Isotopic Exchange of CO Adsorbed on Pt(111)

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The isotopic exchange of CO adsorbed on Pt(111) was studied using polarization modulation IR reflection absorption spectroscopy (PM-IRRAS) and temperature programmed desorption. It was found that the rate constants for the exchange reaction are much higher than would be expected from previous investigations of CO adsorbed on Pt nanoparticles. The adsorption of CO on Pt(111) under elevated pressures of CO and H_2 was also studied using PM-IRRAS. It was seen that CO pressures above 1 mbar lead to a shift in the absorption peak arising from CO adsorbed on a bridge site from 1850 to 1875 cm^{-1}. Exposing the CO-covered Pt(111) surface to 1000 mbar H_2 did not lead to any significant desorption of CO at room temperature, whereas at 363 K H_2 exposure did lead to a significant desorption of CO, due to the increased chemical potential of H_2. In a mixture of CO and H_2 with partial pressures of 0.01 mbar and 1000 mbar, respectively, no significant effect of H_2 on the PM-IRRAS spectrum was seen at temperatures below 423 K.

Introduction

The adsorption of CO on platinum has been examined extensively throughout the years, both under ultrahigh vacuum (UHV) conditions and at elevated pressures, as this system has high relevance within the field of catalysis. Another reason for the attention given to this system is the large dipole moment of the CO molecule, causing the system to be a perfect model system for vibrational spectroscopy. In recent years, the adsorption of CO on platinum has gained renewed interest, due to its relevance with respect to the proton exchange membrane fuel cell (PEMFC). The poisoning effect of trace amounts of CO on hydrogen splitting taking place on the platinum anode is one of the problems that needs to be overcome if the PEMFC is to meet its full potential of commercialization.[1] With the aim of gaining knowledge about the mechanisms behind CO poisoning, work with emphasis on isotopic CO exchange on carbon-supported platinum nanoparticles has been carried out in our laboratory.[2] The aim of the current work is to examine the effect of structure on the rate of isotopic exchange of CO and to study the influence of hydrogen on the adsorption of CO on the Pt(111) surface.

It is well-established that on Pt(111) CO chemisorbs with the molecular axis perpendicular to the platinum surface with the carbon atom toward the surface.[3−5] When Pt(111) is exposed to more than 4 L of CO, it is known from low-energy electron diffraction (LEED) experiments, that a c(4 × 2) structure with a coverage θ_{CO}, defined as the number of CO molecules per Pt surface atom, of 0.5 is obtained. One-half of the CO molecules occupy on-top sites, and the other half occupy bridge sites.[4,6] Electron energy loss spectroscopy (EELS), IR reflection absorption spectroscopy (IRAS), and sum frequency generation (SFG) experiments have shown vibrational adsorption bands at around 2095 and 1850 cm^{-1}, which have been assigned to on-top site adsorbed CO and bridge site adsorbed CO, respectively.[6−10] At elevated CO pressures, the coverage increases, and scanning tunneling microscopy (STM) measurements have been

performed at CO pressures up to 1000 mbar.[11,12] At this CO pressure, $\theta_{CO} = 0.7$.[11] SFG experiments performed on Pt(111) at CO pressures up to 400 Torr have shown little effect of the CO pressure on the on-top-site peak, while a peak originating from bridge-site CO was not observed in these experiments.[12−15] The influence of hydrogen on the adsorption of CO on Pt(111) has been investigated by Gland et al.,[16,17] who by using fluorescence yield near edge spectroscopy (FYNES) found that significant CO replacement took place at H_2 pressures higher than 2×10^{-2} Torr. This is somewhat surprising since CO poisoning is known to occur on a PEMFC anode, where the H_2 pressure is approximately 1 bar.

In this work, the isotopic exchange of CO on Pt(111) has been examined using temperature programmed desorption (TPD) and polarization modulation IR reflection absorption spectroscopy (PM-IRRAS).[18−20] Our results show a strong dependence of the observed exchange rate on the CO pressure and a significant difference between the results obtained from nanoparticles and the results obtained for the single-crystal surface. The influence of an applied pressure of H_2 on the adsorption of CO on Pt(111) was also studied using PM-IRRAS. It was found that when a Pt(111) surface precovered with CO is exposed to a H_2 pressure of 1000 mbar, the change in the PM-IRRAS spectrum is temperature-dependent. At 300 K, the effect is very small, while a significant effect is seen at 363 K. In a gas mixture with partial pressures of H_2 and CO of 1000 mbar and 0.01 mbar, respectively, an influence of H_2 on the spectrum was seen only at temperatures above 423 K. The observed influence grew at higher temperatures. We have also measured the PM-IRRAS spectra of CO adsorbed on Pt(111) for CO pressures ranging from 10^{-10} to 500 mbar.

Experimental Section

The apparatus used in this work consists of an UHV chamber equipped with a high-pressure cell (HPC), which can be separated from the main chamber by a high-pressure lock utilizing a Cu gasket.[21] The UHV chamber has a base pressure of ∼10^{-10} mbar and is equipped with instruments for standard UHV surface analysis methods including X-ray photoelectron

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spectroscopy (XPS), low-energy ion scattering spectroscopy (LEISS), and quadrupole mass spectrometry (QMS). The apparatus has been described in detail elsewhere.[22] The Pt single crystal is mounted at the end of a vertical manipulator, allowing transfer between the UHV chamber and the HPC. The crystal can be heated resistively to above 1373 K and cooled by liquid nitrogen stored inside the hollow manipulator. The HPC is used for the in situ PM-IRRAS experiments. PM-IRRAS[18-20] is a development of IR absorption spectroscopy (IRAS) utilizing the fact that p-polarized radiation can be absorbed by vibrational excitation of surface species whereas s-polarized radiation cannot. In short, the difference between the reflectivities of p- and s-polarized light is measured and normalized with the sum of the reflectivities. Hereby a spectrum, which only includes contributions from vibrations related to surface species, is obtained, while contributions from absorption by the isotropic gas phase are removed from the spectrum. The IR source and interferometer are contained in a Nexus spectrometer supplied by Thermo Nicolet. The beam is focused by a focal lens placed before the polarizer and modulator. After the beam is passed through the HPC, it is focused onto a liquid-nitrogen-cooled MCT detector. The HPC is fitted with ZnSe windows to allow transmission of the IR beam used for PM-IRRAS, and the angle of incidence between the beam and the crystal surface is 82°. The photoelastic modulator was supplied by Hinds Instruments and has a modulation frequency in the 100 kHz range. The optical material of the modulator is ZnSe. The lenses, polarizer, modulator, and detector outside the Nexus module were exposed to air, and absorption bands arising from atmospheric water and CO_2 are present in the unmodulated spectra but not in the PM-IRRAS demodulated spectra.

The hydrogen quality used in the experiment was N60, and the gas was passed over a reduced Cu catalyst and a liquid-nitrogen cooling trap prior to being admitted to the HPC. The isotopically unlabeled CO used was also of N60 quality and was passed over activated carbon and a liquid-nitrogen cooling trap before being used in the HPC. Even though unlabeled CO contains approximately 1% ^{13}CO and 0.1% $C^{18}O$, the notation "$C^{16}O$" will be used for the unlabeled CO mixture for simplicity. The tubing after the cooling trap is made from Cu, and the HPC is made from Ni-free steel, to avoid formation of Ni−carbonyl. Sample cleanliness was checked daily by LEISS and in regular intervals by XPS. No indications of Ni−carbonyl were detected. The isotopically labeled CO, $C^{18}O$, contained approximately 5% $C^{16}O$ according to mass 28 and mass 30 areas measured by TPD from the sample immediately after dosing 6 L of $C^{18}O$.

The Pt single crystal was cleaned by annealing in 10^{-6} mbar oxygen at 850 K for 5 min, then the sample was sputtered with argon at 1273 K for 5 min followed by annealing for 2 min at 1273 K. When the sample was badly contaminated, this procedure was repeated until no impurities could be detected with XPS or LEISS. At the end of every cleaning and after every exchange experiment, the sample was annealed in 10^{-6} mbar oxygen at 850 K for 5 min and flashed to 1273 K, resulting in a clean surface as judged from XPS and LEIS spectra.

Results

Isotopic CO Exchange. After the Pt crystal was exposed to 6 L of CO at room temperature, the known C(4 × 2) structure with $\theta_{CO} = 0.5$ was obtained.[4,6] In agreement with this result, the area of the TPD spectra as a function of CO dose was found to saturate at a dose of 6 L. The shapes of the TPD spectra were found to agree with those reported in the literature.[4,23] It was found that if the crystal is dosed with 6 L of $C^{18}O$ as described above, then transferred to the HPC, and exposed to a partial pressure of $C^{16}O$ of 0.01 mbar, then a complete exchange of the $C^{18}O$ on the surface occurs within the 3 min it takes to measure a single PM-IRRAS spectrum. This immediately suggests that the exchange rate at comparable CO pressures is at least 2 orders of magnitude faster for the Pt(111) surface than that in the experiments on Pt nanoparticles.[2] As a consequence of this, it was decided to study the isotope exchange by measuring the TPD areas of $C^{18}O$ and $C^{16}O$ as a function of the dose of $C^{16}O$, after the surface had been preexposed to 6 L of $C^{18}O$ at 294 K. Under the conditions of interest here, the following reactions take place on the surface.

$$C^{18}O^* + C^{16}O(g) \rightleftharpoons C^{16}O^* + C^{18}O(g) \qquad (1)$$
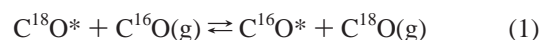
Here, the asterisk and CO* denote an adsorption site and adsorbed CO, respectively. For this system, we have the reactions

$$C^{16}O(g) + * \rightleftharpoons C^{16}O^* \qquad (2)$$
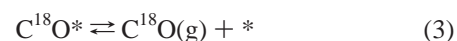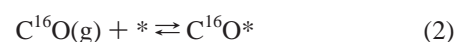
$$C^{18}O^* \rightleftharpoons C^{18}O(g) + * \qquad (3)$$

Since the $C^{18}O$ pressure is negligible, the exchange rate can be described by the expression

$$r_{ex} = \theta_{C18O} \nu_{C18O} \, e^{-E_{des}/kT} \qquad (4)$$

As the desorption energy is coverage-dependent[24-26] and the coverage varies with CO pressure, the exchange rate will be dependent on the CO pressure. However, in each of the experiments presented, the total CO pressure is constant, and hence the total CO coverage and the desorption energy will be constant. Therefore, the desorption of $C^{18}O$ can be described by the first-order desorption equation

$$\theta_{C18O} = \theta_{C18O}^0 \, e^{-k_{des}t} \qquad (5)$$

$$k_{des} = \nu_{C18O} \, e^{-E_{des}/kT} \qquad (6)$$

Here, θ_{C18O}^0 is the initial coverage of $C^{18}O$. To enhance the accuracy of the measurement and to confirm the validity of eq 5, exposure times of up to 1 h were used for a number of pressures of $C^{16}O$ at a sample temperature of 294 K. The coverages of the CO isotopes were obtained from TPD spectra obtained 3 min after the CO leak valve had been closed. This waiting period allowed the pressure in the chamber to drop to 10^{-9} mbar, thereby improving the accuracy of the TPD measurement. Since the pressure dropped within 30 s after the CO leak valve was closed, no significant exchange occurred during the waiting period. Figure 1 shows the TPD curves measured after exposure to 1.2×10^{-5} mbar of $C^{16}O$ for varying periods of time. Because of background exchange occurring in the chamber, it was not possible to use the mass spectrometer signal for $C^{18}O$ as a function of time to determine the rate constant for the exchange, as was done in ref 2.

The coverage of $C^{18}O$ was calculated as the ratio between the area of the TPD curve for $C^{18}O$ and the total area of the TPD curves for $C^{18}O$ and $C^{16}O$ under the assumption of a constant total CO coverage at the beginning of all TPD measurements. Figure 2 shows the results and the fits to eq 5. Test experiments showed that no $C^{18}O$ was exchanged after leaving the crystal for up to an hour in the chamber after dosing $C^{18}O$, as can be seen from the upper curve in Figure 2.
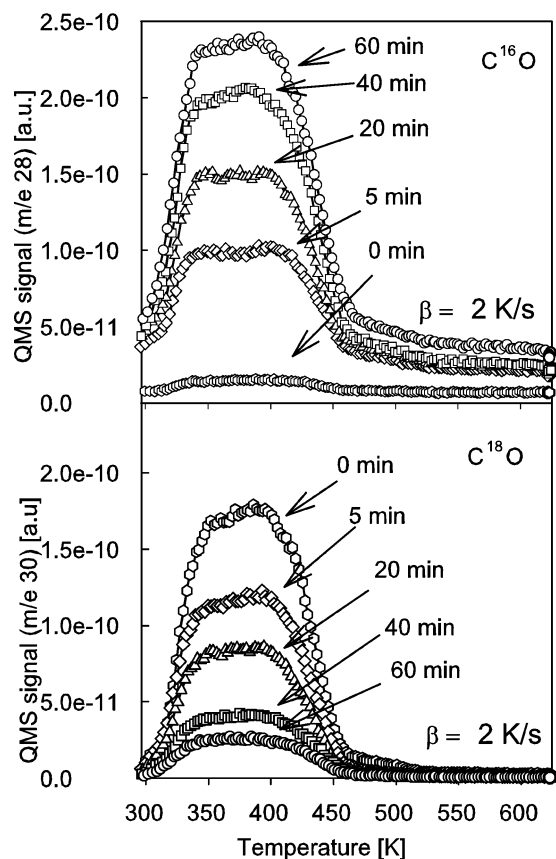
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Figure 1. $C^{18}O$ and $C^{16}O$ TPD spectra after exposure to 6 L of $C^{18}O$ at 294 K followed by exposure to 1.2×10^{-5} mbar of $C^{16}O$ at 294 K for between 0 and 60 min.
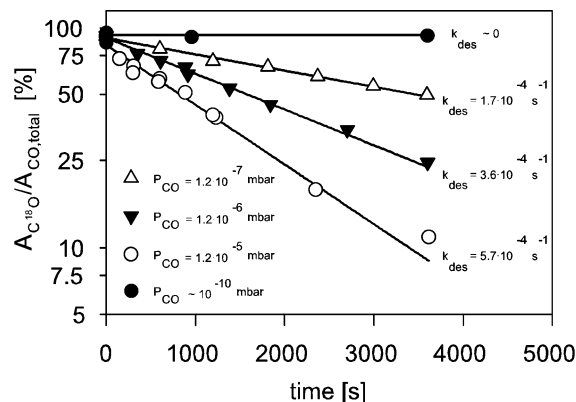

Figure 2. $C^{18}O$ TPD areas as a function of time and the $C^{16}O$ pressure at 294 K. The surface was dosed with 6 L of $C^{18}O$ at 294 K before the exposure to $C^{16}O$.

To investigate the effect of impurities, a series of exchange experiments were carried out without cleaning the sample after leaving it in the chamber for more than 10 h. These experiments led to exchange rate constants with values up to 10 times larger than those obtained from experiments performed on a cleaned sample, even though no significant change in the area or appearance of the TPD spectra was observed. The rate constants were obtained using eq 5 for only one exposure time and therefore only one TPD spectrum. This was done since there was no guarantee that subsequent measurements could be carried out with equivalent amounts of impurities present on the surface. It was assumed that $\theta^0_{C^{18}O} = 0.5 \times 0.95 = 0.48$. Here, the factor 0.95 is due to the fact that about 5% of the initial coverage of labeled CO is actually $C^{16}O$, as obtained from TPD measurements immediately after dosing $C^{18}O$. The procedure
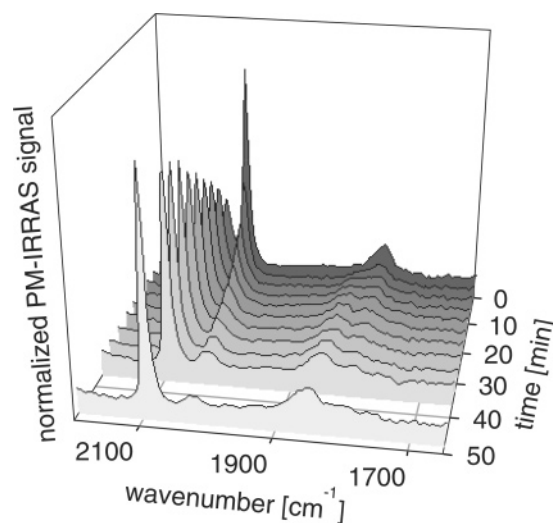

Figure 3. PM-IRRAS spectra for a Pt(111) surface precovered with 6 L of $C^{18}O$ at 294 K during exposure to 1.2×10^{-6} mbar of $C^{16}O$ at 294 K

of obtaining these rate constants from only one exposure time for each pressure can be justified since the rate constants measured for the clean surface are in good agreement with eq 5. The impurities causing the increase in exchange rate could not be detected by XPS, and LEIS spectra showed only a very small peak at mass 12 and a small increase in background at low kinetic energies. A test was carried out by exposing the Pt(111) to small amounts of O_2 before dosing $C^{18}O$, this did not influence the reaction rate, and oxygen does not seem to be the reason for the increased reactivity. As no other impurity was detected after the initial cleaning of the crystal, small amounts of carbon seem to be a possible explanation for the higher rate constants obtained for the uncleaned surface. The effect of steps and kinks was examined by performing exchange experiments after sputtering the sample for 10 and 25 min at room temperature to create defects in the surface. The observed exchange rate was not lowered compared to the results on the clean Pt(111) surface, even though TPD measurements showed that up to 28% of the CO was adsorbed at sites with higher adsorption energies.[27]

The TPD measurements do not reveal information about the surface during reaction; therefore a series of PM-IRRAS experiments were carried out by exposing the Pt(111) sample to 6 L of $C^{18}O$ and measuring the PM-IRRAS spectra when exposing the sample to a pressure of 1.2×10^{-6} mbar of $C^{16}O$. A typical series of spectra can be seen in Figure 3. Initially, a broad peak with a maximum at 1809 ± 2 cm^{-1} and a narrow peak with a maximum at 2052 ± 2 cm^{-1} are seen. During the exchange reaction, the maxima of these peaks decline, and two new peaks arise and reach maxima at 1852 ± 2 and 2094 ± 2 cm^{-1}, which are the well-known peak positions for $C^{16}O$ adsorbed on Pt(111) at bridge sites and on-top sites when θ_{CO} is 0.5.[6-10] This leads to the conclusion that both bridge-site and on-top-site CO adsorbates are exchanged and basically at the same rate. The total peak areas for on-top-site and bridge-site CO have standard deviations of less than 3% and 8%, respectively, but the signal intensities are not proportional to the ratio of the coverages of the two isotopes as intensity borrowing by the high-frequency peaks leads to a significant exaggeration of the high-frequency peaks arising from $C^{18}O$.[28-30] As the total coverage of CO molecules on the surface remains unchanged as long as the CO pressure is kept constant, the shifts in peak position are due to dipole–dipole interactions, as
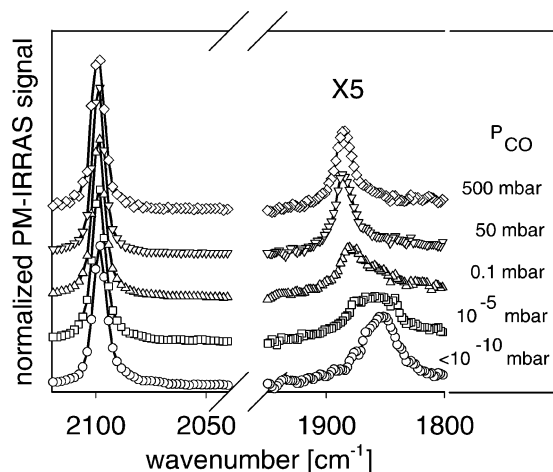
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Figure 4. PM-IRRAS spectra for a Pt(111) surface exposed to various pressures of CO at room temperature.
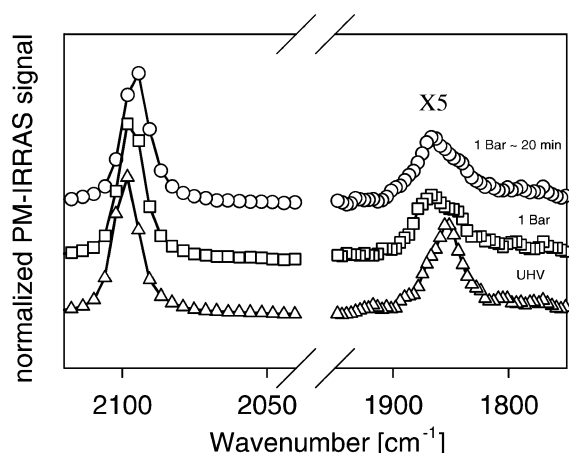

Figure 5. PM-IRRAS spectra for a Pt(111) surface precovered with CO while in UHV, just after exposure to 1 bar of H_2 and after about 20 min of exposure to 1 bar of H_2. The experiment was carried out at room temperature.

no chemical shift will be observed. The observed shift for the on-top-site peaks is roughly 27 cm^{-1}, which is in good agreement with observations done by Olsen et al.,[8] who observed a shift of 25.1 cm^{-1} for the $^{13}CO-^{12}CO$ system on Pt(111), but slightly higher than results published by Schweizer et al., who for the $C^{16}O-C^{18}O$ system on Pt(111) found a shift of around 20 cm^{-1}.[31]

Influence of the CO and H_2 Pressures. The influence of the CO pressure on the observed vibrational spectra was examined over a range in pressure of 12 orders of magnitude. Figure 4 shows representative spectra taken with a resolution of 2 cm^{-1}. The on-top signal appears unchanged within the experimental error. The signal arising from bridge-site CO is initially rather broad, at CO pressures above 1 mbar, it is completely shifted from 1850 to 1875 cm^{-1}, and the line width becomes slightly smaller. This is completely reversible, and the original spectrum reappears upon pumping out the CO.

The influence of H_2 on the PM-IRRAS spectrum was tested by dosing of 6 L of CO, followed by exposure to 1 bar of H_2 at room temperature. Representative spectra can be seen in Figure 5. After 15 min, the system stabilized, and the spectra remained unchanged for up to 2 h, after which point no more spectra were taken. The signal from bridge-site-bound CO is shifted 25 cm^{-1} upward, while the signal from on-top-site-bound CO is shifted 3 cm^{-1} downward. When the sample was precovered with CO, transferred to the HPC, exposed to 1000

mbar H_2, and then heated to 363 K, the influence of the H_2 was more pronounced as can be seen in Figure 6a. The first spectrum was obtained at room temperature, while the rest of the spectra were obtained at 363 K. To distinguish the effect of H_2 at 363 K from the effect of heating the crystal, another experiment was conducted, in which the crystal was covered with CO and transferred to the HPC, which was then sealed off before the crystal was heated to 363 K. The resulting spectra can be seen in Figure 6b. The inserts in Figure 6 show the peak areas as functions of time. The ratio of the intensities of the on-top CO signal and the bridge-site CO signal at room temperature is constant and approximately equal to 3, which is in reasonable agreement with the ratio of 2.7 found by Schweizer et al. at $\theta_{CO} = 0.5$.[31] Ideally, the area is proportional to the polarizability of the molecules and the number of molecules per surface area; however, as the polarizability of adsorbed CO may change with the coverage of CO and H,[28,32] one has to be careful in deducing conclusions about the CO coverage on the basis of peak area. The immediate conclusion that can be drawn on the basis of frequency shift and peak area is that the applied H_2 pressure has a very limited effect at room temperature but leads to a significant desorption of CO at 363 K. The system used here is closed after introduction of H_2, and one has to take the rise in partial pressure of CO due to any desorbing CO into account. On the basis of the surface area of the single crystal and the volume of HPC, we estimate a maximum partial pressure of CO of 6×10^{-8} bar, equivalent to 0.06 ppm of CO in 1 bar of H_2.

As we have an interest in the conditions relevant for the PEMFC, the influence of H_2 in a mixture containing 10 ppm of CO in H_2 was examined at temperatures varying from room temperature to 483 K. The total pressure in the system was 1000 mbar, and reference measurements were made in 1000 mbar of argon also containing 10 ppm of CO. The results can be seen in Figure 7. At each temperature, the measurements were repeated, and no variation with time was seen. As a control experiment, a spectrum was obtained at room temperature before increasing the temperature. All of the spectra obtained at room temperature were equal within the experimental error. In this mixture of 10 ppm of CO in H_2, it was necessary to raise the temperature to 423 K before a significant influence of H_2 on the spectrum was seen. The effect of H_2 was found to increase with temperature.

Discussion

Isotopic CO Exchange. The CO pressures necessary to achieve a significant isotopic exchange rate on Pt(111) are surprisingly low. Figure 8 shows the relationship between the pressure and the rate constant found for Pt(111) in this work and the rate constants reported by Davies et al.[2] The results presented from platinum nanoparticles were obtained by adsorbing ^{13}CO on Pt nanoparticles with an average size of 2.5 nm. The nanoparticles were then subjected to a flow of CO or CO in argon, and the rate of ^{13}CO desorption was measured using a QMS. As can be seen in Figure 8, it was found that the logarithm of the desorption rate constant was directly proportional to the logarithm of the CO partial pressure. We also observe this relationship between the CO pressure and the rate constant. However, the CO pressures needed for achieving similar rate constants are 5 orders of magnitude lower for the single-crystal surface than those for the nanoparticles.

The exchange rate at constant CO pressure will mainly be determined by the desorption energy and the number of the sites with the lowest adsorption energy that are filled at a particular
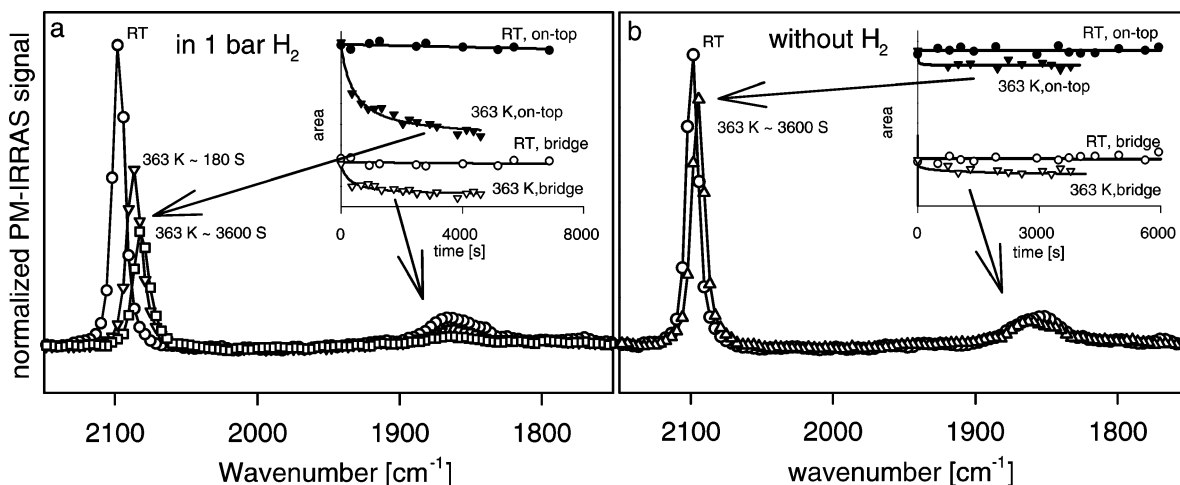
Figure 6. Selected PM-IRRAS spectra of a Pt(111) surface precovered with CO at room temperature and heated to 363 K (a) in 1000 mbar of H_2 and (b) without H_2. The inserts show the development of the peak areas.
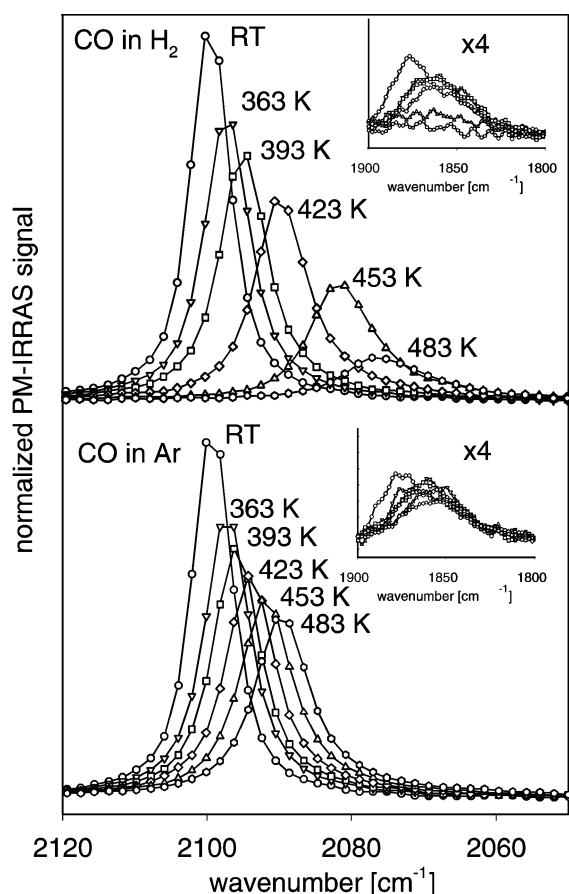

Figure 7. PM-IRRAS spectra for for a Pt(111) surface exposed to 1000 mbar of 10 ppm of CO in (top) H_2 and (bottom) argon at different temperatures.

Figure 8. CO desorption rate constants as functions of CO pressures. P_0 is 1 bar.

pressure. This does not mean, however, that CO bound to sites with a higher binding energy are not exchanged, since scrambling due to diffusion of CO molecules to and from adsorption sites at steps and kinks has been shown to occur in isotope experiments on Pt.[27] If the curves in Figure 8 are extrapolated into the pressure range $10^{-8}-10^{-4}$ mbar, then it follows that the Pt(111) single-crystal surface has many more sites with desorption energies low enough to allow exchange than the Pt nanoparticles. STM measurements by Longwitz et al. have shown that increasing CO pressure leads to a continuous rise in θ_{CO} on Pt(111) due to incommensurate superstructures.[11] On the nanoparticles, however, the CO coverage is quantized due
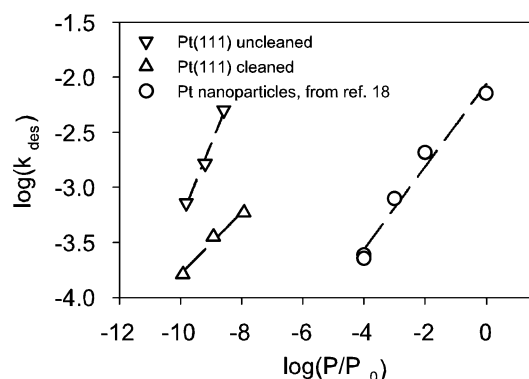
to the limited number of adsorption sites and hence CO molecules present on a particle. To illustrate, a facet with 20 Pt atoms will have a θ_{CO} of 0.5 when 10 CO molecules are adsorbed, adsorption of one more molecule will lead to a CO coverage of 0.55, which is a very significant increase in coverage. This quantization is a possible explanation to the observed difference in exchange rate between the Pt(111) surface and the nanoparticles.

The amount of impurities present on the Pt(111) surface after 10 h of exposure to UHV was found to increase the rate constant about 1 order of magnitude, as seen in Figure 8. The increased desorption rate constant is probably due to the introduction of new sites with low CO adsorption energies. The limited size of this effect and the fact that the rate on the nanoparticles is lower than that on the Pt(111) surface at comparable pressures make it highly unlikely that impurities (probably C) present on the Pt(111) surface are the cause of the difference in rate constants found in this work and the rate constants found by Davies et al.[2] The fact that the exchange rate was not affected by the introduction of defects in the Pt(111) surface can be explained by the single-crystal surface remaining widely extended even with defects. As explained above, the sites with high adsorption energy created by sputtering are probably not rate-limiting in the exchange experiment.

Influence of the CO and H_2 Pressures. In agreement with SFG studies published in the literature, the absorption band from on-top CO is not affected dramatically by the applied CO pressure.[12-14] The signal from bridge site CO is shifted 25 cm^{-1} upward. These shifts on going from $\theta_{CO} = 0.5$ to 0.7 have previously been studied by IRAS under UHV conditions at

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100 K.[9] In ref 9, a peak at 1841 cm^{-1} was found at $\theta_{CO} = 0.6$; this peak was assigned to bridge-site species experiencing decreased dipole−dipole coupling causing a lowering of the frequency. We have seen no sign of such a phenomenon. Apart from this, nothing points toward differences between high coverages achieved at low temperatures and under high CO pressures. This lack of a pressure gap for the Pt(111) system is in agreement with the conclusion of Longwitz et al. based on STM studies.[11] However, as pointed out by Longwitz et al., Persson et al. conclude that the low-temperature system at 0.7 CO coverage consists of ordered strips with the c(4 × 2) structure separated by domain walls of higher CO density, whereas Longwitz et al. conclude that at CO coverages above 0.5 at room temperatures incommensurate, or in some cases commensurate, uniform overlayers are formed. Still, we observe the same shift; therefore one should be careful about drawing conclusions about the chemical shift or dipole−dipole interactions leading to the shift of the peak arising from bridge-site species. It is striking that the same shift is observed in both CO high-coverage systems and the system with CO and H$_2$ coadsorbed, indicating that the shift is in all cases a result of compression of the adsorbed CO molecules. The mechanism is not fully understood. Persson et al. suggest that interaction between bridge-adsorbed CO molecules and on-top-adsorbed CO molecules at the domain walls could be the reason. This cannot be the case at our high-pressure and room-temperature system, since this system consists of a uniform CO overlayer. The effect of H$_2$ observed is much smaller than previously reported by Gland et al.[16,17] At room temperature, we see a limited effect of H$_2$ when applying a H$_2$ pressure 4 orders of magnitude larger than that used by Gland et al. Even at 1 bar of H$_2$ and at 363 K, the effect that we observe is much smaller than that reported by Gland et al. for a H$_2$ pressure of 0.2 Torr at 348 K. However, as mentioned in the Results section, CO desorbing from the crystal will give rise to a low CO pressure (less than 6×10^{-8} mbar) in our experiment. This could be part of the explanation for the apparent discrepancy between our results and those reported by Gland et al.[16,17] As H$_2$ seems not to influence the PM-IRRAS spectra at temperatures below 423 K when the gas contains 10 ppm of CO, it is obvious, as is also known from practical experience,[1,33] that adsorbed CO will occupy a significant part of the surface and hence present a serious problem under the conditions relevant to the PEMFC. An increase in temperature will lead to a reduction of the CO coverage. The result that H$_2$ does influence the PM-IRRAS spectra at temperatures above 423 K can be rationalized if it is assumed that a certain fraction of free sites is needed for dissociation of H$_2$. The resulting hydrogen replacement of CO is a simple consequence of the increased chemical potential of the adsorbed hydrogen induced by the increased hydrogen pressure. Experiments performed for lower initial CO coverages did show a lowering of the PM-IRRAS signal at room temperature during exposure to 1000 mbar of H$_2$, indicating that the replacement of CO by H$_2$ is related to the initial CO coverage. Since our results clearly show that the influence of H$_2$ on CO adsorption on Pt(111) is very limited under the conditions relevant to the PEMFC, we have not pursued this matter any further.

Conclusion

Using PM-IRRAS and TPD, we have found that significant isotopic CO exchange takes place on the Pt(111) surface at CO partial pressures down to 10^{-7} mbar. This is in contrast with results reported for Pt nanoparticles where CO pressures several orders of magnitude larger are needed to achieve comparable rates, which suggests the presence of a structure gap. The PM-IRRAS spectra of CO on Pt(111) for CO partial pressures varying over 12 orders of magnitude are reported and compared to IRAS spectra observed at similar CO coverages in a vacuum at 100 K. No significant differences were observed, leading to the conclusion that there is no true pressure gap in the Pt(111)−CO system. When the Pt(111) surface precovered with CO ($\theta_{CO} = 0.5$) was exposed to 1 bar of H$_2$ at room temperature and at 363 K, it was found that the effect of H$_2$ is limited at room temperature, while there is a significant replacement of CO at 363 K. If the H$_2$ gas contains just 10 ppm of CO, then no effect is seen at temperatures below 423 K, clearly demonstrating the poisoning effect of CO on a PEMFC.

References and Notes

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