Weighing Fractions of Monolayers: Application to the Adsorption and Catalytic Reactions of H_2, CO, and O_2 on Pt

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The adsorption and catalytic reactions of H_2, CO, and O_2 on Pt were investigated with a quartz-crystal microbalance having a sensitivity of $\sim 10^{-10}$ g/cm^2 ($< 10^{-2}$ monolayers of oxygen). At zero coverage the sticking coefficients for H_2, CO, and O_2 were 0.62, 0.54, and 0.38, respectively. The catalytic oxidation reactions all exhibited Langmuir-Hinshelwood behavior. Detailed rate curves were measured for the H_2-O_2 reaction. The maximum reaction probability was 0.32 per impinging H_2.

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Our intention with this Letter is (1) to describe how catalytic reactions on surfaces may be studied with the quartz-crystal microbalance (QCM) (whose capabilities for such studies are unappreciated), (ii) to present results for the adsorption *and* reactions of three different reactants on the *same* Pt catalyst, and (iii) to present detailed and absolute-reaction-rate data for the H_2-O_2 reaction on Pt.

The principle of the QCM (see, e.g., Stockbridge[1]) is that mass added to one of the electrodes of an oscillating quartz crystal changes the frequency of oscillation in proportion to the added mass. The mass of the deposit may thus be determined if the proportionality factor is known. Even the small mass change caused by adsorption of gases on the sample may be measured. The measurements were performed in a modified version of the equipment used previously to investigate the oxidation of thin Ti films.[2] The frequency of the ~ 10-MHz QCM crystal (AT cut, temperature stabilized at 0 °C), was in this work measured by period-average measurements of the small difference frequency between the QCM frequency and that of a very stable reference crystal. This improved both the sensitivity and the time constant by about an order of magnitude, in comparison with the conventional frequency measurements used previously. The sensitivity and accuracy in these measurements were 0.01–0.1 Hz corresponding to $\sim 10^{-3}$–10^{-2} monolayers of oxygen. The experiments were performed in an ion-pumped, stainless steel UHV chamber[2] with a base pressure of $<10^{-10}$ Torr. High-purity platinum (99.99%) was evaporated from a W crucible onto one of the electrodes of the quartz crystal. The sample thickness and diameter were ~ 300 Å and 5 mm, respectively.

Figure 1 shows the surface coverage as a function of exposure when a Pt film was exposed to O_2 and CO at pressures of 2.4×10^{-7} and 1.8×10^{-7} Torr, respectively. Unity coverage ($\theta_{CO}{}^{sat} \equiv 1$) is defined as the saturation coverage of irreversibly adsorbed CO at 273 K. At CO pressures $> 10^{-6}$ Torr the coverage increased above this value, but decreased to the saturation coverage, $\theta = 1$, by CO desorption when the pressure was lowered. To convert θ to number of molecules per cm^2, we note that the saturation density of CO molecules is about the same on several metals (Pt, Ni, Pd, Ru, Ir, and Cu) and is furthermore rather independent of the crystallographic orientation.[3] Comparing these data, we found 8.0×10^{14} (± 10%) CO molecules/cm^2 to be a most likely saturation density at 273 K.

The saturation coverage of (atomic) oxygen was $\theta_O{}^{sat} = 0.82\theta_{CO}{}^{sat}$ (6.6×10^{14} atoms/cm^2) indicating a slightly smaller number of adsorption sites for O atoms than for CO molecules (it is generally agreed that O_2 adsorbs dissociatively on Pt). This is in good agreement with the results re-

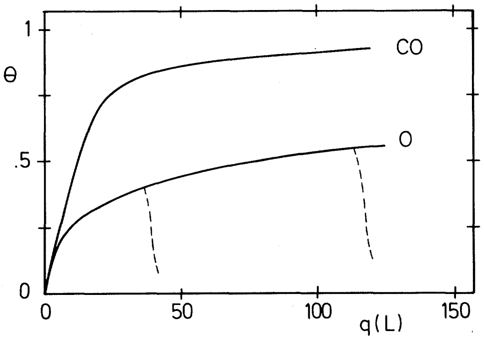

FIG. 1. Coverage of CO molecules and O atoms on Pt vs gas exposure ($P_{CO} = 1.8\times 10^{-7}$ Torr, $P_{O_2} = 2.4\times 10^{-7}$ Torr). $\theta = 1$ is defined as the saturation coverage of CO molecules ($\approx 8\times 10^{14}$/cm^2). The dashed curves show the decrease in oxygen coverage due to H_2O formation when the sample was exposed to H_2 gas (see Fig. 3). (1 L $= 10^{-6}$ Torr s.)

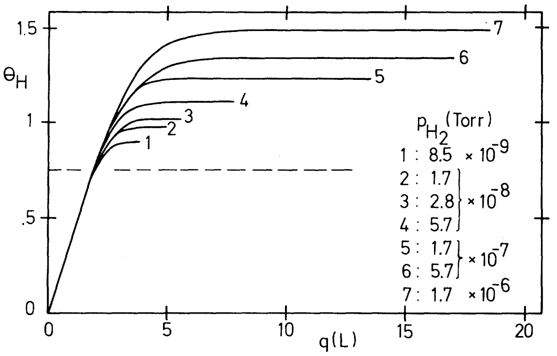

FIG. 2. Hydrogen coverage vs exposure at different pressures. The dashed line corresponds to the saturation coverage in the limit $P_{H_2} \rightarrow 0$.

ported by Joebstl[4] for Pt(111), by Nishiyama and Wise for Pt foil[5] and by Weber, Fusy, and Cassuto[6] for Pt filaments but considerably larger than Norton's results for Pt foil.[7]

Figure 2 shows the increase in coverage of (atomic) hydrogen with exposure at different hydrogen pressures. The saturation coverage of hydrogen increased with increasing pressure, but when the H_2 leak was closed the coverage decreased by desorption to a common, lower coverage. This behavior may be explained by either the presence of two different adsorption sites with different binding energies for hydrogen, or a decrease in the adsorption energy with increasing coverage. A plot of the pressure-dependent saturation coverage versus the square root of the pressure yielded a straight line at the lower pressures, which supports the former interpretation. From the intercept of the straight line with the θ axis a saturation coverage (atomic hydrogen) of $\theta_H{}^{sat} = 0.75\theta_{CO}{}^{sat}$ ($6.0 \times 10^{14}/cm^2$) at zero pressure was obtained, in good agreement with one reported value for Pt foil[5] and intermediate between results for various single-crystal planes.[8]

The zero-coverage sticking coefficients were obtained from the measured adsorption rates at $\theta = 0$. To obtain absolute values the sensitivity of the QCM and the ion gauge were needed. The ion gauge was calibrated with a very accurate capacitance manometer calibrated by the volume-expansion method, while the sensitivity of the QCM was taken from an earlier calibration.[2] We then arrived at sticking coefficients at $\theta = 0$ of 0.62, 0.54, and 0.38 (± 10%) for H_2, CO, and O_2, respectively. (In Fig. 1 the oxygen curve has a steeper slope than the CO curve at $\theta = 0$ because it displays the coverage of O *atoms*.) Sticking coefficients of 0.3 and 0.12 have been reported for H_2 on Pt foil[5,9] while common values for single-crystal planes[8] are in the range 0.1–0.4. Reported sticking coefficients for oxygen vary over a large range but are usually $\gtrsim 0.1$ in well-controlled experiments. In a recent paper Gland and Korchak[10] reported a sticking coefficient of 0.5 at the step sites of a stepped Pt(111) surface while values of 0.25 and 0.16 have been reported for polycrystalline samples.[5,11] Norton's value of ~0.01 for Pt foil seems too small.[12,13] The CO adsorption curve is characterized by an almost constant sticking coefficient in the range $0 \leq \theta \leq 0.5$ which indicates adsorption via a precursor state in the second adsorption layer. Similar observations have been made by other authors.[3] Reported sticking coefficients for CO at $\theta = 0$ are usually 0.1–1 on all surfaces.[3,14]

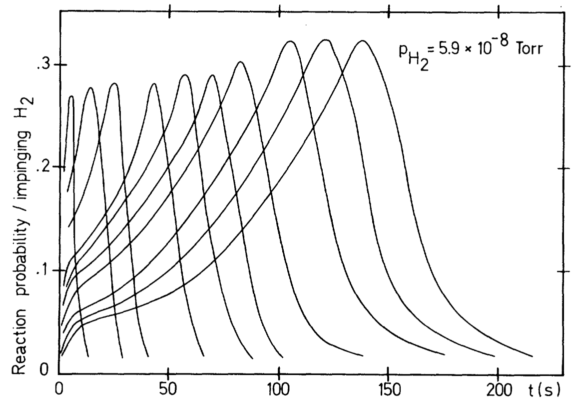

FIG. 3. Each curve shows the H_2O production rate as a function of time when a partly oxygen-covered Pt surface was exposed to H_2 at constant pressure. The oxygen coverages, θ_O, at $t = 0$ were (from left to right): 0.07, 0.16, 0.21, 0.31, 0.40, 0.45, 0.55, 0.65, 0.70, and 0.75.

The catalytic reaction between hydrogen and oxygen to water on Pt was studied by exposing partly oxygen-covered surfaces to H_2 gas at constant pressure. The oxygen coverage then decreased (as indicated by the broken curves in Fig. 1) due to the overall reaction $H_2{}^{gas} + O^{ads} \rightarrow H_2O^{gas}$ until all the oxygen was removed. The rate curves in Fig. 3 were obtained by differentiating such coverage decrease curves with respect to the time of H_2 exposure ($p_{H_2} = 5.9 \times 10^{-8}$ Torr). Each curve corresponds to a different starting coverage of oxygen and approximately gives the rate of decrease of the oxygen coverage, or equivalently the rate of water production, as a function of H_2 exposure. The appearance of a maximum is a strong indication that the reaction is a Langmuir-Hinshelwood (LH) reaction, i.e., a reaction between adsorbed oxygen and adsorbed hydrogen. The so called Eley-Rideal reaction (adsorbed oxygen + gas-phase hydrogen) would show a monotonically decreasing rate with increasing H_2 exposure. The rate at maximum, which slowly increases with increasing initial oxygen coverage, corresponds to a reaction probability of around 0.32 per incident H_2 molecule. The partial-pressure curves of H_2O recorded by the mass spectrometer were in general agreement with the QCM rate curves but the former decreased more slowly after the maximum, because of H_2O desorption from the chamber walls.

When the experiments were instead performed by exposing hydrogen-covered films to O_2, a somewhat different technique had to be used because of the large atomic mass ratio M_O/M_H. The sample was exposed to small doses of O_2 and the mass decrease due to each dose was recorded. The observed net mass decrease for each dose was then solely due to the removal of hydrogen by production of H_2O. The reaction rate again showed a maximum (LH reaction).

Also the CO oxidation reaction was studied in a few runs by exposing partly CO (O) covered surfaces to small doses of O_2 (CO) and recording the mass decrease due to desorption of CO_2. Both reactions showed a maximum and an induction period (LH mechanisms) which for large θ_{CO} was extremely long. With an initial CO coverage of 0.85 an oxygen dose of 1.8×10^4 L (1 L = 1 μTorr sec) was required to reach the maximum rate of CO_2 production. The reaction probabilities at maximum were about 0.5 and 0.05 per impinging molecule with preadsorbed oxygen and CO, respectively.

Our reaction rate data for the hydrogen-oxygen reaction agree quite well with the x-ray photoemission-spectroscopy studies by Norton and Norton, Tapping, and Goodale[12] and with the data of Pacia and Dumesic[9] for Pt foil. The reaction probability at maximum was, however, considerably larger in our work than in Ref. 12, 13, and our data could not be described by the proposed simple rate law. Our reaction probability at maximum, ≈ 0.32, is on the other hand in close agreement with that of Ducros and Merrill for Pt(110).[15] Collins, Lee, and Spicer[16] reported a high reaction probability ~ 1, which contrary to our findings was claimed to be coverage independent. Initially, we also arrived at this erroneous result because of bad control of the H_2 pressure.

The adsorption and reaction measurements were carried out on many different films and the results were very reproducible. Adsorption-reaction-adsorption cycles with H_2 and O_2 could be repeated many times (> 10) on the same film, showing that irreversible changes of the surface and poisoning effects were small. A prerequisite was a very low background pressure for other gases than H_2O and that exposures were determined by partial pressure measurements and not from recorded total pressures. The only systematic variation during the experimental series was a variation in the surface roughness of the Pt films as deduced from CO titration.[17] However, the sticking coefficients and relative coverages for H_2, CO, and O_2 were reproduced within 10% independent of the surface roughness.

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