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Real-time monitoring of catalytic surfaces using a mass/heat flow sensor: Hydrogenation of ethylene on platinum and palladium

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A quartz crystal microbalance/heat conduction calorimeter has been used to monitor simultaneously the heat of reaction and the change in surface mass when H_2 and C_2H_4 in a N_2 carrier react on palladium and on platinum surfaces at temperatures of 25–50 °C. The measured turnover rate of the $H_2 + C_2H_4$ reaction on platinum at 50 °C is consistent with literature values.

KEY WORDS: quartz crystal microbalance; calorimetry; hydrogenation; ethylene; platinum; palladium.

1. Introduction

Virtually all heterogeneous catalysts used in chemical manufacturing and petroleum refining consist of thin films of active materials on high surface-area substrates [1]. In order for a catalyst to be robust and efficient, the catalytic surface must increase the rate of the desired reaction while remaining unpoisoned by the build-up of carbonaceous or other surface films that inhibit catalytic activity. Somorjai [2,3] has recently reviewed the characterization of surface materials used as catalysts; he states "…Over 60 techniques have been developed, most recently, techniques that can scrutinize, on the molecular level, the buried interfaces, solid–high pressure gas, solid–liquid, and solid–solid." Virtually all of the techniques mentioned by Somorjai are structural or spectroscopic, as opposed to calorimetric or kinetic. Yet *every* heterogeneously catalyzed chemical reaction either liberates or absorbs heat at the catalyst surface. High-temperature cracking reactions are endothermic whereas most petrochemical synthesis reactions occur at lower temperatures and are exothermic [4]. The rate of heat flow to the catalytic surface is thus a direct measure of the catalytic reaction rate. Dumesic and co-workers [5] have reviewed the widespread application of microcalorimetry to study adsorption energetics and kinetics of heterogeneous catalysts.

Until recently, no isothermal calorimetric/gravimetric technique existed which had the ability to measure the rate of heat production at surfaces and in thin films at ambient pressure, while at the same time and on the same sample measuring mass changes at the surface with monolayer sensitivity. The apparatus for measuring mass change and heat flow at thin film surfaces exposed to gases is termed the quartz crystal microbalance/heat conduction calorimeter (QCM/HCC). Details of the construction and operating principles of this device are published elsewhere [6–9]. In this work, the QCM/HCC was used to monitor the efficiency of catalytic hydrogenation of ethylene at a palladium surface at 25 °C, and at a platinum surface at 30–90 °C.

A comparison of the specifications of one flow microcalorimeter [10] with the QCM/HCC is given in table 1. While the Dumesic heat flow calorimeter operates on ~ gram samples of supported catalysts in powder or pellet form, the QCM/HCC operates directly on sub-mg amounts of the catalytic metal in the form of a thin film.

2. Experimental

The mass measurement sensor is a 5.000 MHz quartz plate resonator oscillating in the transverse shear mode (the QCM). When a thin film is deposited on the resonator the frequency decrease is proportional to the change in mass per unit area of the film, and measuring this frequency shift permits mass determinations to a precision of a few nanograms. At a 5.0 MHz, the relationship between frequency change and mass change at the surface is given by the Sauerbrey relationship,

$$\Delta f(\mathrm{Hz}) = -56.6\,\Delta m/A\ (\mu g/cm^2) \qquad (1)$$

where $\Delta m/A$ is the change in mass per unit surface area of the QCM. The surface area of the platinum catalyst exposed to the gas mixture is 2.0 cm^2. The QCM is tightly coupled thermally to a heat sink through a Peltier thermopile. Any heat flow generated by chemical processes in the thin film on the QCM surface is detected

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Table 1

Comparison of performance of two calorimetric instruments used in catalytic studies

Apparatus	Heat flow microcalorimeter[a]	QCM/HCC[b]
Transducers	Heat flux	Heat flux and mass
Heat flux sensitivity	0.015 V/W	0.806 V/W
Mass sensitivity	N/A	1×10^{-9} g
Solid sample geometry	Bulk powder, catalytic surface on solid support	Catalytic surface applied directly to microbalance
Solid sample size	4 cm^3	2×10^{-4} cm^3 (film 2 cm^2 area 1 μm thick)
System response time	105 s	50 s
Minimum detectable thermal power	50 μW	0.5 μW
Minimum detectable energy	5.5 mJ	25 μJ
Gas dose for adsorption	$1–3 \times 10^{-6}$ mol	$1–3 \times 10^{-8}$ mol

[a] Ref. 10]

[b] See refs. [6–9,11], and http://www.mass

as a voltage change by the thermocouple plate – the heat conduction calorimetry (HCC) principle. The thermopile is a custom bismuth–telluride Peltier thermoelectric module designed for high sensitivity. By using the heat generated by the QCM crystal when driven at resonance, the sensitivity coefficient of this thermopile in position in the apparatus was measured to be 0.806 W/V. Isolating the QCM/HCC in a quasi-adiabatic thermal environment provides simultaneous thermal power and mass change measurements on the film during sorption or reaction of gases with the surface. The sensitivity of the QCM/HCC is sufficient to measure the enthalpy of formation of a self-assembled monolayer of alkylthiol molecules on a gold surface [8].

Figure 1 show the mass/heat flow sensor and the full first-generation apparatus [11], used to do measurements on the palladium-catalyzed reaction. A bare quartz blank (i.e., without RF electrodes) was used in the reference chamber, so no mass measurements could be made on the reference side and no catalytic heat was generated.

Three-component gas mixtures were generated from three 1–10 mL/min mass-flow-controllers, one each for N_2, H_2, and C_2H_4. The gas mixture was flowed through a heat exchanger in the base of the calorimeter and then into a tee that split the flow equally between the sample and the reference chambers.

3. Hydrogenation of ethylene on palladium

We have used the QCM/HCC to monitor the observed rate of the hydrogenation of ethylene over hydrogenated palladium as a function of both hydrogen and ethylene partial pressures at 25 °C and 1 atm total pressure. The reversible dissolution of hydrogen in palladium at 25 °C has been well studied [12], and the room temperature phase Pd/H_2 phase diagram has been determined [13]. A Pd film 141 nm thick and of 1.3 cm^2 area of was electroplated on the gold surface of a QCM, then placed in the sample chamber.

Figure 2 shows two sorption cycles of hydrogen in the palladium film. Each cycle consisted of six sorption/desorption steps for $0 < pH_2 < 0.15$ atm. Notice that the total mass increase due to H_2 sorption is only 0.3 μg and that the noise in the mass trace is only a few ng. The slow downward drift in the mass trace in figure 2 has been observed by other QCM researchers [13] and is attributed to residual elastic stresses in the palladium film. The thermal trace in figure 2 shows that when the dissolved H_2 content of the Pd film increases there is an exothermic heat pulse generated, due to the enthalpy of sorption of H_2 in Pd. Likewise, each stepwise decrease in hydrogen partial pressure causes H_2 to be desorbed endothermically from the Pd. In such sorption experiments it can be shown [6] that the thermal trace is proportional to the first derivative of the mass trace, with the proportionality constant containing the sorption enthalpy. Analysis of the data of figure 2 yields enthalpies of sorption of H_2 in thin Pd films consistent with prior measurements on bulk Pd [13]. A fuller treatment of these data is presented elsewhere [9].

During the catalytic hydrogenation of ethylene over Pd, dissolution of hydrogen into the bulk palladium proceeds concurrently with chemiadsorption of ethylene on the palladium surface. Studies on single crystals of palladium have shown the formation of both π- and σ-adsorbed ethylenic species above room temperature [14]. During the reaction these ethylenic surface species pick up hydrogens from the palladium hydride solid phase and form ethane. Although the details of the individual steps involved in this reaction are complex, the net energetics for ethylene hydrogenation can easily be determined from calorimetric measurements of the heat of combustion of the reactants and products: $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$, $\Delta_{\text{reaction}}H^0 = -136.4$ kJ/mol. If this reaction occurs at a constant *rate* at the Pd surface of the coated QCM, then a constant *heat flow* is generated through the Pd film and the QCM to the thermopile, thus generating a constant *thermal power signal.*

Figure 3 shows experimental data from one set of QCM/HCC experiments with a three-component gas mixture, $H_2/C_2H_4/N_2$. The H_2 partial pressure was kept constant at 0.41 atm, and the partial pressure of C_2H_4

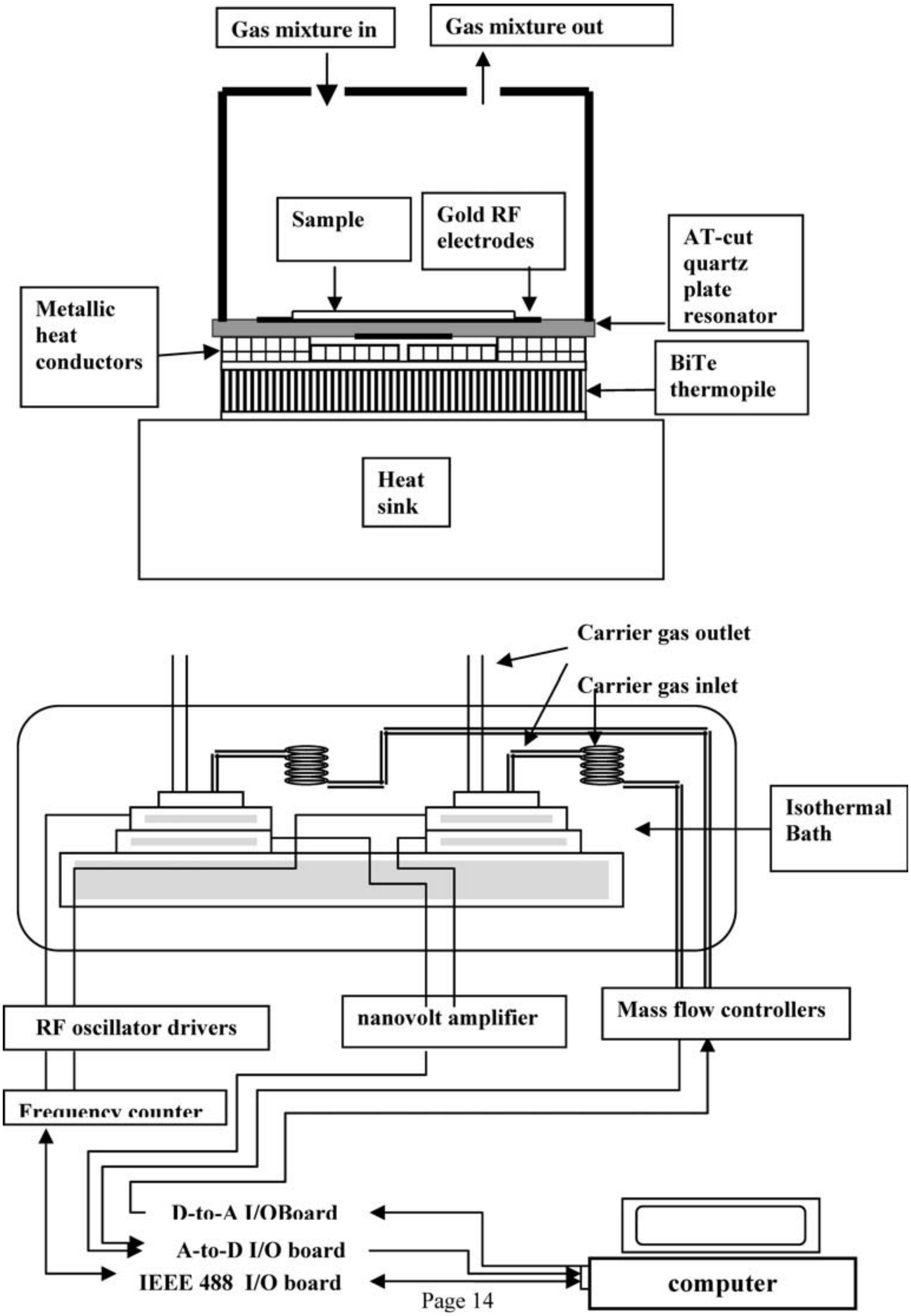

Figure 1. Block diagram of Drexel University quartz crystal microbalance/heat conduction calorimeter.

was varied from 0.25 to 0.59 atm in five steps. The thermal power signals in this experiment look quite different from those obtained with no ethylene present (figure 2). Because the hydrogen pressure was constant, the composition of the hydrogenated Pd solid phase was constant. Notice that the maximum exothermic (i.e. negative-going) signal was obtained when the C_2H_4 pressure was highest (0.59 atm), and that the signals are of constant power while $P_{C_2H_4}$ is held constant. Thus, the thermopile is measuring directly the *rate* of hydrogenation of ethylene on the Pd surface. Using the above information and a rate expression for the catalytic hydrogenation of ethylene gas over palladium previously derived by Tysoe [14], we compared the measured thermal power signal at different H_2 and C_2H_4 partial pressures to those estimated from the known rate expressions for the hydrogenation of ethylene over Pd [11], thus determining the catalytic activity of the

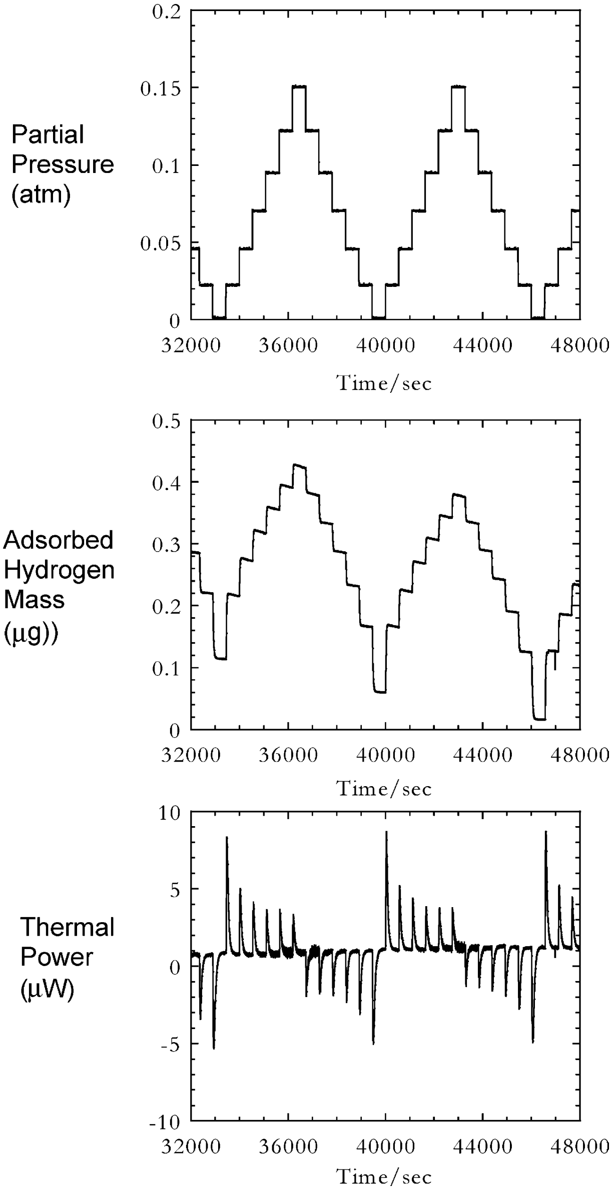

Figure 2. Mass sorption and heat generation when a palladium film at 25 °C is exposed to hydrogen.

palladium film sample. From the thermal signals we calculate that the rate of the reaction is ~10^{-11} mol C_2H_4 s^{-1} cm^{-2} on the Pd surface. It can be determined from these data that the reaction rate increases with $P_{C2}H_4$ at an order less than 1.0.

Figure 3 shows that there is an *increase* in mass of 5–10 ng as $P_{C2}H_4$ varies from 0.25 to 0.59 atm; we believe that some carbonaceous species is building up on the Pd surface. Assuming this, a 5–10 ng mass increase corresponds to 2–4×10^{14} C atoms/cm^2 on the surface, a fractional coverage of less than 0.1 monolayer of carbon. The mass change is partially reversible, although over the duration of the experiment there is a steady increase in adsorbed mass. In these experiments the mass build-up does not appear to affect the reaction rate.

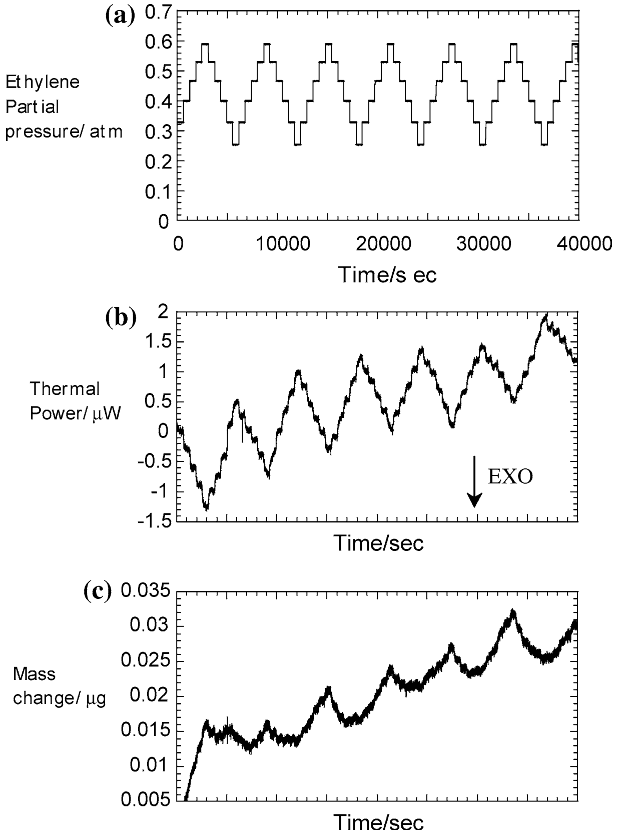

Figure 3. Mass change and heat generation due to reaction of ethylene and hydrogen catalyzed by palladium surface at 25 °C. Partial pressure of hydrogen held constant at 0.41 atm.

4. Hydrogenation of ethylene on platinum

The second-generation QCM/HCC used in these experiments was a prototype of the Masscal Model G1, introduced as a commercial product by Masscal Corporation. It is described more fully on the Masscal web-site, http://www.masscal.com.

About 5 MHz quartz plate resonators were coated with a 100 nm film of platinum using vacuum evaporation by the crystal manufacturer, Maxtek Inc., and were used in the G1 without any pretreatment. Thirty-eight runs of 2–3.5 h duration were taken using the 2 cm^2 coated area of these crystals to catalyze the reaction $H_2 + C_2H_4 \rightarrow C_2H_6$ at temperatures between 30 and 90 °C. A typical procedure was to set the flow of the carrier gas N_2 and one of the other gases early in the run, then vary the third gas flow in steps. Large exothermic heat flows were observed only when both reactants were present, although there were some runs at higher temperature in which thermal power signals were seen only with H_2 present. An example of this behavior is shown in figure 4. With the platinum-coated QCM crystal at 323 K in a flow of N_2 at 5 mL/min, introduction of 0.09 atm of ethylene at 7.5 min produced no discernible changes in thermal power or mass signals, but repetitive introduction of 0.045 atm H_2 at 18, 78, and 123 min produced large exothermic thermal power

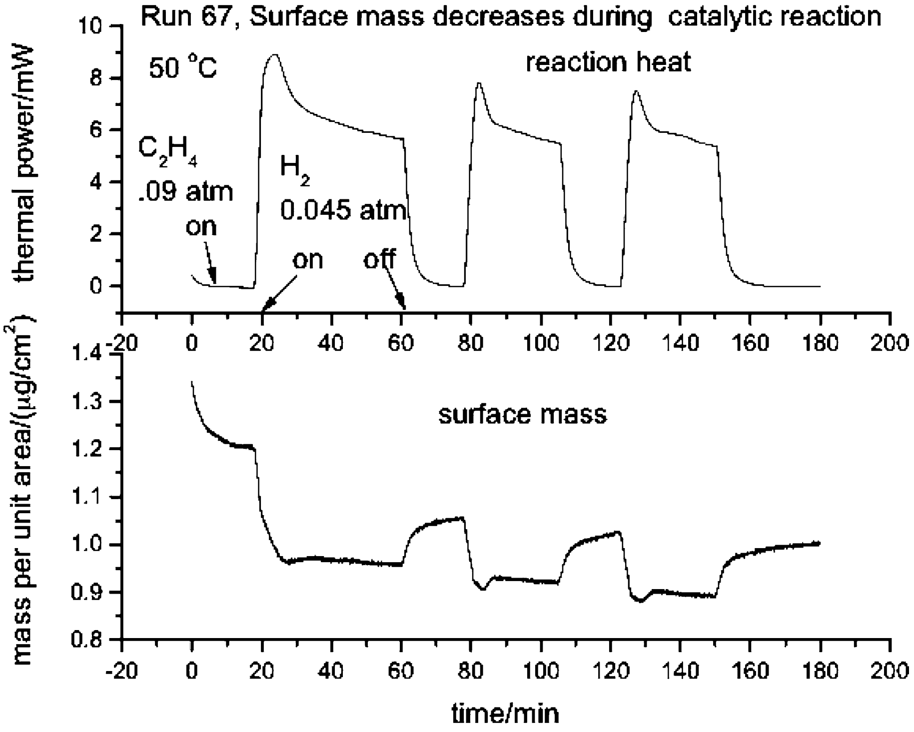

Figure 4. Mass change and heat generation due to reaction of ethylene and hydrogen catalyzed by platinum surface at 323 K. During the catalytic reaction, the partial pressure of ethylene was 0.090 atm and of hydrogen was 0.045 atm.

signals, accompanied by a corresponding *increase* in QCM frequency (i.e., a *decrease* in mass).

One possible explanation for the frequency increase when hydrogen is introduced must be explored. Kanazawa and Gordon [15] showed that for an infinite viscoelastic fluid such as a gas in contact with the QCM, the frequency difference between a QCM in vacuum and in contact with the fluid is

$$\Delta f = -(2\rho_q h_q)^{-1}(\rho_f \eta_f f_0/\pi)^{1/2} \qquad (2)$$

where ρ_f and η_f are the density and viscosity of the fluid. Tsionsky and Gileadi have verified this relationship experimentally for gases [16]. For N_2, H_2, and C_2H_4 at 298 K and 1 atm, the frequency shift from equation (2) is calculated to be −3.38, −0.63, and −2.57 Hz, respectively. When the reagent gases H_2 and C_2H_4 are added to the carrier gas stream in figures 3 and 4, the change in composition of the gas stream will produce a small frequency shift of the QCM independent of any gas adsorption. If this frequency shift is misinterpreted as a change in adsorbed mass, then through the Sauerbrey equation this corresponds to a mass per unit area change of −0.004 μg/cm^2 for figure 3 and +0.002 μg/cm^2 for figure 4 respectively. The observed change in mass in figure 3 is of the order 0.005 μg/cm^2 for the two extremes in gas composition, which agrees with the estimate from equation (2). However, for figure 4 the observed mass change between the two gas mixture states is ~0.1 μg/cm^2, 50 times that calculated from equation (2). We conclude that the observed change in mass of the surface when H_2 is admitted is due the actual *decrease* in mass of the surface film.

A consistent observation throughout all runs with platinum-coated crystals is that the resonant frequency was lower than that of the platinum-coated crystal at the beginning of the runs, and that it increased when both reagents were present. From the Sauerbrey equation we conclude that a thin film of surface mass was present during all runs, and that the film mass *decreased* when heat due to the catalytic reaction was evolved. This is the effect illustrated in figure 4. This suggests to us that the catalytic reaction was occurring not on the bare platinum but on some adsorbed, reactive molecular layer. Assuming one ethylene adsorbed per Pt atom, a monolayer of ethylene has a mass per unit area of 0.07 μg/cm^2, comparable to the change observed in figure 4 when H_2 is admitted to the system.

With the assumption that the heat liberated at the Pt surface is due entirely to the reaction $H_2 + C_2H_4 \rightarrow C_2H_6$, for which $\Delta H^0_{298} = -136$ kJ, the thermal power of 6.0 mW with both gases present (figure 4) can be used to determine the turnover rate of the catalyzed reaction. For this thermal power, the partial pressure of ethylene is 0.090 atm, the partial pressure of hydrogen is 0.045 atm, and the reaction temperature is 323 K. The turnover rate is defined as

$$\mathrm{TOF} = [dN(C_2H_6)/dt]/N_{\mathrm{Pt}} \qquad (3)$$

where $dN(C_2H_6)/dt$ is the rate of production of ethane molecules and N_{Pt} is the surface atom density of platinum. N_{Pt} for vacuum-evaporated polycrystalline Pt is assumed to be 3.0×10^{15} atoms/cm^2, and the Pt coating exposed to the gas mixture has an area of 2.0 cm^2. A thermal power of 6 mW thus corresponds to turnover rate in our experiments of

$$\begin{aligned}&(6\times10^{23})(6\times10^{-3}\,\mathrm{J/s})/(1.36\times10^{5}\,\mathrm{J/mol})(3.0\times10^{15}\\&\quad \mathrm{atoms/cm^2}) = 9\,C_2H_6\,\mathrm{molecules/(Pt\ atoms)}\ .\\&\quad = 9\,\mathrm{s}^{-1}\end{aligned}$$

The problem of defining and measuring turnover rates in heterogeneous catalysis has been reviewed by Boudart [17]. Ribeiro *et al.* [18] have addressed the question of whether turnover rates can be measured reproducibly, using a number of examples from heterogeneous metal catalysis. They conclude that the hydrogenation of ethylene on Pt is a "structure insensitive" reaction, for which turnover rates can be measured reproducibly on single crystals, foils, and supported catalysts prepared in different laboratories. Dumesic *et al.* [19] have measured turnover rates and kinetic reaction orders for ethylene hydrogenation over platinum catalysts from 223 to 336 K, and hydrogen pressures between 0.066 and 0.86 atm and ethylene pressures between 0.007 and 0.79 atm. They reference all rate measurements to standard conditions of 25 Torr (0.033 atm) C_2H_4 and 150 Torr (0.20 atm) H_2. From Table 2 of Dumesic and co-workers we take the order of the reaction with respect to ethylene to be −0.33 at $T=323$. From their Table 3 we take the order with respect to hydrogen to be 1.0 at 323 K. From their figure 3, the TOR at 323 K is 15/s at standard conditions. Correcting for the non-standard pressures in our experiments, we get the following turnover rate from the work of Dumesic *et al.* for the hydrogenation of ethylene at 323 K:

$$\mathrm{TOR}=\mathrm{TOR}_{\mathrm{std}}\left(\frac{\mathrm{P}(C_2H_4)}{\mathrm{P}(C_2H_4)_{\mathrm{std}}}\right)^{-0.33}\left(\frac{\mathrm{P}(H_2)}{\mathrm{P}(H_2)_{\mathrm{std}}}\right)^{1.0}=2.4\,\mathrm{s}^{-1}$$

Our turnover rate, 9 s^{-1}, is a factor of 3.75 higher than that of Dumesic and co-workers. We believe that such an agreement is reasonable at this preliminary state of experimentation, particularly because we have not characterized the evaporated thin film platinum surface we used.

5. Conclusion

(1) The QCM/HCC can easily detect both the mass change and the heat generated during the sorption of H_2 in thin Pd films at room temperature and ambient pressure.
(2) The QCM/HCC is capable of real-time monitoring of the reaction rate of hydrogenation of ethylene at both a palladium and a platinum surface. The resulting turnover frequencies are 3.75 times larger than those reported by Dumesic at comparable reagent partial pressures and temperature.
(3) The QCM/HCC detects sub-monolayer mass changes on both palladium and platinum surfaces during the catalytic reaction.

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