Hydrogen and Deuterium Exchange on Pt(111) and Its Poisoning by Carbon Monoxide Studied by Surface Sensitive High-Pressure Techniques

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Abstract: Catalytic hydrogen/deuterium exchange on a platinum (111) single crystal and its poisoning with carbon monoxide was studied using scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), sum frequency generation vibrational spectroscopy (SFG), and mass spectrometry under reaction conditions at pressures in the mTorr to atmospheric range. At 298 K and in the presence of 200 mTorr of hydrogen and 20 mTorr of deuterium the surface is catalytically active, producing HD with activation energy of ~5.3 kcal/mol. Addition of 5 mTorr of CO stops the reaction completely. In situ STM images reveal an ordered surface structure of chemisorbed CO. At 353 K the addition of 5 mTorr of CO slows the reaction by 3 orders of magnitude, but HD production continues with an activation energy of 17.4 kcal/mol. Changes in coverage and adsorption site of CO were followed by XPS and SFG up to a temperature of 480 K. From these data, a CO dominated, mobile and catalytically active surface model is proposed

Introduction

The poisoning of catalysts is a problem that despite its economic and environmental importance is still not understood completely. Poisoning is a complex phenomenon involving a variety of effects, the simplest one being site blocking, where a strongly bound species prevents adsorption of the reactants. However, site blocking is rarely complete, and numerous vacancies are still present on the catalyst surface. These residual vacancies may form ensembles that are too small to allow adsorption of reactants or the formation of reaction intermediates. In that case, mobility of the poison species at sufficiently high temperatures might unblock the catalyst surface by allowing reactants to diffuse and vacancies to aggregate into sufficiently large ensembles. This is an interesting situation since the poison either becomes a passive spectator species or generates patterns of vacancies with special geometries. It might also control, through its diffusion parameters, the rate and selectivity of the reaction. To investigate these important issues the molecular-scale structure of the surface during reaction must be determined. Until recently most molecular-scale surface science studies have been performed at low pressures because the techniques used to obtain such information cannot operate under the high-pressure conditions required for catalysis.

This situation has changed dramatically in recent years due to the development of microscopy and spectroscopy techniques that can operate under realistic pressure and temperature conditions. Here we have employed three such techniques: high-pressure scanning tunneling microscopy (HPSTM), high-pressure X-ray photoelectron spectroscopy (HPXPS), and sum frequency generation vibrational spectroscopy (SFG) to study a catalytic system near ambient conditions. HPSTM provides atomically resolved images of the surface under high pressures and temperatures,[1-3] thus revealing the structure and dynamics of adsorbed layers. High-pressure XPS (HPXPS), also known as ambient pressure photoelectron spectroscopy (APPES), provides quantitative chemical information and specific binding sites at pressures currently up to 5 Torr.[4,5] SFG, a nonlinear optical technique, provides vibrational spectra and reveals chemical environmental changes in adsorbate structure. The H_2/D_2 exchange reaction is an important probe reaction to study a catalytic surface's activity and, thus, its ability to dissociate hydrogen. The use of these three powerful surface-sensitive techniques to probe the system while concurrently monitoring catalyst activity can give a comprehensive view of the structure of active and poisoned catalyst surfaces.

Experimental Section

High-pressure STM experiments were performed in an instrument that has been described in detail elsewhere.[6,7] The system combines a UHV surface analysis/preparation chamber with a variable temperature (298−675K) and pressure (10^{-10} to 10^3 Torr) chamber housing an STM head from RHK. The base pressure of the system was 1×10^{-10} Torr with a background mostly made up of H_2, CO, and H_2O. By using

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gate valves the STM chamber can be isolated from the rest of the system and filled with gases. A mass spectrometer (Stanford Research Systems, RGA 200) connected to the chamber by a leak valve was used to monitor the gas composition.

The sample was a platinum single crystal of (111) orientation from Matek Corporation with a miscut angle of <0.3°. Before each experiment the sample was sputtered with Ar ions of 500 eV and a current of 4 μA for 15 min. After sputtering, the sample was heated with an electron beam to 1073 K for 10 min. This process was repeated a few times before transferring the sample to the reaction chamber. The surface composition was monitored by Auger electron spectroscopy and checked with STM prior to gas introduction.

During experiments the STM chamber was isolated from the rest of the system while various combinations of hydrogen, deuterium, and carbon monoxide were introduced. Hydrogen was always introduced first followed by CO and deuterium. In the presence of reactive gases a 150 W projector bulb without any mechanical contact radiatively heated the sample. A type K thermocouple spot-welded to the side of the crystal monitored sample temperature. The sample was always allowed to equilibrate at least 5 min prior to imaging. Blank experiments were run under identical conditions (by removing the crystal) in order to check for background reactions. Electrochemically etched tungsten tips were used for imaging.[8] STM settings during image acquisition were $I = 0.05$ to 0.2 nA and $V = 50-100$ mV. A Baratron model 722A from MKS was used to monitor chamber pressure.

The HPXPS experiments were performed at beamline 11.0.2 at the Advanced Light Source in Berkeley. The system uses a differentially pumped electrostatic lens system that has been described previously.[5,9] The platinum 4f, carbon 1s, and oxygen 1s peaks were recorded at incident photon energies of 230, 450, and 690 eV, respectively, so that the photoelectron kinetic energies, and therefore the surface sensitivity, are the same. After normalization, the peak areas were used to monitor the surface coverage of CO. The hydrogen, deuterium, and carbon monoxide flows were regulated with three leak valves, which continuously replenished the gases lost through the spectrometer aperture. Sample heating was accomplished using a button heater directly beneath the sample, which was turned off during measurement.

The SFG experiments were carried out in a system consisting of a UHV chamber with base pressure of 2×10^{-9} Torr and a high-pressure cell isolated from the UHV chamber by a gate valve. Two CaF$_2$ windows on the HP cell allow transmission of infrared (IR), visible (VIS), and sum frequency radiation for SFG experiments. A Nd:YAG laser produced 1064 nm photons in 20 ps pulses and 20 Hz repetition rate. This was used to create a tunable IR (1800-4000 cm^{-1}) and a visible second harmonic VIS (532 nm) beam. The VIS (200 μJ) and the IR (200 μJ) beams were spatially and temporally overlapped on the Pt(111) surface with incident angles of 55° and 60°, with respect to the surface normal. All spectra were taken using a ppp polarization combination (SFG, VIS, and IR beams were all p-polarized). The SFG beam was sent through a monochromator and the signal intensity measured with a photomultiplier tube and gated integrator, while the IR beam was scanned over the range of interest. By using a previously reported procedure[10,11] the spectra were curve fit to a form of the equation

$$I_{SFG} \propto |\chi_{NR}^{(2)} e^{i\phi_{NR}} + \sum_q \frac{A_q}{\omega_{IR} - \omega_q + i\Gamma_q} e^{i\gamma_q}|^2 \quad (1)$$

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Table 1. Turnover Frequencies for H$_2$/D$_2$ Exchange on Pt(111) over a Range of Temperatures

(a) In the Presence of 5 mTorr of CO

temp (K)	CO coverage (monolayers)	surface mobile?	H$_2$/D$_2$ exchange rate (molecule/site/s)
298	0.6	N	below detection limits
353	0.46	Y	0.031
375	0.45	Y	0.064
393	0.44	–	0.125
422	0.42	–	0.478
440	0.38	–	1.775
458	0.36	–	13.17

(b) In the Absence of CO

temp (K)	surface mobile?	H$_2$/D$_2$ exchange rate (molecule/site/s)
298	Y	4.3
325	Y	15.0
345	–	39.1
373	–	83.6
420	–	122.4
464	–	100.9

where $\chi_{NR}^{(2)}$ is the nonresonant nonlinear susceptibility, $e^{i\phi_{NR}}$ is the phase associated with the nonresonant background, A_q is the strength of the qth vibrational mode, ω_{IR} is the frequency of the incident infrared laser beam, ω_q is the frequency of the qth vibrational mode, Γ_q is the natural line width of the qth vibrational transition, and $e^{i\gamma_q}$ is the phase associated with the transition. Detailed descriptions on the system can be found elsewhere.[12-15]

Results and Discussion

Reactivity Studies. The catalytic activity for H$_2$/D$_2$ exchange on the Pt(111) crystal was studied in the presence and absence of CO over a temperature range of 298-480 K. It was found that at room temperature and in the presence of 200 mTorr of H$_2$ and 20 mTorr of D$_2$, the surface is catalytically active, producing HD at a rate of ~4.3 molecules/site/s. Upon introduction of 5 mTorr of CO, however, the production of HD dropped below the detection limits of our mass spectrometer, and no products could be detected over the course of 1.5 days. At 345 K the turnover frequency in the absence of CO increased to 39 molecules/site/s, which is about 10 times higher than that at room temperature. Addition of 5 mTorr of CO at this temperature decreased the reactivity dramatically, but unlike in the room-temperature case, catalytic activity was still observed at the rate of 0.03 molecules/site/s. Turnover rates for HD production with and without CO as a function of temperature are shown in Table 1 and in the Arrhenius plot of Figure 1. The activation energy for the H$_2$/D$_2$ exchange reaction in the absence of CO is 5.3 kcal/mol, slightly above the value obtained at low pressure for Pt(111)[16] and similar to that found also at low pressure on polycrystalline samples.[17] The introduction of CO into the system causes the activation energy to more than triple to 17.4 kcal/mol. A similar result was obtained for the poisoning of ethylene hydrogenation on Pt(111). In this case

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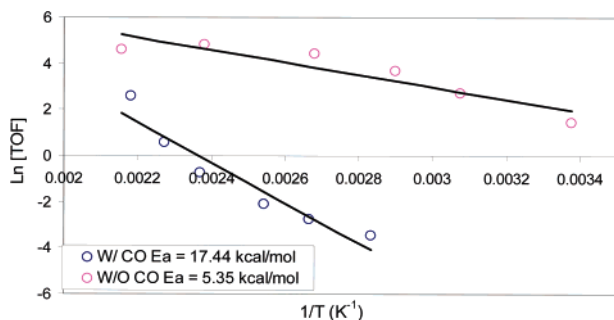(17) Norton, P. R.; Richards, P. J. *Surf. Sci.* **1974**, *41*, 293.

Figure 1. Arrhenius plot of the H_2/D_2 exchange turnover frequency (TOF) on a Pt(111) surface in the presence of a gas mixture consisting of 200 mTorr H_2 and 20 mTorr D_2 (top curve). The bottom curve is for a similar experiment after addition of 5 mTorr of CO to the gas mixture. The activation energy increases from 5.35 kcal/mol to 17.44 kcal/mol upon the addition of CO.

the activation energy increased from 9.6 kcal/mol for the clean surface to 20.2 kcal/mol for the CO-poisoned surface.[18,19] The heat of desorption of CO at high coverage is also about 20 kcal/mol.[20] Although a bit smaller, the high value of the activation energy for H_2/D_2 exchange suggests that the rate-limiting step in the reaction may be the desorption of CO, which is necessary for adsorption of gaseous species.

The lower activation energy of the H_2/D_2 poisoned system versus the poisoned ethylene hydrogenation system is likely due to the smaller vacancy aggregates that are necessary for H_2/D_2 exchange. The reaction rates for the poisoned and unpoisoned H_2/D_2 exchange reactions, initially differing by more than 3 orders of magnitude, begin to approach each other at the highest temperature studied, as the lower coverage of CO liberates surface sites for reactant adsorption and surface dynamics.

The reactivity studies performed illustrate the nonlinear relationship between surface reactivity and coverage of a poison molecule, thus indicating that multiple surface sites are necessary for reaction.

Scanning Tunneling Microscopy Studies. STM images acquired at room temperature under reaction conditions (200 mTorr H_2, 20 mTorr D_2) show a surface with no discernible order (Figure 2a) as the adsorbate species are diffusing much faster than the scanning rate of our instrument ($\sim$10 μm/s). STM images of the surface after introducing 5 mTorr of CO to poison the reaction revealed an ordered surface with hexagonal symmetry (Figure 2b), which is similar to that formed by pure CO on Pt(111)[3] in this pressure range. The structure is incommensurate with that of the Pt(111) lattice and has a coverage of about 0.6 monolayer (ML). A schematic of the proposed structure is shown is Figure 2c.

Imaging the surface at 345 K under 5 mTorr of CO showed no periodic structure indicative of the highly mobile nature of the CO overlayer. Cooling the sample to room temperature produced an ordered structure similar to that observed previously (Figure 2b).

In previous studies of hydrogenation/dehydrogenation of cyclohexene and ethylene hydrogenation reactions under similar pressure conditions[21,22] we have shown that, although the STM
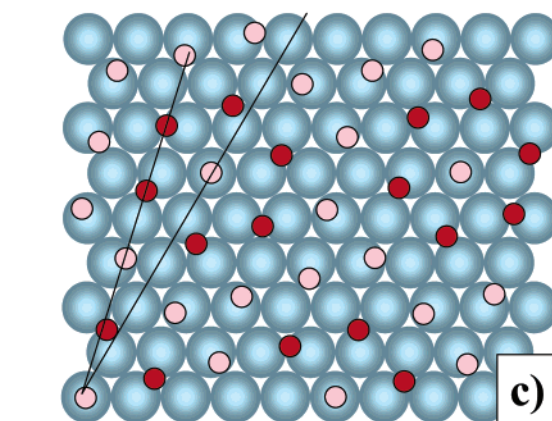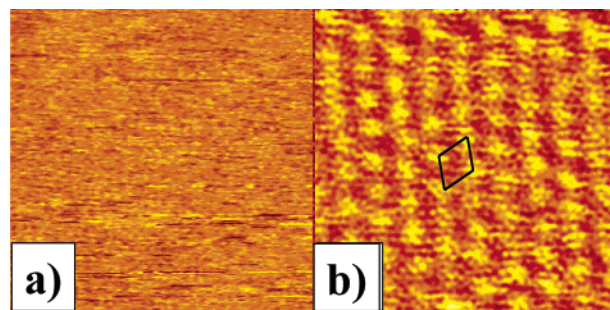
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Figure 2. 90 Å × 90 Å STM images of Pt(111) at 298 K: (a) in the presence of 200 mTorr H_2 and 20 mTorr D_2. The catalyst is actively producing HD. (b) in the presence of 200 mTorr H_2, 20 mTorr D_2, and 5mTorr CO. The production of HD has ceased. The structure observed is due to a CO monolayer forming an incommensurate structure, as shown in the diagram in (c). CO molecules are represented by the small circles and color coded according to their proximity to a top site (dark) or to a bridge site (light).

images indicated surface disorder upon heating, no products were observed until the temperature was near 400 K.[23,24] The appearance of disorder due to enhanced mobility is a result of the creation of vacancies. Vacancies are necessary for the adsorption of reactants and also to permit mobility of adsorbates so that they can collide and react. The fact that catalytic activity is still observed at 353 K for H_2/D_2 exchange but not for cyclohexene and ethylene hydrogenation reactions suggests that to react these hydrocarbon reactants require larger vacancy ensembles than H atoms do, which should be more difficult to produce on a CO crowded surface. These STM studies show the clear relationship between surface mobility and reactivity.

X-ray Photoelectron Spectroscopy Studies. HPXPS spectra of the C1s and O1s peaks from adsorbed CO at 298 K in equilibrium with gas at a pressure of 200 mTorr H_2, 20 mTorr D_2, and 5 mTorr CO are shown in Figure 3. Two XPS peaks can be resolved in the C1s region, at 286.8 and 286.1 eV, and in the O1s region at 531.5 and 533.5 eV. Similar values for the C1s and O1s peaks were obtained in low-pressure studies at 200 K[25,26] for the $c(4 \times 2)$ CO on Pt(111) structure, although in that case the peaks were about 30% narrower. They were assigned to top site (286.8 and 533.5 eV) and bridge-site adsorption (286.1 eV and 531.5 eV). In the $c(4 \times 2)$ structure each CO molecule is bound to either a top site or a bridge site.

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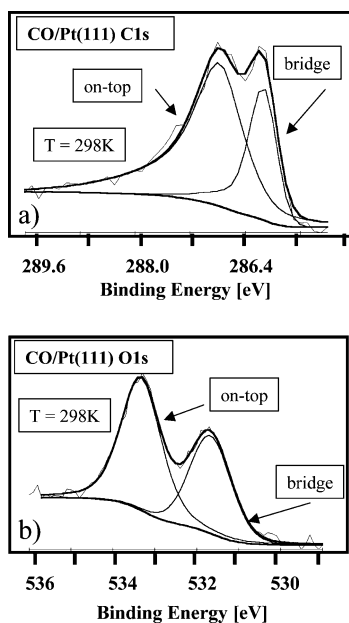
CO/Pt(111) C1s

on-top

bridge

T = 298K

a)

289.6   288.0   286.4
Binding Energy [eV]

CO/Pt(111) O1s

T = 298K

on-top

bridge

b)

536   534   532   530
Binding Energy [eV]

Figure 3. XPS spectra of Pt(111) at 298 K acquired in the presence of 200 mTorr H_2, 20 mTorr D_2, and 5 mTorr CO. (a) C1s region. (b) O1s region. The peaks can be deconvoluted into two components that are assigned to near-top and near-bridge positions.

In the model shown in Figure 2c, however, the CO molecules occupy sites that vary from top to bridge and many intermediate positions. The observation of two well-resolved XPS peaks is therefore surprising. It suggests that the CO molecules might not be rigidly constrained to occupy the exact position shown in the schematic of Figure 2c and that small lateral displacements might be present that bring the molecules closer to top or bridge sites. For example, the lightly shaded circles in Figure 2c represent CO molecules that are close to a top site, while the dark ones represent those close to a bridge site. Our XPS results suggest that small displacements from the top and bridge sites produce only small changes in binding energy.

The XPS peaks were monitored as the surface temperature was increased from 298 to 480 K in the presence of 200 mTorr H_2, 20 mTorr D_2, and 5 mTorr CO. For quantitative analysis the total C1s and O1s peaks areas were normalized to the known initial coverage of 0.6 ML of CO.[3,20] Due to the larger splitting, the O1s peaks were used for quantitative analysis. The resulting data are plotted in Figure 4. As the temperature is increased, the total coverage decreases from 0.6 ML at 298 K to 0.47 ML at 345 K, followed by a plateau and a further decrease above 400 K to reach 0.34 ML at 480 K. The ∼20% decrease of CO coverage from 298 to 345 K is accompanied by an increase in surface reactivity from below the detection limit to 0.03 molecule/site/s. While measurable, it is still 3 orders of magnitude smaller than in the absence of CO, indicating that the reactivity does not scale proportionally to the area free of CO (0.2 ML). If dissociative adsorption is the rate-limiting step, one explanation could be that aggregates of several vacancy sites are needed for that reaction to occur. Such an effect has indeed been observed at low temperature for the dissociation of H_2 on Pd(111), which requires ensembles of three or more
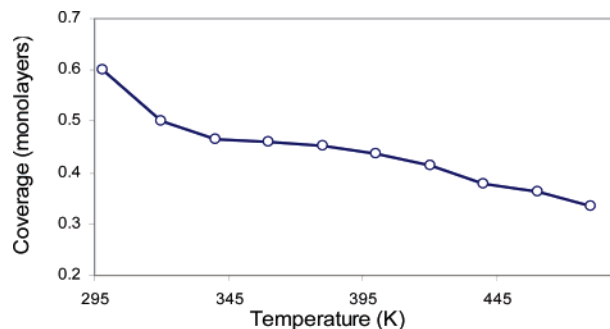

Figure 4. CO coverage on Pt(111) in the presence of 200 mTorr H_2, 20 mTorr D_2, and 5 mTorr of CO as a function of temperature. The coverage was obtained from the XPS peak intensity of the O1s peaks and normalized to 0.6 at 298 K corresponding to the known coverage under these conditions.

free sites.[27] If a similar argument is valid for vacancies in a CO-covered surface, the coverage of 0.2 ML vacancies would generate n-vacancy sites in proportion to 0.2^n. The observed decay in reactivity of 10^{-3} relative to the clean surface would imply $n \approx 4$. Another possible explanation is that CO simply limits the ability of H and D to diffuse across the surface and collide. Optical diffraction studies of the independent diffusion of hydrogen atoms and CO molecules on Pt(111) give low-coverage diffusion constants for hydrogen that are more than 3 orders of magnitude higher than for CO.[28,29] Clearly, a hydrogen atom adsorbed on a surface covered to 80% of saturation by CO will have its ability to diffuse severely hindered.

Given the similarity in activation energy of the exchange reaction on the poisoned surface to the desorption energy of CO, it appears that the creation of vacancy aggregates is the rate-limiting step. The relative population of CO molecules on top and bridge positions can be obtained from the areas of the XPS spectra. We found that the ratio of peak areas of top sites and bridge sites for the O1s peaks (which show the least overlap) remained essentially constant around 1.50 ± 0.08 between 298 and 380K. Above 380 K the ratio decreases to 1.32 ± 0.07. However, this ratio does not represent the population ratio of the two types of sites since it is affected by diffraction effects, which alter differently the areas of the two energy components of the XPS peaks.[25,30] In the low-temperature studies by Bjorneholm et al.[26] on a surface covered by 0.6 ML of CO, spectra similar to ours were obtained. The structure proposed is a $c(5 \times \sqrt{3})$rect,[31] with a 2:1 ratio of top to bridge sites. The STM data in Figure 2 however, show that this is not the structure present in our experiments, which instead is described by a hexagonal unit cell with large periodicity similar to that found by Longwitz et al.[3] These authors showed that as a function of coverage a nearly continuous variation of the size of the large hexagonal unit cell is produced. They proposed that the CO molecules form hexagonal close-packed arrangements incommensurate with the substrate lattice, such as the one in Figure 2c. The large unit cells are the result of Moire interference patterns between the CO and Pt lattices. The constant value of

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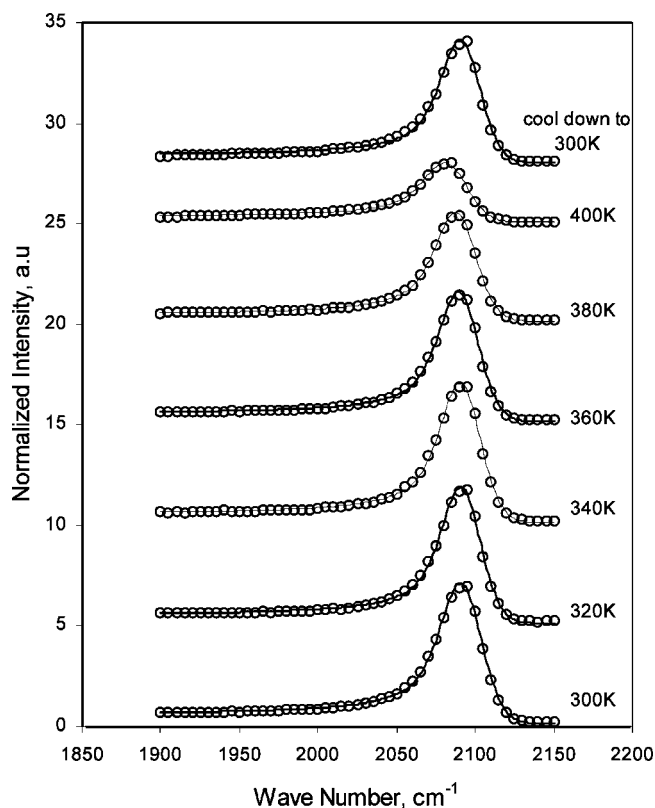(31) Persson, B. N. J.; Tushaus, M.; Bradshaw, A. M. *J. Phys. Chem.* **1990**, *92*, 5034.

Figure 5. Sum frequency generation (SFG) spectra showing the top site CO stretch resonance mode on Pt(111) in the presence of 200 mTorr H_2, 20 mTorr D_2, and 5 mTorr CO. The frequency of the peak at 2097 cm^{-1} remains constant up to 360 K at which point it begins to red-shift. Solid lines represent the curve fits to eq 1 in the text.

Figure 6. (a) CO vibrational resonance frequency, ω_{CO}, and (b) amplitude of the resonant contribution, A_{CO}, plotted against the metal surface temperature. Solid lines are drawn as a visual guide.

the ratio of peak areas between 298 and 360 K indicates that as the CO coverage decreases a similar distribution of near-top and near-bridge sites is maintained, which according to Figure 2c should be 7:6 or a ratio of 1.17. Above 360 K there is a loss of top sites relative to bridge sites, indicating a possible change of structure. The less dense CO structures formed above room temperature must also contain numerous defects where hydrogen and deuterium can adsorb. The defects also make possible the diffusion of adsorbates.

Sum Frequency Generation Vibrational Spectroscopy. Sum frequency generation was also employed to investigate the same system. Figure 5 shows a series of SFG spectra of the Pt(111) surface exposed to 200 mTorr of H_2, 20 mTorr of D_2, and 5 mTorr of CO. The resonant contribution to the SFG spectrum originating from adsorbed CO can be fit to eq 1. In Figure 6 the frequency of the vibrational mode ω_{CO} (a), and its amplitude A_{CO} (b), are plotted against the surface temperature. The peak located at 2097 cm^{-1} corresponds to the top-bound CO molecule.[27] As the temperature is raised from 300 to 360 K, a small shift of the peak to lower frequencies and no discernible decrease in intensity is observed. Heating above 360 K results in a noticeable shift and broadening of the peak. This is also the temperature at which XPS shows a plateau in the coverage and a change of structure due to loss of top site CO molecules. Similar broadening and red-shifts of the CO peak have been previously observed on Pt(111) in the presence of 40 Torr of CO,[32] although the changes were observed at higher
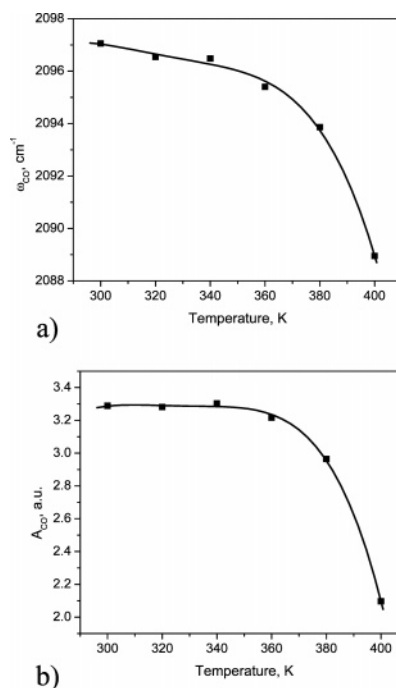
temperatures. This is understandable as the higher pressure allows for a higher surface coverage at increased temperatures. UHV studies have revealed a similar trend in resonant mode shifting, peak broadening, and amplitude reduction.[33] The temperature dependence of the peak width is explained by dephasing, in which a rapid energy exchange occurs between low-frequency modes of the metal surface and low-frequency modes of the adsorbate, which are anharmonically coupled to the higher-frequency mode investigated in this study. However, comparison of the peak widths obtained in this study, ~15 cm^{-1}, to that of CO adsorbed on a well ordered Pt(111) surface, ~8 cm^{-1},[34] implies significant inhomogeneous broadening. This broadening can be attributed to the creation of defect sites from sputtering procedures. Furthermore, step-site vibrations have been assigned to 2065–2078 cm^{-1}.[35] In both our current study and the previous high-pressure study, cooling the sample back to room temperature returned the initial spectrum, indicating as did STM that the initial incommensurate CO structure is restored.

In summary, the SFG spectra show that, as the surface temperature is increased, the CO peak position red-shifts, showing that adsorbed CO is becoming more mobile on the surface. Furthermore, as the surface temperature is cooled to 300 K, the SFG spectrum reveals the reversibility of the system, implying that hydrogen and deuterium are readsorbing onto the surface. Had hydrogen and deuterium been blocked by the adsorbed CO molecules, the CO peak position would have been blue-shifted upon cooling.

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Conclusions

The adsorption of CO on the Pt(111) catalyst surface increases the H_2/D_2 activation energy from ~5.3 to 17.4 kcal/mol, similar to the findings from studies of CO-poisoned ethylene hydrogenation. As the temperature is raised, the reactivity in the presence of CO approaches that of the CO-free system.

The only condition studied in which catalytic H_2/D_2 exchange was not detected was at room temperature in the presence of 200 mTorr of H_2, 20 mTorr D_2, and 5 mTorr of CO. Under these conditions an immobile and ordered monolayer of CO molecules was detected by STM. The immobile structure is composed of CO forming an incommensurate structure relative to the Pt(111) substrate. Removing a small fraction (~20%) of the CO layer via heating the sample allowed the surface to become mobile and also catalytically active. The surface structure remains similar to that at room temperature, according to the XPS and SFG spectra, but now contains vacancies that allow for the dissociative chemisorption of hydrogen as well as for surface mobility of the adsorbed species. The strong poisoning effect of CO can be explained by the need of three or more vacancy ensembles for the dissociative hydrogen and deuterium adsorption, which can form only when numerous vacancies are present. The vacancies allow also for the needed mobility of the reactant atoms.

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