_2$  for 4 h at room temperature, the main  $O_{1s}$  binding energy was still located at 531.2 eV (spectrum not shown), while the intensity became weaker. Finally, the above result obtained after sole introduction of  $CO_2$  also ruled out the possibility of reverse CO disproportionation reaction, namely, no CO was produced through the following reaction:



even though some carbonaceous material is observed on the surface of platinum (see below). Thus the new adsorbed species can only be the result of surface interaction between pre-adsorbed  $H_2$  and  $CO_2$  at room temperature. Several possible

oxygen containing species can be listed as follows:



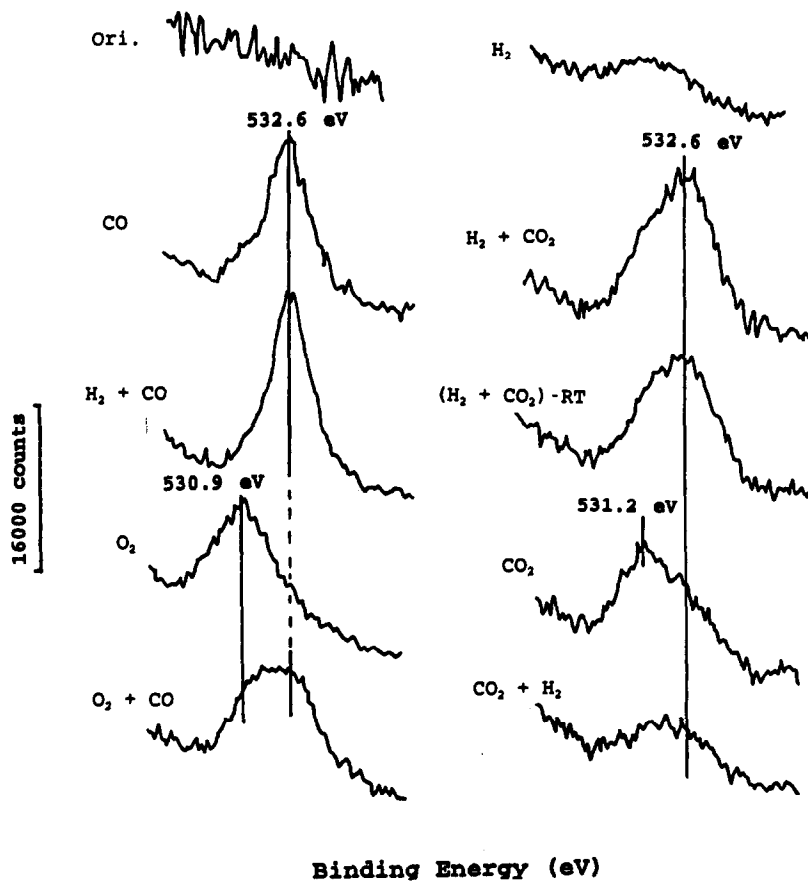
The  $\text{O}_{1s}$  binding energy for linearly and bridged adsorbed CO species on Pt is located at 532.7 and 531.0 eV, respectively. The  $\text{O}_{1s}$  binding energy for surface species  $-\text{COH}$  and  $\gtrsim\text{COOH}$  on carbon black is well known in the literature (Table 3 [24,25]). Since Pt possesses an electronegativity which is comparable to that of the carbon atom (2.2 for Pt and 2.5 for C [23]), it is then expected that their influence on  $\text{O}_{1s}$  binding energy of these adsorbed species should be similar. Table 3 summarizes these data. Clearly, the  $\text{O}_{1s}$  binding energy of the new species suggests that it may be the adsorbed  $-\text{CO}$  or  $\gtrsim\text{COH}$  species. Similarly, the new peak at 531.2 eV (Fig. 1,  $\text{CO}_2$ ) may suggest a species such as bridged adsorbed CO or a  $\text{C}=\text{O}$

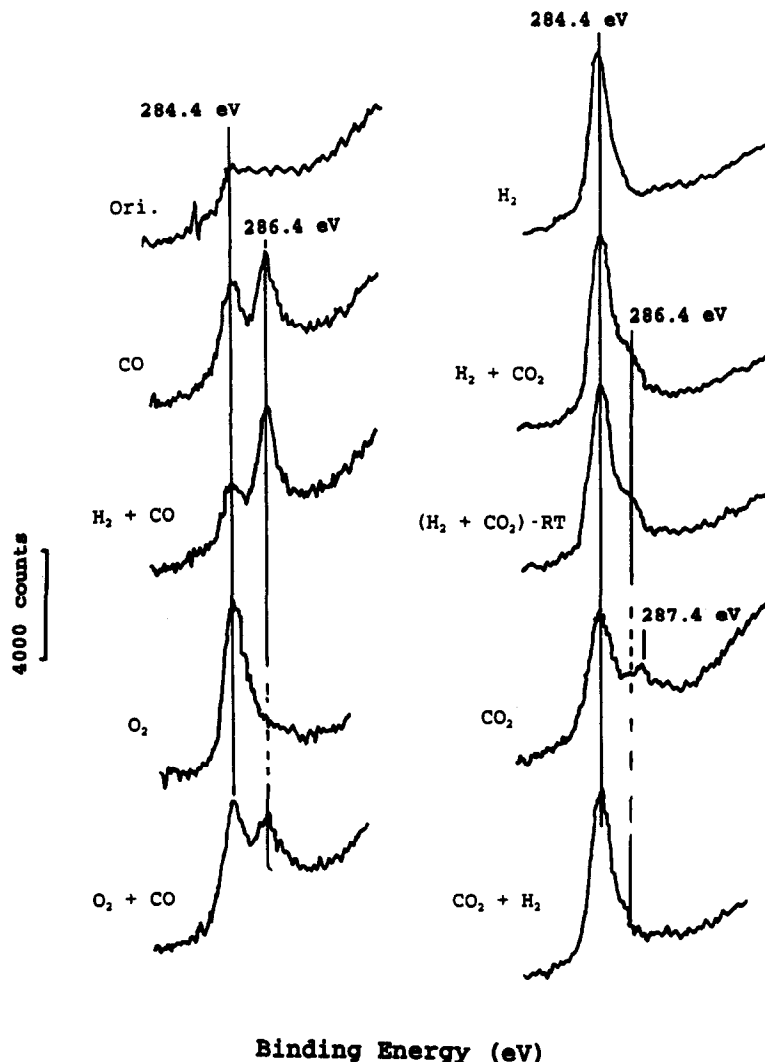
Table 3

The  $\text{O}_{1s}$  and  $\text{C}_{1s}$  binding energy of some surface species

Species	$\text{O}_{1s}$ (eV)	$\text{C}_{1s}$ (eV)	Ref.
$-\text{C}\equiv\text{O}$	532.7	286.6	[1–3,22]
	532.6	286.4	this work
$\equiv\text{C}-\text{O}-\text{H}$	532.6	285.9	[24,25]
$=\text{C}=\text{O}$	531.0	287.4	[22]
$-\text{C}(=\text{O})-\text{O}-\text{H}$	531.2	288.6	[24,25]
new species	532.6	286.4	this work

group in an organic species [24,25] such as  $\text{COOH}$ . However, it is very unlikely that an organic species could be formed on the Pt surface upon sole adsorption of  $\text{CO}_2$ . The appearance of a 531.2 eV peak then suggests a partial decomposition of  $\text{CO}_2$  on the Pt surface. However, only bridged CO species is formed from this decomposition and subsequent exposure to hydrogen removes these bridged CO species.

Fig. 1.  $\text{O}_{1s}$  XP spectra.

Fig. 2.  $C_{1s}$  XPS spectra.

A weak  $O_{1s}$  signal located at 534.5 eV was obtained [1] upon adsorption of  $CO_2$  on Pt at 77 K. It was assigned to adsorbed  $CO_2$ . The same author later concluded [3] that  $CO_2$  was only physisorbed on the Pt surface. The  $O_{1s}$  of adsorbed water was also located at around 535.0 eV [2]. In this work, no  $O_{1s}$  component due to adsorbed  $CO_2$  or water was distinguished from the spectra even for XPS data recorded at 77 K. Further computer deconvolution results suggest that these species, adsorbed  $CO_2$  and water, may exist in the cases of  $CO_2$  and  $(H_2 + CO_2)$  adsorption; and the molar portion of these species is about 10% of the surface oxygen species. The appearance of adsorbed water

in the case of  $(H_2 + CO_2)$  is reasonable, since it should be another surface product of  $H_2 + CO_2$  reaction, no matter which one of adsorbed  $-CO$  or  $\geq COH$  is the new species.

The  $C_{1s}$  binding energy yields more information about the  $H_2 + CO_2$  interaction.  $C_{1s}$  literature results are also listed in Table 3. The  $C_{1s}$  lines recorded after different treatments are shown in Fig. 2. When  $CO$  was introduced to the platinum foil (Fig. 2:  $CO$ ,  $H_2 + CO$  and  $O_2 + CO$ ), a common peak was detected at 286.4 eV, which is in good agreement with the literature results. Another peak located at 284.4 eV was always detected in all cases of the study. For example,

after adsorption of pure oxygen or hydrogen, an even stronger peak appeared at this position. This peak may be due either to elemental carbon or to hydrocarbon carbon [20]. However as shown in Fig. 2 this peak was very weak in the spectrum of the initial sample indicating a minor contribution from the residual hydrocarbons in the spectrometer. Then there is a possibility that traces of hydrocarbons would have been introduced as impurities in the adsorbed gases. We however do not believe that such is the case because changing the hydrogen gas to ultrahigh purity (99.9999%) did not result in decrease of the intensity of this line. Therefore we believe that this 284.4 eV line is due to elemental carbon. The purity of the platinum foil used in this work is 99.99%, and a weak  $C_{1s}$  peak was still detected after sputtering. Therefore the appearance of elemental carbon upon adsorption of oxygen or hydrogen may be a phenomenon of surface concentration of bulk carbon impurity. Bulk carbon atoms would be attracted to the surface upon adsorption of oxygen or hydrogen. In any case, the location of the  $C_{1s}$  line of elemental carbon is quite far from that of chemisorbed CO and/or COH (2 eV).

When  $CO_2$  was adsorbed after pre-adsorption of hydrogen, a shoulder at 286.4 eV appeared (Fig. 2,  $H_2 + CO_2$ ). Therefore, in agreement with  $O_{1s}$  results, the  $C_{1s}$  line also revealed the formation of chemisorbed  $-CO$  or  $\geq COH$  upon reaction of  $CO_2$  with adsorbed hydrogen at room temperature. Since the  $C_{1s}$  binding energy of the new species is closer to that of CO (Table 3), it is likely to be adsorbed CO rather than adsorbed COH. An interesting result came from the direct exposure to  $CO_2$  (Fig. 2,  $CO_2$ ), where a new and weak peak at 287.4 eV was detected, which is the same as that of bridged adsorbed CO. As reported above, this  $O_{1s}$  results also suggests the formation of bridged CO species from partial decomposition of  $CO_2$ . It is noted that the subsequent introduction of  $H_2$  caused an apparent change in the spectrum of  $C_{1s}$  signals (Fig. 2,  $CO_2 + H_2$ ). The peak responsible for the C=O group disappeared, while a weak shoulder peak is displayed at 286.4 eV, which was already assigned to the linearly adsorbed CO.

The  $C_{1s}$  binding energy of chemisorbed  $CO_2$  was reported at 291.0 eV [1]. However, the intensity of this reported signal was very weak even though it was recorded at 77 K. In our cases, no distinguishable peak at this position was detectable throughout this work. This is also consistent with the above  $O_{1s}$  result, namely, no  $CO_2$  could be directly detected from  $O_{1s}$  signals.

#### 4. Conclusion

In agreement with literature,  $CO_2$  is very weakly adsorbed on the Pt foil at 77–298 K. However, direct spectroscopic evidence is obtained for the interaction of  $CO_2$  with pre-adsorbed  $H_2$  at room temperature, which results in a new adsorbed surface species strongly held by the Pt surface and which cannot be removed by evacuation at room temperature under high vacuum ( $10^{-9}$  Torr). Based on the literature results and also on a series of blank experiments in this work, the new adsorbed species is suggested to be linearly chemisorbed CO.

Chemisorbed CO is also produced in a relatively small amount on Pt foil upon pre-adsorption of  $CO_2$  followed by adsorption of  $H_2$ . The C=O group was detected in the adsorption of pure  $CO_2$ , which may suggest a partial decomposition of  $CO_2$  over the Pt foil. However, mainly a bridged CO species was formed from this decomposition.

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