INFRARED STUDIES OF CO ADSORPTION ON REDUCED AND OXIDIZED PT/TI--ETC(U)

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by

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Infrared Studies of CO Adsorption on Reduced and Oxidized Pt/TiO₂

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concentration of bridged species lies below detection limits. On oxidized Pt/TiO$_2$ samples, some Pt atoms are covered with oxygen atoms and the density of step sites is enhanced. On these surfaces there are two kinds of linear CO species assigned to terraces (2130 cm$^{-1}$) and steps (2101 cm$^{-1}$) and a bridged CO species at 1880 cm$^{-1}$. In addition, several CO species are also detected on reduced samples. These species show intensity variations during lengthy exposures. Preadsorbed linear CO species (2130 cm$^{-1}$, 2094 cm$^{-1}$ and 2077 cm$^{-1}$ bands) on oxidized samples are also sensitive to H$_2$ exposures.
Infrared Studies of CO Adsorption on Reduced and Oxidized Pt/\text{TiO}_2

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Abstract
Carbon monoxide adsorption experiments were studied on reduced and oxidized Pt/TiO_2 with FT-IR. On reduced samples two kinds of linear CO species were observed and assigned as adsorption on Pt close-packed (terrace) sites (2094 cm\(^{-1}\)) and on Pt open (step) sites (2077 cm\(^{-1}\)). In addition a bridged CO species was found at 1854 cm\(^{-1}\). Both linear species show increasing frequencies with coverage. Saturation CO uptake decreases with increasing substrate reduction temperature and there is a preferential decrease of linear CO species on terrace sites and the concentration of bridged species lies below detection limits. On oxidized Pt/TiO_2 samples, some Pt atoms are covered with oxygen atoms and the density of step sites is enhanced. On these surfaces there are two kinds of linear CO species assigned to terraces (2130 cm\(^{-1}\)) and steps (2101 cm\(^{-1}\)) and a bridged CO species at 1880 cm\(^{-1}\). In addition, several CO species are found which are also detected on reduced samples. These species show intensity variations during lengthy exposures. Preadsorbed linear CO species (2130 cm\(^{-1}\), 2094 cm\(^{-1}\) and 2077 cm\(^{-1}\) bands) on oxidized samples are also sensitive to H_2 exposure.
1. Introduction

The adsorption of CO is typically used in the characterization of supported metal catalysts. Since Henschel et al reported adsorbed CO species on Y-Al$_2$O$_3$ and SiO$_2$ supported Pt, Pd, Ni and Fe catalysts,\(^{(1)}\) much attention has been given to the type of CO, i.e., linear, bridged and weak species.\(^{(2)}\) In general, it is found that the CO adsorption depends on the metals themselves, their dispersion and oxidation state, as well as the support. Taking Pt catalysts for example, linear and bridged CO species are observed at 2060-2110 cm$^{-1}$ and 1815-1865 cm$^{-1}$ irrespective of their supported or non-supported character, i.e., on Pt/Y Al$_2$O$_3$,\(^{(1,3)}\) evaporated Pt films,\(^{(4)}\) Pt(111)\(^{(5)}\) and Pt/Pt-alumite.\(^{(6)}\) An exception is the Pt/SiO$_2$ system where only a linear CO species is seen.\(^{(11)}\) Koper and Horn performed ELS and LEED measurements on Pt(111) and Pt 6(111)x(111) systems and observed linear CO species at 2099 cm$^{-1}$ when the LEED pattern shows the $\sqrt{3}$x$\sqrt{3}$ R20$^\circ$ structure while bridged species at 1895 cm$^{-1}$ were involved in the C(4x2) structure.\(^{(7)}\)

It is reported that Pt supported on high temperature pretreated TiO$_2$ shows a high catalytic activity for the photo-assisted water decomposition and water gas shift reactions.\(^{(8)}\) TiO$_2$-supported metal catalysts also show striking CO and H$_2$ uptake decreases with increasing reduction temperature, called the strong metal support interaction (SMSI).\(^{(9)}\) and high amenable activity and selectivity are reported for such systems.\(^{(10)}\)

The aim of this paper is to characterize the CO adsorption sites both on oxidized and reduced Pt/TiO$_2$. Quadrosoption experiments using CO$^{13}$CO and CO$^{18}$O(171) and CO$^{18}$O exchange reaction

\[ \text{CO}^{18}\text{O} \rightarrow \text{CO}^{18}\text{O} \]

were performed on reduced catalysts and the subsequent effect of H$_2$ introduction was observed.\(^{(18)}\)

2. Experimental

A commercial anodesample (HCB) was used as the support after overnight reduction with H$_2$ at 800$^\circ$C. This is the same procedure used to obtain high activity for the photoassisted water decomposition reaction.\(^{(3)}\) The main impurities in the sample were Ag(0.00003%), Cu(0.001%), Al(0.002%) and In(0.01%). Reduced TiO$_2$ was soaked in dilute chloroplastic acid solution to prepare wet Pt loaded catalysts. This solution was dried at 100$^\circ$C and the supported catalyst was washed with distilled water at 25$^\circ$C until no chlorine was detected in solution. Carbon monoxide was purified through a 5A molecular sieve trap maintained at 77K.

An infrared cell, with CaF$_2$ windows, was designed to prepare the sample in situ.\(^{(11)}\) Infrared spectra were recorded in absorbance using a Nicolet 7199 Fourier transform infrared spectrometer with 2 cm$^{-1}$ resolution. Three hundred scans were taken to get good S/N. Absorption due to the windows and the gas phase were subtracted. CO was introduced to each sample at 25$^\circ$C and infrared spectra were recorded at the same temperature.

Palladium for infrared experiments were prepared between pieces of paraffin paper moistened, using stoichiometric, to the forms of
a one inch diameter die. A pressure of 5000 lb in$^{-2}$ was applied to 130 mg in$^{-2}$ of powder. Without paraffin paper, attempts to prepare pellets were unsuccessful. There are advantages and disadvantages in this procedure. Metal contamination from the pellet die in the final and sturdy infrared pellets are formed. However, pellets show paraffin adsorption bands which must be removed by evacuation at 400$^\circ$C overnight. While we cannot rule out subtle changes in substrate structure as a result of this procedure, no qualitative difference was observed for CO adsorption on Pt supported on unreduced anatase and the pre-reduced, reduced TiO$_2$ described above.

Carbon monoxide adsorption experiments were carried out on these kinds of samples: oxidized, reduced at 200$^\circ$C and reduced at 450$^\circ$C. In each case the final step was evacuation at 400$^\circ$C for 30 minutes. The three types are denoted as 400-0-400, 400-200-400 and 400-450-400, where each number shows the treatment temperature in the following order: oxidation, reduction with H$_2$ and evacuation. Oxidation and reduction treatments were done in a static system. During reduction, 1 atm of purified hydrogen was replaced at least 5 times. The quantitative analysis of CO uptake gave 0.64% on Pt/TiO$_2$ (400-200-400).

3. Results and Discussion

In the sections below several CO stretching frequencies are assigned. These are summarized in Table 1, and the assignments of each band are summarized in Table 2.

3.1. CO adsorption on Pt/TiO$_2$ (400-200-400)

CO adsorption spectra on Pt/TiO$_2$ reduced at 200$^\circ$C with H$_2$ overnight and subsequently evacuated at 400$^\circ$C (400-200-400) are shown in Fig. 1. Introduction of 5 torr CO, Fig. 1(a), showed infrared absorption bands at 2185 cm$^{-1}$, 2019 cm$^{-1}$ and 1854 cm$^{-1}$. The 2092 cm$^{-1}$ and 1854 cm$^{-1}$ bands can be assigned to linear and bridged CO on Pt respectively in agreement with the work of Kishina and Plikin. The 2185 cm$^{-1}$ band was observed in CO adsorption on TiO$_2$ and was assigned as a physisorbed species; however, the gas phase CO frequency is 2168 cm$^{-1}$ so that it may be better to assign 2185 cm$^{-1}$ as a weakly chemisorbed species. Upon evacuation at 25$^\circ$C, Fig. 1(a) is converted to Fig. 1(b); the 2185 cm$^{-1}$ band disappears, the linear Fe-CO species shifts down to 2078 cm$^{-1}$ and the bridged CO remains at 1854 cm$^{-1}$ but with lower intensity. This is quite different from the behavior on alumina-supported Pt catalysts, where the bridged species is easily removed during evacuation at 25$^\circ$C. (3a) Spectrum 1(c), after evacuation at 85$^\circ$C, showed no bridged species and an absorption maximum at 2063 cm$^{-1}$ with a shoulder at 2074 cm$^{-1}$. After 150$^\circ$C evacuation this shoulder disappeared leaving a single peak at 2060 cm$^{-1}$, Fig. 1(d). No CO remained after evacuation at 200$^\circ$C, Fig. 1(e). In order to check the reproducibility, 5 torr CO was introduced after experiment 1(d). As shown, Fig. 1(f) reproduces Fig. 1(a) except the shoulder at 2082 cm$^{-1}$ is resolved and there is a 20% decrease in intensity.

The downward frequency shift of linear CO frequency with decreasing CO coverage is a common observation. One of the earliest observations was for CO on Pt/TiO$_2$ where the shift was from 2087 to 2060 cm$^{-1}$, a shift attributed to dipole-dipole
interactions. However, Ely and Bulke(13) proposed that the
formation of a strong bond enhances back donation from metal
6-orbitals to antibonding 2p* orbital of the CO molecule, thereby
weakening the C-O bond. This would cause the frequency to shift
downward. Since the metal-CO bond energy typically decreases
with coverage, we would expect the stretching frequency to
decrease as the coverage decreases. As Hollis and Pettit(14)
suggest, this kind of explanation is chemical in nature and has a
great deal of analogy with dipole-dipole interactions.

Reflection-absorption infrared spectra for CO on polycrystalline Pt, de-activated by the (111) face, show a frequency shift from 2055 to 2101 cm⁻¹ as the coverage increases to saturation(15). Cottrell and Kite(16) use a model, first developed by Hammet and al.(13) to account for this frequency shift. In honor of experimental vibrational spectra, from isotope mixtures of ¹²CO and ¹³CO. If the shift of the ¹²CO band to higher frequency with increasing coverage is due only to dipole-dipole interactions, then successive substitution of ¹²CO
with ¹³CO at constant total coverage as the metal-CO interaction
in constant, should reduce the frequency. They obtained this result experimentally. The essential feature of the model is the
frequency shifts, which is proportional to the lattice sum, \( \sum r_{ij} \),
where \( r_{ij} \) is the distance between the centers of two dipoles i and
j. Similar coverage induced frequency shifts have been reported for
linear CO on evaporated Ir(15) in SiO₂ prepared from
Nickel-iron(16), and γ-oxides supported Pt.(16) Frequency shifts
were also detected for bridged CO on Ir(17) and Pt.(18)

To test whether or not the shift shown in Fig. 1 was due to
dipole-dipole interactions, equimolar C¹⁶O and C¹⁸O (6 torr) was
introduced on Pt/TiO₂ (400-200-400). As shown in Fig. 2(a),
linear C¹⁶O and C¹⁸O species on Pt were observed at 2074 cm⁻¹ and
at 2007 cm⁻¹. On TiO₂, C¹⁶O and C¹⁸O gave bands at 2105 cm⁻¹ and
2135 cm⁻¹. Isotopically different bridged species were not
observed here; however, bridged C¹⁶O and C¹⁸O species were
observed at 1854 cm⁻¹ and 1810 cm⁻¹ using a different procedure
(Fig. 3). After evacuation at 250°C, the 2074 cm⁻¹ band shifted to
2061 cm⁻¹, while the relative intensity of the shoulder at 2007
cm⁻¹ grew with no frequency shift. These two bands shifted to
lower frequency with lower CO coverage as the evacuation
temperature was increased to 80°C (Fig. 2(b), and to 150°C, Fig. 2(d).
Evacuation at 200°C, Fig. 2(e), left only a detectable adsorbed CO.
Comparing 1a with 2a, and 1b with 2b, we note that under
similar coverage conditions the C¹⁶O stretching frequency is
always reduced in the presence of C¹⁸O.

Elichsen et al.(11) observed two bands at 2074 cm⁻¹ and 2012
cm⁻¹ when a mixture of C¹⁶CO and C¹³CO was adsorbed on a Pt/TiO₂
catalyst. (Note that the isotope effect of C¹³CO/C¹⁶O is almost
the same as C¹⁸O/C¹⁶O so results can be compared directly.) They
find that chemisorbed CO is pumped out at 200°C and that the
relative intensities of the two bands depends on the surface
coverage with the high frequency band becoming relatively more
intense as the surface coverage increases, just as we observe in
Fig. 2. This is interpreted in terms of dipole coupling variations.
Our results are quite consistent with theirs. To conclude
that for CO on Pt/TiO₂ (400-600-600) the 2023 cm⁻¹ band is a
linear species and the frequency shift of this species can be
interpreted completely in terms of dipole-dipole interactions
between adsorbed species.

The exchange of c¹⁸O with c¹⁶O preadsorbed on Pt/TiO₂ at 25°C
was used as a complement to the adsorption experiment described
above. First 0.3 Torr of c¹⁸O was dosed onto a 400-600-600 Pt/TiO₂
sample, Fig. 3(a), and followed by evacuation at 25°C, Fig. 3(b)
then this surface was exposed to 3 Torr c¹⁶O, the linear c¹⁶O
species on Pt changed to the c¹⁸O homologue at 2042 cm⁻¹, with a
shoulder at 2087 cm⁻¹, and bridged c¹⁶O at 1854 cm⁻¹ changed
gradually (5 min.) to bridged c¹⁶O at 1816 cm⁻¹, Fig. 3(c). The
shoulder at 2087 cm⁻¹ gradually decreased in intensity with time
of exposure to c¹⁸O, Fig. 3(d) is after 30 min. and Fig. 3(e) is
after 18 hr. During this same period the bridged CO species moved
towards 1880 cm⁻¹. The average frequency ratios of the 1810 cm⁻¹/1854
and 2042 cm⁻¹/2084 cm⁻¹ bands are consistent with the
classical values (δ.9700).

According to X-ray diffraction results for the Pt/TiO₂
system, the surface of supported Pt is comprised mainly of (111)
faced with a small amount of the (200) face (64.19). It is also
well known that the (111) face is dominant for annealed
crystalline Pt (20). Therefore it is worthwhile considering CO
adsorption experiments done on Pt(111). Several studies (21-22)
of CO adsorption on Pt(111) indicate that the activation energy
for desorption drops monotonically with CO coverage and that the
activation energy for desorption, extrapolated to zero coverage,
is about 33 kcal mol⁻¹. In these experiments there is no
evidence for the different kinds of species and sites that would
account for the distinctly different isotope exchange rates that
this c¹⁸O species is adsorbed strongly and remains, with a
frequency shift to 2050 cm⁻¹, after evacuation at 200°C, Fig. 3(g).

The equilibrium of isotopic species in the exchange is heavily
weighted in favor of adsorbed c¹⁸O because of the dominance (.50/1)
of c¹⁸O in the gas phase. These results imply that adsorbed
C¹⁶O species which rapidly exchange with gas phase C¹⁸O at 25°C
are those species removed by evacuation at 200°C. Moreover, the
evidence suggests that the CO species at 2060 cm⁻¹ remains after
evacuation at 150°C, Fig. 1(f), and after the exchange reaction
with C¹⁸O, Fig. 3(g). (g) is not the same species as that showing
a strong band at 2094 cm⁻¹, Figs. 1(a), 3(a). We propose that the
2094 cm⁻¹ band is due to CO on terrace sites while the band at
2050 cm⁻¹ involves step site adsorption. In the following
paragraphs we relate this idea to observations on unsupported
metals.
we observe.

Staged or kinked Pt(111) does show site heterogeneity in CO desorption: two peaks appear (7,24-26), and the intensity ratio follows the step/terrace concentration ratio. While there are significant variations in the quoted activation energies for desorption, there is agreement that desorption from step sites involves at least 3 kcal mol⁻¹ higher activation energy than desorption from the terrace sites. Consequently, it is not unreasonable to expect some variations in isotropic molecular exchange rates. If CO adsorbed at step (and other defect) sites exchanges slowly, compared to CO adsorbed at terrace sites, then we would expect this to be reflected in experiments like those summarized in Fig. 3. Thus we interpret the 2050 cm⁻¹ band in Fig. 3(g) as CO on Pt(111) adsorbed on step sites. Note the similarity between Fig. 2(a) and Fig. 3(g).

Because connections to single crystal work involving the step/terrace concepts are made here we have chosen to use this language. It should be recognized that one could also use the language of closed-packed (111) and open (higher index) crystallite faces.

Recently Bartosh et al. (27) found adsorption-desorption hysteresis curves in CO on Pt supported cob-o-all systems, where high frequency "desorptive CO" is assigned to disordered species while low frequency "desorptive CO" is assigned to ordered species. According to their results, CO molecules migrate from low Miller index planes, terraces, to high Miller planes, steps and kinks, prior to desorption. Their observations with respect to surface heterogeneity are consistent with our results.

3.2 CO adsorption on Pt/TiO₂ (400-400-400)

Adsorption of CO was carried out on Pt/TiO₂ after overnight oxidation followed by reduction and evacuation, all at 400°C (Fig. 4). We selected 400°C as the maximum hydrogen/evacuation temperature which gives a mild BMR system because a complete BMR system (400°C) is known to reduce the CO uptake at 25°C by as much as a factor of 20. (9,19) Under these conditions, CO bands are difficult to detect. In an ambient of 100 torr CO, Fig. 4(a), infrared absorption was recorded at 2185 cm⁻¹ and 2020 cm⁻¹ which correspond to CO on Pt(111) and linear CO on Pt, respectively. It is noteworthy that the intensity of the CO species on Pt decreased by about 20% relative to the spectrum of Fig. 1(a). Moreover, no bridged CO species was seen. This is not merely a signal-to-noise problem since a 50% reduction of the 1854 cm⁻¹ band of Fig. 1(a) would still be easily measurable. As shown in Fig. 4(b), the linear CO species on Pt at 2081 cm⁻¹ shifted to 2072 cm⁻¹ upon evacuation at 25°C for 30 min. Following this procedure, 1 atm CO was added, Fig. 4(c). Approximately the same intensity CO band as observed in Fig 4(a) was seen at 2081 cm⁻¹ with some complicated bands at around 2170 cm⁻¹. Evacuation at 25°C and 150°C; Fig. 4(d), (e), caused a frequency shift of the linear CO species on Pt from 2081 to 2075 cm⁻¹ and 2063 cm⁻¹ with accompanying losses of intensity. In Fig. 4(d) two small intensity bands were detected around 1940 and 1940 cm⁻¹. These are not associated with CO since they often appear on reduced samples in the absence of CO. Although the origin of these bands...
in unknown, they may be associated with overtones of Ti-O lattice vibrations. The 2080 cm⁻¹ peak remained following evacuation at 200°C, Fig. 4(c). This is quite different from the behavior shown by Pt/TiO₂ reduced at only 250°C, Figs. 1-3, where all the CO bands disappear after evacuation at 200°C.

After the spectrum of Fig. 4(c) was taken, the sample was exposed to 6 torr of CO in order to check reproducibility. As indicated in Fig. 4(g), the frequency of CO on Pt shifted to 2075 cm⁻¹ as compared to 2083 cm⁻¹ in Fig. 4(a). Moreover, the intensity decreased about 50%. Evacuation at 25°C led to the expected downshift frequency shift, Fig. 4(h). Taking difference spectra (not shown), i.e. 4(h) - 4(a) and 4(h) - 4(g), clearly indicates that these species giving the 2080 cm⁻¹ band partially reappeared and partially desorbed with evacuation to give the bands in the 2075 - 2071 cm⁻¹ range. This suggests that either: (1) CO molecules on a terrace migrate and is stabilized on a step or defect site or (2) CO molecules adsorb primarily on step sites and, upon evacuation, the frequency of this band moves down due to lesser dipole-dipole interactions. In favor of the former explanation.

The uptake of both H₂ and CO on TiO₂ supported noble metal catalysts is strongly diminished by H₂ reduction at 500°C. This is not the result of metal agglomeration on the TiO₂ support since more than 2/3 of the original CO and H₂ uptake are recovered by reoxidation at 550°C. This phenomenon, called the strong oxygen-promoted insulation (SOP) effect, has been shown to give significant effects in CO hydrogenation activity and selectivity. (10)

The morphology of the Pt particles is significant. Baker, et al., (22) conclude from transmission electron microscopy that Pt on TiO₂ (in the PbO state) is in the form of thin hexagonal pillboxes grown on a partially reduced titania, Ti₃O₇. The faces of these thin structures have Pt(111) character with mainly terrace sites. It is this structure which shows only weak CO chemisorption. Our results then suggest that a selective decrease in CO binding on terrace sites, perhaps due to changes in the Pt electronic structure, leads to the loss of CO chemisorption activity.

From LEED and high resolution electron energy loss spectroscopy (HREELS) data, there are two ordered structures showing different CO binding on Pt(111). (7) For the $\sqrt{3} \times \sqrt{3}$ R30° structure, only linear binding is found while for the c(4 x 2) structure, both the linear (2089 cm⁻¹) and bridged (1855 cm⁻¹) structures are found. On a stepped surface, 6(111) x (111), a linear species at 2089 cm⁻¹ is also found even when the thermal desorption spectra clearly indicate that CO is bound only to step sites. The relatively low resolution of HREELS (900 cm⁻¹) may have prevented observation of shifts due to bonding differences on terraces and steps. (23) These results are not inconsistent with the notion that, in the PbO system, terrace sites become dominant, that no bridge bonded CO is present on step sites and that linear CO binding on residual steps is still strong.

3.3 CO adsorption on Pt/TiO₂(400-500-600)

Adsorption of CO on Pt/TiO₂ that was oxidized at 400°C and
reduced with CO and the formation rate of the 2080 cm⁻¹ intensity is inversely proportional to the intensity of the 2130 cm⁻¹ band.

The results of a series of experiments, like those of Fig. 5, can be summarized as follows (see Table 1 for assignments):

(a) On a Pt/TiO₂ surface poisoned with O₂ at 400°C exposure to CO leads to bands associated with and without interacting oxygen. The former is found at 2130 cm⁻¹ (Fig. 5a) and the latter at 2097 and 2077 cm⁻¹ (Fig. 5g). The formation rate of the 2077 cm⁻¹ band is dependent on the CO pressure.

(b) On the same surface there are two kinds of bridged CO (1800 and 1854 cm⁻¹). The intensities of the 1800 and 2130 cm⁻¹ bands are related. These are assigned (see below) to CO adsorbed in bridged and linear forms that also involve chemisorbed oxygen.

(c) With exposure time, the 2130 cm⁻¹ band reaches a maximum intensity and shifts to lower frequency. This species is ascribed to linear CO on Pt with interacting oxygen since the intensity decreased sharply following surface reduction.

(d) The intensity decrease with time of the physically adsorbed CO species on TiO₂ at 2185 cm⁻¹ is associated with the formation of coordinated CO₂ at 2349 cm⁻¹, as well as some carbonate species, on TiO₂.

In the previous sections we suggested two kinds of CO on Pt/TiO₂: terrace and step Pt(111) sites. This also appears to be the case for oxygen poisoned Pt/TiO₂. Before considering the details, we briefly consider the interaction of O₂ with Pt. Molecularly adsorbed, atomically chemisorbed and subsurface oxide are all known to exist in the O₂/Pt(111) system. In our system molecular adsorption is negligible since the sample is evacuated at 400°C. We expect the oxygen to be predominantly chemisorbed atomic species although, for small Pt particles on TiO₂, subsurface oxygen may be formed. This remains an open question deserving further study. We attribute the 2130 cm⁻¹ band to CO on Pt in the presence of atomic oxygen.

On well-characterized bulk single crystals, dissociation of O₂ on Pt takes place mainly on step sites, as compared to terrace sites. Examining these systems, it is observed that oxygen atoms are chemisorbed primarily on step sites in our system, we expect selective CO adsorption on terrace sites (2094 cm⁻¹) until the oxygen atoms at the steps are removed. The CO pressure dependence of the 2080 cm⁻¹ band (Fig. 6), which is assigned to CO on step sites, can be interpreted in terms of selective adsorption of oxygen atoms on these sites followed by a slow reaction with CO, removal as CO₂ and, finally, CO adsorption at the same sites.

In a supporting experiment, a (400-480-400) sample was exposed to 1 atm of O₂ for 30 min at 25°C, evacuated at 25°C and exposed to 7 torr of CO at 25°C. Comparing Fig. 7(a) and (b) with Fig. 5(a) and (b), there are no qualitative differences suggesting that the adsorbed oxygen reactivity and structure does not depend on either the adsorption or evacuation temperature between 25 and 400°C. Figure 7(c) shows that the 2080 cm⁻¹ band intensity grew in during evacuation at 25°C. We take this to mean that step sites were vacated during evacuation by reaction of CO with O₄ and removal as CO₂, thereby allowing terrace CO to migrate to the step sites. Spectrum 7(d), taken after evacuation at 100°C, shows...
that the 2130 cm\(^{-1}\) band is composed of two species with
frequencies at 2130 and 2101 cm\(^{-1}\).

The presence of two kinds of CO on oxygen-covered Pt reminds us
that there are two kinds of CO on reduced Pt, terrace and step
species. If it is assumed that the 2130 and 2101 cm\(^{-1}\) bands
correspond to terrace and step adsorption on oxygen-covered Pt,
then the downward frequency shift of mixtures of these two species
in Fig. 3 can be accounted for as the result of enrichment of the
2132 cm\(^{-1}\) band. This assignment is supported by another
experimental result. In Fig. 6 there is a linear relationship
between the absorbances of the 2094 and 2130 cm\(^{-1}\) bands during the
first two hours of the exposure, where the frequency of the CO on
oxygen-covered Pt remains at 2130 cm\(^{-1}\).

The remaining assignments involve the bands at 2060 and 1942
cm\(^{-1}\). These may be assigned to dicarbonyl species. If present,
such species should give a pair of bands (symmetric and
asymmetric) as in Ir(CO)\(_2\) \(^{16}\) and Rh(CO)\(_2\) \(^{17}\). These species
formed on Y-alumina are thought to be on partially oxidized
isolated metal sites like Rh\(^{b}\). The formation of such species
would require extensive coordinative unsaturation as expected at
steps, kinks and other defects. McClain et al. \(^{26}\) suggest that
for the Pt(331) surface made of rough steps which have a high
density of kinks, 40% of the surface Pt atoms are coordinatively
unsaturated. Such surface sites could account for the formation of
dicarbonyl species.

The results of introducing H\(_2\) to a Pt/TiO\(_2\) surface, prepared
with CO and evacuated at 250°C, are shown in Fig. 8. Prior to the
introduction of H\(_2\), the intensity of the 2094, 2077 and 2130 cm\(^{-1}\)
bands were 0.144, 0.033 and 0.028, respectively. Adding H\(_2\) gave
rise to a rapid intensity increase in the 2094 cm\(^{-1}\) band and an
abrupt decrease of the 2077 and 2130 cm\(^{-1}\) bands. With H\(_2\) exposure
time, Fig. 8 shows that the 2094 and 2077 cm\(^{-1}\) band intensities
increase gradually, while the band at 2130 cm\(^{-1}\) decreased slowly.
After a 2 hr exposure, the frequencies of these three bands
shifted down to 2080, 2062 and 2118 cm\(^{-1}\). The combined intensity
of the 2094 and 2077 cm\(^{-1}\) bands was 0.176 at the start and rose to
0.196 after 2 hr. This increase matches nicely the intensity lost
(0.019) in the 2130 cm\(^{-1}\) band and indicates that CO molecules on
oxygen-covered Pt are converted to CO species on step and terrace
sites on reduced Pt during H\(_2\) exposure. The growth of the 1620
cm\(^{-1}\) band, indicating water formation, is consistent with the
above frequency shifts in the sense that surface reduction is
occurring. Covenagh and Yates\(^{32}\) as well as Apple and Dymowski\(^{33}\)
studied the effect of coadsorption of CO on the adsorption of H\(_2\)
on Rh/Al\(_2\)O\(_3\) and Pt/TiO\(_2\) and concluded that preadsorbed CO inhibits
the adsorption of "spillover" hydrogen. Applied to our system, we
expect no reduction of TiO\(_2\) and interpret the water indicated in
Fig. 8 as arising from reaction with oxygen on Pt (hydrogen
titration).

Two of the more interesting results of the experiment
described in Fig. 8 are the downward frequency shift with time of
the CO species on both step and terrace sites and the abrupt
intensity changes in some of the bands just after hydrogen
introduction. Downward frequency shifts are also observed in
coadsorption of H₂ and CO. This is explained in terms of
strengthened chemisorbed bonds between Pt and CO. Though there is no
desorption data that compares the characteristics of
terrace and step sites, our intensity redistribution data suggests that:
(a) most CO molecules on Pt are mobile and (b) hydrogen
desorbs in a way that removes some CO from step sites. Since H₂
adsorption is not likely to induce CO desorption, we expect that
CO molecules removed from step sites will migrate to terrace
sites. This result implies that CO and H on step sites have
different adsorption structures than their counterparts on terrace
sites. The initial sticking coefficient for H₂ is reported to be
0.2 for clean Pt(111) and 0.4 for oxygen-covered Pt(111); however,
the adsorption coverage for H(a) is nearly the same in both
cases.[23] Taking this result over to our supported Pt system,
hydrogen adsorption would occur more readily on step sites since
hydrogen atoms prefer to adsorb there.

4. Summary

The IR data reported here show clearly that a variety of
adsorbed CO species are observed on platinumed titania depending
on the pretreatment of the adsorbate. The adsorption bands are
interpreted in terms of the traditional bridged and linear CO
species. Here, we find two types of linear CO species which are
assigned to adsorption on terrace (close-packed) and step (open)
sites. Resonable frequency shifts in both are found in the
presence of interacting oxygen. Exchange experiments involving
C¹³O and C¹²O demonstrate that the species attributed to step
site exchange were slower than those at the terrace species.

This is confirmed by thermal desorption experiments showing that
the higher frequency linear CO component (terrace site) is less
stable. In the strongly reduced SMSI state, Pt(111) adsorbes small
amounts of CO, bridged CO is not detected and adsorption at
terrace sites is lost preferentially. On oxidised Pt(111),
several kinds of adsorbed CO form and intensities are time
dependent reflecting oxygen removal by reaction with CO to form
CO₂, particularly at step sites. Under some conditions, weak
bands assigned to dicarbonyl are found. Finally, exposure of a
CO-poisoned sample to H₂ causes marked changes in the intensities
of certain CO bands indicating surface reduction to form water and
a redistribution of linearly bound CO between step and terrace
sites.
References

25

Table 1. Experimental Conditions and Observed CO Band Frequencies.

<table>
<thead>
<tr>
<th>Experimental Conditions</th>
<th>Observed Frequency (cm⁻¹)</th>
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<tbody>
<tr>
<td>(1) 400-200-400 (Fig. 3)</td>
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<tr>
<td>5 torr CO ads. 25°C</td>
<td>2185 2094 1854</td>
</tr>
<tr>
<td>Evacuation at 25°C</td>
<td>-   2076 1854</td>
</tr>
<tr>
<td>Evacuation at 80°C</td>
<td>-   2074 2063</td>
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<tr>
<td>Evacuation at 150°C</td>
<td>-   -   2060</td>
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<tr>
<td>Evacuation at 200°C</td>
<td>-   -   -</td>
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<tr>
<td>5 torr CO ads. 25°C</td>
<td>2185 2094 2080 1854</td>
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<td>(2) 400-400-400 (Fig. 4)</td>
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<tr>
<td>10 torr CO ads. 25°C</td>
<td>2185 2083</td>
</tr>
<tr>
<td>Evacuation at 25°C</td>
<td>-   2072</td>
</tr>
<tr>
<td>Evacuation at 150, 200°C</td>
<td>-   -   2065</td>
</tr>
<tr>
<td>6 torr CO ads. 25°C</td>
<td>-   2075</td>
</tr>
<tr>
<td>(3) 400-40-400 (Fig. 5)</td>
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<tr>
<td>0.8 torr CO 25°C 5 min.</td>
<td>2185 2097 1854 2130</td>
</tr>
<tr>
<td>0.8 torr CO 25°C 120 min.</td>
<td>2185 2097 1854 2130 1880</td>
</tr>
<tr>
<td>37 torr CO 25°C 150 min.</td>
<td>2185 2097 2077 1854 2130 1880</td>
</tr>
<tr>
<td>37 torr CO 25°C 63 hrs.</td>
<td>-   2094 2077 1854 2132 (1880) 2069 1942</td>
</tr>
<tr>
<td>Evacuation at 25°C</td>
<td>-   2094 2072 1854 - - - (1842)</td>
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<tr>
<td>Evacuation at 150°C</td>
<td>-   -   2099</td>
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<td>Evacuation at 200°C</td>
<td>-   -   -</td>
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<td>5 torr CO 25°C 5 min.</td>
<td>2185 2096 2080 1854 2131 -</td>
</tr>
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<td>(4) O, 400-80-400 (Fig. 7)</td>
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<td>7 torr CO 25°C 7, 80 min.</td>
<td>2185 2098 1854 - 2130</td>
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(continued on next page)
Table 3. Assignment of CO bands.

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<tr>
<th>Frequency/cm⁻¹</th>
<th>Species</th>
<th>Site</th>
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<tr>
<td>2185</td>
<td>L (a)</td>
<td>TiO₂</td>
</tr>
<tr>
<td>2130</td>
<td>L</td>
<td>Pt(O₂)/Terrace</td>
</tr>
<tr>
<td>2181</td>
<td>L</td>
<td>Pt(O₂)/Step</td>
</tr>
<tr>
<td>2094</td>
<td>L</td>
<td>Pt/Terrace</td>
</tr>
<tr>
<td>2077</td>
<td>L</td>
<td>Pt/Step</td>
</tr>
<tr>
<td>1980</td>
<td>B</td>
<td>Pairs of Pt(O₂)</td>
</tr>
<tr>
<td>1954</td>
<td>B</td>
<td>Pairs of Pt</td>
</tr>
<tr>
<td>2050, 1942</td>
<td>T</td>
<td>Edge Pt</td>
</tr>
</tbody>
</table>

(a) L, B, and T denote linear, bridge and twist sites. Pt(O₂) denotes oxygen-covered Pt.
**FIGURE CAPTIONS**

**Figure 1.** Spectra for CO adsorption on Pt/TiO₂ reduced at 200°C (400-200-400). (a) 5 torr CO. (b) Evacuation of (a) at 25°C. (c) Evacuation at 80°C. (d) Evacuation at 200°C. (e) 5 torr CO after (d).

**Figure 2.** Adsorption of an equimolar mixture of C¹³O and C¹⁸O on Pt/TiO₂ (400-200-400). (a) 6 torr of mixture. (b)-(g) Evacuation of (a) at 25, 80, 150 and 200°C respectively.

**Figure 3.** Exchange of C¹³O with presorbed C¹⁸O on Pt/TiO₂ (400-200-400). (a) 6 torr C¹³O. (b) Evacuation of (a) at 25°C. (c)-(g) Exposure of (b) to 3 torr C¹⁸O for 5 min, 30 min and 18 hr, respectively. (h)-(l) Evacuation of (g) at 25 and 80°C, respectively.

**Figure 4.** CO adsorption on Pt/TiO₂ (400-400-400). (a) 10 torr CO. (b) Evacuation of (a) at 25°C. (c) 1 atm CO after (b). (d)-(f) Evacuation of (c) at 25, 150 and 200°C, respectively. (g) 6 torr CO after (f). (h) Evacuation of (g) at 25°C.

**Figure 5.** CO adsorption spectra on oxidized Pt/TiO₂ (400-400-400). CO pressure was increased from 0.8 to 37 torr after 120 min. Exposure times were: (a) 5 min, (b) 60 min, (c) 120 min, (d) 125 min, (e) 180 min, (f) 270 min, and (g) 65 hr. After (g) the system was evacuated at: (h) 200°C. (i) 80°C, (j) 150°C, and (k) 200°C. (l) 5 torr CO after (k).

**Figure 6.** Time dependence of intensity changes for spectra of Fig. 5.

**Figure 7.** CO adsorption on oxidized Pt/TiO₂ (400-400-400) reduced with O₂ at 25°C. Exposure of 7 torr CO for (a) 7 min and (b) 80 min. Evacuation of (b) at: (c) 25°C, (d) 100°C, and (e) 200°C.

**Figure 8.** Effect of H₂ (1 atm) introduction on a Pt/TiO₂ sample reduced with CO.
The images show infrared spectra with wave numbers in cm$^{-1}$, and absorbance graphs over time. The absorbance peaks at 2080 cm$^{-1}$ and 2100 cm$^{-1}$ are highlighted. The graphs compare absorbance at different pressures, with labels for $P_{CO} = 0.8$ torr and $P_{CO} = 37$ torr. The absorbance values range from 0 to 0.2.
<table>
<thead>
<tr>
<th>Name</th>
<th>Institution</th>
<th>Address</th>
<th>City, State, Zip Code</th>
</tr>
</thead>
<tbody>
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