DISSOCIATIVE ADSORPTION OF CO2 ON OXIDIZED AND REDUCED Pt/TiO2.

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by

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On both oxidized and reduced Pt/TiO₂, carbon dioxide decomposes at room temperature to form chemisorbed oxygen atoms and carbon monoxide. In the absence of Pt, no decomposition was found. On reduced samples, the oxygen atoms were stabilized on the titania support and reacted further with CO₂ to form adsorbed bidentate carbonate. On reduced Pt/TiO₂, the adsorbed CO produced in the decomposition reaction produced a linearly bound species at step sites in the initial stages of the reaction. As the reaction proceeded, CO adsorbed linearly on terrace sites was found. On oxidized Pt/TiO₂, the decomposition rate was much slower.
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1. Introduction.

Since the discovery by Prins et al. (1) of frequencies associated to adsorbed CO after exposure of Rh/Al₂O₃ catalysts to CO₂, many papers have been published dealing with the interaction of CO₂ with Rh-based catalysts. Somorjai et al. (2-4) studied CO₂ adsorption on several Rh single crystal and polycrystalline samples and found evidence for dissociation of CO₂ using electron energy loss vibrational spectra. However, several other groups find no evidence for dissociated CO₂ on Rh. (5-7) Recently, Itoh et al. (8) reported that CO₂ interacting with Rh/Al₂O₃ dissociates in the presence, but not in the absence, of H₂. There is disagreement on this point as Fisui and Tanaka (9) find on a similar substrate that CO₂ is dissociated at 300K and moderate CO₂ pressures even in the absence of H₂.

In this paper, we report the dissociation of CO₂ on both reduced and oxidized samples of Pt/TiO₂. A discussion of the latter involved in the dissociation of CO₂ as well as those involved in the retention of the reaction products is presented. Previously, we have reported that CO₂ is not adsorbed at no substrate. Species are formed on reduced TiO₂. (10) Upon exposure of Pt/TiO₂ to CO₂, we have found two kinds of adsorbed linear CO species attributed to step and terrace sites. (11) Here we find that CO₂ dissociates leads to several kinds of carbonate species on Pt, and both step and terrace CO species on Pt.

2. Experimental.

All the procedures used here were identical to those reported in another paper from this laboratory. (11) Infrared spectra were taken on a Nicolet FT-IR spectrometer and were recorded in absorbance with 2 cm⁻¹ resolution. Spectra reported here have been corrected by subtraction for absorption of the gas phase, the solid adsorbent before adsorption and the CaF₂ windows. All spectra were recorded at room temperature.

Anastase (MCM) was reduced with H₂ at 400°C and soaked in dilute chloroplatinic acid solution to get 2 wt.% Pt/TiO₂. The sample was dried at 100°C and then washed with distilled water until no chloride could be detected in the wash water. The same procedure has been followed to obtain active catalysts for photo-assisted reactions. (12-16)

Pellets for IR analysis were pressed between two pieces of paraffin paper; the advantages and disadvantages of this procedure have been discussed previously. (11) Each pellet was oxidized at 400°C in the IR cell in order to remove paraffin fragments.

Three kinds of Pt/TiO₂, each with a different reduction temperature were used in this work. For simplicity each sample is denoted by three temperatures, the oxidation, reduction and evacuation temperatures. For example, the notation 400-300-400 signifies oxidation at 400°C, reduction at 300°C and evacuation at 400°C.

Reactant CO₂ was degassed and purified by pumping through two cold traps maintained at 77 and 195K. These procedures were performed with great care to eliminate any residual CO that might be present in the reactant gas. All interactions of CO₂ with the substrates were carried out at 300K.
3. Results and Discussion.

Carbon dioxide adsorption on a 400-200-400 substrate is shown in Fig. 1. When 20 torr of CO$_2$ was introduced, Fig. 1a, bands at 2354, 2243, 2273, 1251 and 1245 cm$^{-1}$ were observed. After 15 min, Fig. 1b, a new band was found at 2092 cm$^{-1}$. After 1 hr, Fig. 1c, the 2354 cm$^{-1}$ band intensity decreased about 10% and the 2077 cm$^{-1}$ band increased by about a factor of 2. A 23 hr exposure, Fig. 1d, led to an order of magnitude decrease in the intensity of the 2354 cm$^{-1}$ band and a shift to 2145 cm$^{-1}$. In addition, new bands appeared at 1671 and 1617 cm$^{-1}$ while the intensity of the 2077 cm$^{-1}$ band increased by a factor of 3. Subsequent evacuation at 20°C for 30 min. Fig. 1e, left only the bands at 2092, 2077 and 1617 cm$^{-1}$.

The bands of Fig. 1 are assigned as follows. In accord with the work of Matzner et al.\(^{17}\) and our previous work\(^{10}\), the 2354 and 2243 cm$^{-1}$ peaks are assigned to coordinated CO$_2$ and $^{13}$CO$_2$ (natural abundance), the 1245 and 1673 cm$^{-1}$ bands to bidentate carbonate and the 1598 and 1245 cm$^{-1}$ bands to bicarbonate, respectively. No monodentate carbonate was detected in these experiments.

The bands at 2077 and 2092 cm$^{-1}$ are assigned to linear CO species on step and terrace sites, respectively. (The step-terrace language is used here but the results may be discussed equally well in terms of open and close-packed microcrystallite faces.) These band positions are in excellent agreement with those observed on both reduced and oxidized Pt/TiO$_2$.\(^{11}\) The appearance of these two bands and the time dependence of their development indicate clearly that CO$_2$ is dissociating on Pt/TiO$_2$ and that the product CO occupies terrace sites only after the step sites are filled. It is significant that the absorbance of the 2077 cm$^{-1}$ peak, Fig. 1e, is 0.25 which is about 25% of that observed at 2094 cm$^{-1}$ when this substrate is exposed to CO.\(^{11}\) This indicates that the number of adsorbed CO molecules is much larger than could be accounted for on the basis of impurities in the CO$_2$. Additional evidence that the observed CO bands are not due to artifacts, such as CO desorption from the walls, comes from water adsorption experiments where no CO peak was observed.

When this substrate was exposed to CO$_2$ a bridged species at 1854 cm$^{-1}$ was found.\(^{11}\) The fact that it is not found here is ascribed to the relatively low coverage of CO. Peeters and Ibach,\(^{18}\) using high resolution electron energy loss spectroscopy, find that on Pt(111) bridged species appear only at high coverages of CO.

The behavior of the carbonate bands provides insight into the surface processes involving the oxygen atoms formed in the decomposition of carbon dioxide. In the early stages of the reaction, Fig. 1a, b and c, coordinated CO$_2$ dominates the spectrum. Some bicarbonate is found along with a hydrogen bonded species involving two adjacent OH groups of bicarbonate species. 1245 cm$^{-1}$ (not shown here).\(^{10}\) In another paper,\(^{10}\) we show that two interacting bicarbonate species have water and coordinatively unsaturated Ti sites which are active for the formation of bidentate carbonate species in a reaction with CO$_2$.\(^{11}\)
This is shown schematically in the following equation.

\[ 2 \text{Ti}^{2+} + 2\text{CO}_2 \rightarrow 2\text{Ti}^{4+} + 2\text{CO}_2 + \text{H}_2\text{O} \]

\[ \overset{\text{Bicarbonate}}{2\text{C}} \]

\[ \overset{\text{Bidentate Carbonate}}{2\text{C}} \]

\[ \text{CO}_2 \]

Here, □ represents a vacant coordination site on Ti. These processes are also thought to take place here. While the formation of bidentate carbonate is a convenient way to describe the role played by oxygen atoms formed in the decomposition of CO\(_2\), the situation is complicated on 400-200-400 materials since it is not clear whether the oxygen atoms produced in the decomposition process change the surface enough to form bidentate carbonate or whether the reduced sample possesses these sites intrinsically.

To address this question, a 400-400-400 sample was exposed to 10 torr of CO\(_2\) at 300°C. Bidentate carbonate species (1674 cm\(^{-1}\)), bicarbonate (1435 cm\(^{-1}\)), and coordinated CO (2347 cm\(^{-1}\)) were found after 1 min. Fig. 2a, emphasizing that reduced samples do possess sites for bicarbonate formation. This contrasts to interactions in the absence of Pt where no carbonate species are found.\(^{(10)}\) With 1 hr, 20 min and 2 hr as shown in Fig. 2b and 2c, there were slow changes. After 2 hr, Fig. 2c, the intensity of the coordinated CO\(_2\) species dropped by a factor of 3 and a small amount of linear CO appears at 2056 cm\(^{-1}\) indicating dissociation of CO\(_2\).

It is also of interest that, during CO\(_2\) exposure, the intensity of a broad band in the 1000-1200 cm\(^{-1}\) range increased. This is due to Ti-O lattice vibrations and suggests that some of the oxygen atoms derived from the CO\(_2\) decomposition originate on previously reduced TiO\(_2\) surface. Many papers have dealt with the structure of TiO\(_2\) following reduction at 500°C and it is thought to be best described as TiO\(_{2-\delta}\)\(^{(19-22)}\) or Ti\(_3\)O\(_7\)\(^{(22)}\). In addition to oxidizing the surface, oxygen atoms can change the surface coordination to lead to bidentate carbonate as follows.

\[ \overset{\text{Ti}}{\text{O}} + \overset{\text{O}}{\text{Ti}} \rightarrow \overset{\text{O}}{\text{Ti}} + \overset{\text{Ti}}{\text{O}} \]

\[ \overset{\text{Ti}}{\text{O}} \]

\[ \overset{\text{Ti}}{\text{O}} \]

\[ \overset{\text{CO}}{\text{O}} \]

Picking up two electrons corresponds to oxidation of the Ti center.

The very weak intensity of linear CO bands in Fig. 2, as compared to Fig. 1, is related to the strong metal-support interaction (SMSI) effect widely discussed in the literature\(^{(22)}\), and prevailing on strongly reduced Pt/TiO\(_2\). In the early stages of the reaction, Fig. 2, the formation of bidentate carbonate species at 1674 cm\(^{-1}\) is accompanied by the dissociation of CO\(_2\). However, the SMSI effect lowers significantly the adsorption capacity for CO and very little adsorbed CO accumulates. A decrease of 1435 cm\(^{-1}\) intensity and the appearance of the water
bending mode at 1628 cm\(^{-1}\) is readily explained by reaction (1).

Figure 3 shows the results of \(\text{CO}_2\) exposure on a 400-NO-400 sample, i.e. oxidized at 400°C but not reduced. After a 10 min exposure, Fig. 3, to 20 torr of \(\text{CO}_2\) at 25°C, bands were observed at 2154, 1674, 1628, 1557 and 1434 cm\(^{-1}\). These are assigned to coordinated \(\text{CO}_2\) and \(^{13}\text{CO}_2\) bicarbonate, carbonate, water and a set of bands due to bicarbonate, respectively. After 90 min, Fig. 3c, the coordinated \(\text{CO}_2\) intensity (2352 cm\(^{-1}\)) dropped by about one order of magnitude while bands due to water (1628 cm\(^{-1}\)) and carbonate (1674 cm\(^{-1}\)) doubled. These increases were accompanied by a decrease of the bicarbonate (1434 cm\(^{-1}\)) intensity and the relation is understood in terms of reaction (1).

After 3 days, Fig. 3c, the coordinated \(\text{CO}_2\) intensity dropped to a negligible level, a band due to linear \(\text{CO}\) on Pt appeared at 2170 cm\(^{-1}\), step sites, the water band at 1628 cm\(^{-1}\) grew and the bicarbonate bands at 1597 and 1434 cm\(^{-1}\) decreased. The slope observed below 1700 cm\(^{-1}\) is attributed to inadequate subtraction.

The slow formation of adsorbed \(\text{CO}\) species is very interesting. In another paper (24) we reported that \(\text{CO}\) interacted with this kind of support to form \(\text{CO}_2\) and carbonates but the oxygen atoms on step sites were more difficult to remove than those on terrace sites. The results obtained here suggest that some sites are still active for \(\text{CO}_2\) dissociation when the surface is covered with oxygen atoms. However, the reactions are extremely slow. The observed \(\text{CO}\) frequency, 2070 cm\(^{-1}\), indicates adsorption at step sites and is consistent with the results of Fig. 1 where step sites are filled before terrace sites.

These experimental results imply that \(\text{CO}_2\) dissociation takes place either on step sites or at the interface between Pt sites and the \(\text{TiO}_2\) support. If the latter occurs then migration of \(\text{CO}\) to steps must occur subsequently. Such processes are well known on single crystal surfaces. (24) Since adsorbed oxygen atoms cover step sites strongly and selectively (12) it is difficult to see how \(\text{CO}\) is selectively adsorbed on step sites. We ascribe \(\text{CO}_2\) dissociation to all conditions used in this work, to reaction at step sites. This readily accounts for the results of Figs. 1 and 3 where the Pt morphology, non-SMSI, is characterized by rough hemispherical particles with high concentrations of steps and kinks rather than flat particles dominated by Pt(111). (12) As noted in the introduction, there is disagreement about whether or not \(\text{CO}_2\) dissociation occurs on Rh samples. Our results point to surface heterogeneity as one possible explanation for this disagreement. Step sites or open faces, present in significant concentrations, could account for the dissociation.
References


FIGURE CAPTIONS

Figure 1. CO$_2$ adsorption at 25°C on a Pt/TiO$_2$ sample reduced at 200°C (400-200-400). (a)-(d) 20 torr CO$_2$ exposure for 5 min, 15 min, 1 hr and 2 hr, respectively. (e) Evacuation at 25°C for 10 min after (d).

Figure 2. CO$_2$ adsorption at 25°C on a Pt/TiO$_2$ sample reduced at 40°C (400-400-400). (a)-(c) Exposure time of 5 min, 20 min and 72 hr, respectively.

Figure 3. CO$_2$ adsorption at 25°C on an oxidized Pt/TiO$_2$ sample (400-400-400). (a)-(c) Exposure time of 10 min, 90 min and 3 days, respectively.

FIGURE CAPTIONS

Figure 1. CO$_2$ adsorption at $25^\circ$C on a Pt/TiO$_2$ sample reduced at 200$^\circ$C (400-200-400). (a)-(d) 20 torr CO$_2$ exposure for 5 min, 15 min, 1 hr and 2 hr, respectively. (e) Evacuation at $75^\circ$C for 30 min after (d).

Figure 2. CO$_2$ adsorption at $25^\circ$C on a Pt/TiO$_2$ sample reduced at 400$^\circ$C (400-400-400). (a)-(c) Exposure time of 5 min, 15 min and 2 hr, respectively.

Figure 3. CO$_2$ adsorption at $25^\circ$C on an oxidized Pt/TiO$_2$ sample (400-400-400). (a)-(c) Exposure time of 10 min, 90 min and 3 days, respectively.
WAVE NUMBERS (cm⁻¹)

Tschape and White, Fig. 3.
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