Hydrogen-induced CO_2 formation from ethylene deposits on Pt during consecutive O_2 and H_2 exposures

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The oxidation of C_2H_4 deposits on polycrystalline Pt when exposed to consecutive O_2 and H_2 pulses at room temperature has been investigated in a long ($L = 36$ mm), shallow ($d =$ 600–700 nm) micromachined glass–SiO_2–Pt channel. Hydrogen-induced CO_2 formation from species accumulated on the Pt surface was observed. Frequent switching of the O_2/H_2 exposure pulses was found to increase the efficiency of the oxidation of the carbonaceous deposits markedly. The observations may be of general interest for the regeneration of contaminated catalysts.

Keywords: catalysis, carbonaceous contaminants, regeneration of catalyst, ethylene, carbon monoxide, carbon dioxide, platinum, hydrogen, oxygen

1. Introduction

In this work, oxidation and hydrogenation of C_2H_4 deposits on Pt were studied in a long ($L = 36$ mm) and narrow ($d =$ 600–700 nm) micromachined channel. The channel was inserted as the only leak between a high-pressure gas mixing chamber and an ultra-high vacuum mass spectrometer chamber. The experimental setup is similar to that used in spatially resolved measurements, in which reactions at catalytic conditions are monitored with a mass spectrometer through a small quartz glass capillary leak [1]. The channel structure, though, combines the leaking capillary and the model catalyst in one piece. This arrangement, together with the dimensions of the channel, presents unique possibilities. Due to the narrow depth, the flow through the channel will be molecular also at high (about atmospheric) pressures, where the flowing species cover the channel walls to considerable extent. Moreover, the L/d ratio is extremely large (∼50000–60000). This is interesting, since a molecule which transits the channel under molecular flow conditions, will suffer $\propto (L/d)^2$ collisions ($\propto 2.5 \times 10^9$) with the channel walls. We believe that any surface-induced effect, that occurs when a flowing species strikes the channel wall, would be amplified for the transiting molecules, through the very many wall collisions. The channel structure could, thus, be used as an amplifying instrument, which makes small effects discernible. A very short adsorption time would for instance be amplified to a macroscopic time delay upon transmission. Another idea is that a chemical reaction that would occur with a very small probability in a single collision event with the channel wall, might happen with unit probability for those molecules which transit the channel. The yield of the highly purified product transmitted to the low-pressure channel end is given by the transmission probability Tr. If d (depth), w (width) and L (length) are the measures of a channel with rectangular cross-section, d/w is small and the flow through the channel is molecular, the transmission probability can be approximated by [2]

$$\mathrm{Tr} = \frac{d}{L}\left[0.5 + \ln\left(\frac{2w}{d}\right)\right].$$

With $d = 600$ nm, $w = 1$ mm and $L = 36$ mm, the transmission probability is $\mathrm{Tr} = 1.4 \times 10^{-4}$, that is, the throughput is small. The low-transmission probability is accompanied by a large-pressure gradient along the channel and the surface conditions may, thus, vary along the Pt-covered bottom of the channel. This sometimes complicates the evaluation of the measurement results. It has, for instance, proven to be difficult to demonstrate a promoting effect on chemical reactions by the many wall collisions, since we do not control the reactive sticking along the channel. On the other hand, physical evidence might be given for a surface-related process, which rate scales with pressure, due to the low pressure in the downstream part of the channel. We have, for instance, reported on a complete restriction in the transient flow through the channel due to adsorption when oxygen or hydrogen are introduced into the gas mixing chamber [3]. Several other findings, concerning both gas flow and chemical reactions in the channels are presented in [3–8].

A model catalyst must regularly be regenerated with respect to, e.g., carbonaceous contaminants. This procedure would not only standardize the reaction conditions, but would most probably also increase the activity of the catalyst. A commonly used treatment for removal of carbonaceous species on transition metal samples is to expose the samples at elevated temperature to a large O_2 pulse followed by a large H_2 pulse at elevated temperature. In our previous work, we have found that a frequent switching of O_2 and H_2 pulses effectively regenerates transition metal surfaces. The method has succesfully been used on evaporated films, single-crystal samples and polycrystalline foils in large pressure and temperature ranges. The reason for the efficiency of the method has, to our knowledge, never been demonstrated, though. In this work, we present results from hydrogenation and oxidation of C_2H_4 deposits on Pt at room temperature. We demonstrate the virtue in using consecutive O_2 and H_2 pulses for efficient removal of the deposits. A control experiment with carbonaceous contaminants from a CO exposure indicates that the results can be extended to several other applications. We venture, thus, to claim that the frequent switching O_2/H_2 pulse-conditioning procedure in several applications can replace cleaning methods based on a large O_2 exposure, occasionally followed by a H_2 treatment, both in vacuum and at catalytic reaction conditions.

2. The channel structure and the measurement equipment

A cross-sectional view of the channel structure is shown in figure 1. The channel was etched with reactive ion etching (RIE) into a p-doped (100) oriented silicon surface using Al as a masking material. After removal of the Al, the silicon was thermally oxidized to a thickness of 30 nm. A 1 nm thick Pt string was thermally evaporated along the channel bottom. Such a thin Pt film is discontinuous and forms isolated islands [9]. Though polycrystalline, we believe the low-energy (111) facettes to dominate the Pt surface. Finally, a glass (SD2, HOYA) lid was bonded anodically on top of the channel by applying ∼1000 V over the air gap between the glass lid and the silicon structure at 400 °C. A more detailed description of the sample fabrication is given in [3].

The mounting of the channel structure in the vacuum system is schematically shown in figure 2. A quartz capillary is inserted between a high-pressure gas mixing chamber and a high-vacuum mass spectrometer chamber, using a commercially available viton sealed tube fitting which was welded in the wall that separates the chambers. The channel structure was fitted into the quartz capillary orifice. An expoxy seal (E8031, EPO-TEK) fixed the channel structure leak tight to the quartz glass capillary orifice. The tube fitting was tightened by a viton gasket thread around the quartz capillary. Thus, the channel was inserted as the only leak between the chambers. Helium leak detection confirmed that any other (accidental) leak between the chambers was negligible at room temperature. Due to the small channel throughput, the system is extremely sensitive to undesired leaks. Therefore, we have rarely performed any experiments at elevated temperatures, since minute leaks are easily induced in the viton gasket and occasionally in the expoxy joint.

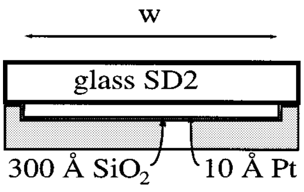

Figure 1. A cross-section of the channel structure. The channel measures were 600–700 nm (d) × 1 mm (w) × 36 mm (L). A 10 Å thick 0.5 mm wide Pt film was evaporated along the channel bottom.

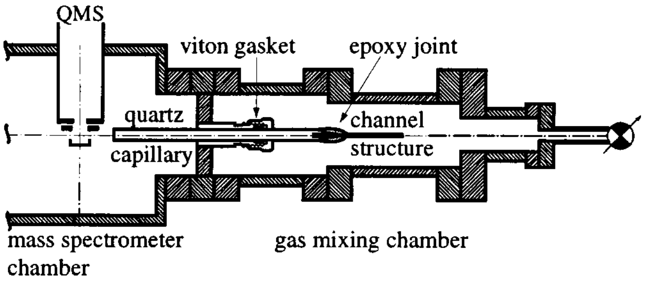

Figure 2. The gas mixing chamber and the mass spectrometer chamber. The channel connects the high-vacuum mass spectrometer chamber (∼3×10^{-9} Torr) to the high-pressure gas mixing chamber (0–500 Torr). The inner diameter of the quartz capillary ($f = 4$ mm) is large compared to the channel depth (d = 600–700 nm), for which reason the diffusion restriction occurs in the channel alone.

A schematic drawing of the measurement system including the gas flow system has been presented previously [3]. The gas mixing chamber can be filled with gases from a gas flow system to desired pressure in the range from 10^{-2} to 2000 Torr. The pressure in the gas mixing chamber is measured with a capacitance manometer and regulated with a downstream pressure control system. Molecules from the gas mixing chamber will enter the channel at its high-pressure end and the molecules (or product molecules formed in the channel) will leave the channel at its both ends. The gas molecules that transit the channel and enter the high-vacuum chamber are analyzed with a mass spectrometer. (Since the channel, apart from its narrow orifices, is completely enclosed, it is, on the whole, impossible to characterize surface species on the channel walls with conventional surface analysis methods.) The pressure in the high-vacuum chamber is measured with an ionization gauge and the base pressure during the measurements was ∼3×10^{-9} Torr.

A 50 Torr argon exposure in the gas mixing chamber induces a pressure increase ΔP_0 of 3×10^{-10} Torr in the mass spectrometer chamber. This corresponds to a leak rate of ∼8 × 108 Torr l/s and a transmission probability of ∼2×10^{-5}, if the pumping speed of the turbo-molecular pump is assumed to be 270 l/s. Since the quartz capillary is directed towards the turbo-molecular pump, the effective pumping speed may be larger. This may, in turn, explain the somewhat small transmission probability.

The mass spectrometric system was originally designed for spatially resolved mass spectrometer measurements and was thoroughly described by Ackelid et al. [10].

3. Experimental

The experiments presented below were performed in three steps, as follows:

- The channel was conditioned by oxygen and hydrogen exposures.
- The conditioned channel was pretreated with a C_2H_4 exposure. (One control experiment was performed, in which the channel was pretreated with CO instead.)
- The C_2H_4-pretreated channel was exposed to consecutive oxygen and hydrogen pulses and the formation of C_2H_6, CO_2 and H_2O was monitored with a mass spectrometer.

The conditioning procedures, the pretreatments and the O_2/H_2 exposures were all performed at room temperature (292 K). Each of the three steps are discussed separately below.

3.1. The surface conditioning procedure

All measurements presented here were preceded by a conditioning procedure, in which the channel wall was exposed to consecutive oxygen and hydrogen pulses. The gas pulses, starting with an oxygen pulse, were flown into the gas mixing chamber at constant rate and pumped away after 20 s. (The pressure signal recorded up-stream of the channel during a conditioning procedure is identical to the signal displayed in the bottom of figure 3.) The oxygen exposure is likely to remove carbon contaminations from the platinum surface through oxidation and desorption. Excess oxygen adsorbed on the platinum surface desorbs as water formed during the hydrogen exposure. The hydrogen exposure may also induce CO_2 formation, as will be demonstrated below. The treatment should preferably be accomplished at enhanced temperature [11]. The (room temperature) conditioning procedure has repeatedly been demonstrated to result in good experimental reproducibility [3–8], though. Still, it is worth noting that the Pt surface may not be atomically clean.

3.2. The ethylene pretreatment

When the channel is exposed to C_2H_4, adsorption and possibly decomposition of C_2H_4 will occur on the Pt surface. From the rich literature on the C_2H_4/Pt system, some suggestions regarding the nature of the C_2H_4 deposits are made below.

When C_2H_4 is exposed to a clean Pt(111) surface at room temperature, some of it adsorbs in a di-σ-fashion while some is converted to ethylidyne and surface hydrogen through dehydrogenation, see [12–14] and further references therein. Some of the surface hydrogen reacts with C_2H_4 and forms C_2H_6, which desorbs. Decomposition of C_2H_4 on Pt is structure dependent, and on other Pt facets yet other species were reported on [15–21]. A mixture of di-σ-ethylene and ethylidyne was found on a 16% Pt/SiO_2 catalyst [22].

The C_2H_4 pretreatments in this work were preceded by the O_2/H_2 conditioning procedure, which ends with a H_2 exposure. In another contribution, we have shown that much of the surface hydrogen remains in the channel for a long time (>15 h) after such exposure [6]. We believe this is due to the many readsorptions in the channel. Due to surface hydrogen from the conditioning procedure, a transient formation of C_2H_6 is initially seen during the C_2H_4 pretreatment exposures. This is in accordance with previous investigations of C_2H_4 interaction with H_2-predosed Pt(111) surfaces [23,24]. C_2H_6 adsorbs weakly on Pt, and spontaneously diffuses out into either of the chambers orders of magnitudes faster than hydrogen ($\sim$1 s). The C_2H_4 pretreatment pulse was always large enough to completely consume the preadsorbed hydrogen.

In conclusion, we assume that C_2H_4 adsorbs and partly decomposes on the Pt surface. A deposit that is likely to be found on the surface is di-σ-ethylene. Other species, such as for instance ethylidyne, may also be present.

3.3. The carbon monoxide pretreatment

When the surface is exposed to CO, the remaining hydrogen from the conditioning procedure will be replaced by CO. This was experimentally confirmed in an experiment in which the hydrogen-pretreated channel was exposed to CO. Hydrogen diffusion out of the channel was registered as a sharp peak with the mass spectrometer well before CO was allowed to transit the channel. We believe that all hydrogen was replaced by CO during the pretreatment exposure.

3.4. Exposing the channel wall to hydrogen and oxygen

In the measurements displayed in the figures below, the C_2H_4-pretreated channel was exposed to consecutive O_2 and H_2 pulses in a way similar to the conditioning procedure. As was mentioned, traces from a H_2 exposure may persist for a long time on the Pt surface. Oxygen adsorbed on Pt desorbs even more slowly at room temperature and is therefore assumed to persist on the surface until it reacts and forms species that desorb at higher rate. The species that formed during the O_2/H_2 exposures were C_2H_6, CO_2 and H_2O. No significant amounts of other species were detected.

The formation of C_2H_6 was monitored with the mass spectrometer $m/e = 26$ signal. This mass number is also a part of the cracking pattern of C_2H_4. Control experiments verify that only C_2H_6 contributes to the signal intensities in the experiments presented in this paper.

The $m/e = 17$ signal (as a measure of H_2O) was recorded during the measurements, but is not displayed in the figures below. The reason for this is the difficulty to interpret the signal, since water interacts with the channel wall in a specific way at room temperature [7,8]. In short, the channel walls act as a sink for water molecules and the response in the mass spectrometer signal upon water formation is therefore delayed. Moreover, H_2O tends to form multiple layers on the channel walls, and the amount of water desorbed into the mass spectrometer is not always proportional to the amounts of H_2O formed and accumulated in the channel. In conclusion, it would be beyond the scope of this report to interpret the mass spectrometer water signal. Nothing in this signal, though, contradicts the suggestions made below.

4. Results

4.1. A presentation of the measurement results

A series of measurements was performed, in which the C_2H_4-pretreated channel wall was exposed to consecutive O_2 and H_2 pulses. The main products formed were CO_2, C_2H_6 and H_2O. The influence of the C_2H_4 pretreatment and the sequence and sizes of the O_2 and H_2 pulses on the oxidation and hydrogenation reactions was investigated.

Figure 3 displays four measurements, in which the C_2H_4-pretreated channel was exposed to a sequence of O_2 and H_2 pulses. The four experiments were identical except that the C_2H_4 pretreatment exposure increases from the bottom (a) to the top (d). Several interesting observations were made. If we compare the CO_2 formation during the first O_2 pulses in the four measurements, respectively, we find that it decreases with increasing pretreatment exposure. The C_2H_4 deposits, thus, poison the surface with respect to oxygen adsorption and/or dissociation. In measurement d, the oxidation reaction is completely inhibited. The following hydrogen pulse, though, readily hydrogenates some of the carbonaceous species, forming C_2H_6. This formation is rapid and reaches its maximum rate well before the maximum H_2 pulse pressure is reached. Almost all C_2H_6 that forms during either of the experiments forms during the first H_2 pulse, but there are still carbonaceous species left on the surface that form CO_2 during the following exposures. We may assume that some C_2H_4 deposits are easily hydrogenated, while others react with hydrogen at much lower rate. A surprising pattern is seen in the CO_2 signal, which frequently displays a broad peak during the O_2 exposure and a sharp peak during the following H_2 exposure. This observation indicates two different mechanisms for CO_2 formation. When CO_2 forms during an O_2 pulse, the following H_2 pulse induces CO_2 formation as well. The latter CO_2 formation is rapid and reaches its maximum rate well before the maximum H_2 pressure is reached, exactly like the C_2H_6 formation described above.

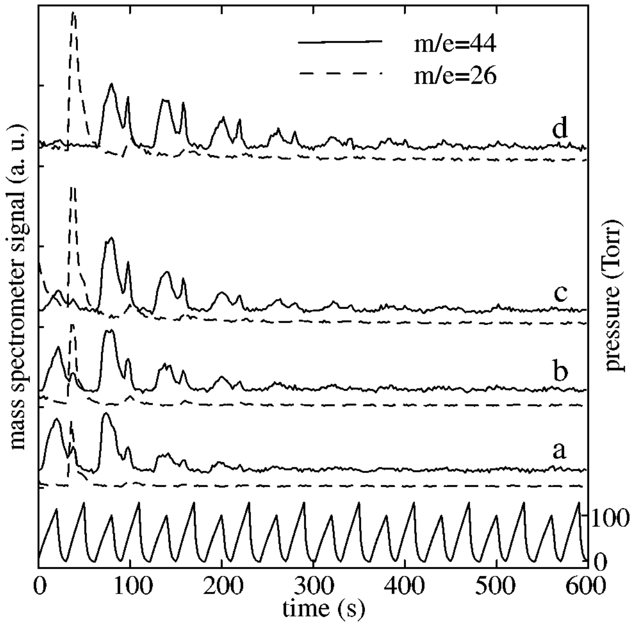

Figure 3. The figure shows four measurements, in which the C_2H_4-pretreated channel is exposed to consecutive O_2 and H_2 pulses. The mass spectrometer $m/e = 26$ (C_2H_6) and $m/e = 44$ (CO_2) signals are displayed as functions of time. The exposure pulse pressure (in the gas mixing chamber) is shown in the bottom of the figure (scale to the right). The grey and white fields in the figure indicate O_2 and H_2 exposures, respectively. The pretreatment pulses were (a) 10 Torr, 100 s, (b) 100 Torr, 100 s, (c) 500 Torr, 500 s, and (d) 1000 Torr, 2 h. (In measurement (c) the $m/e = 26$ signal intensity is initially somewhat elevated (though rapidly declining) due to a too short time delay between the preceding C_2H_4 pretreatment and the start of experiment in this particular case.)

Figure 4 displays six measurements in which the exposure pulse lengths and the first pulse in the O_2/H_2 sequence were varied. The total amount of C_2H_6 formed is obviously larger when the first exposure pulse is H_2 and we may assume that a preceding O_2 exposure consumes species that would otherwise have been hydrogenated. The first hydrogen pulse in measurement II (figure 4(c)) hardly results in any C_2H_6 formation at all. A sharp peak in the CO_2 signal is seen, though, and the maximum CO_2 formation rate during the H_2 pulse actually exceeds the maximum CO_2 formation rate during the preceding O_2 exposure. Besides, if the CO_2 formation rate during the O_2 exposures immediately before and after the hydrogen pulse are compared, we see that the H_2 exposure has a promoting effect on the CO_2 formation. It is, thus, evident that a frequent switching of the O_2/H_2 pulses results in a much more effective oxidation of the surface deposits. In figure 4(c), traces of carbon are seen at 1500 s, while no carbon is traced after 300 s in figure 4(a), where a more rapid switching was used. The removal of carbon contaminants is clearly promoted by a rapid switching of the pulses.

Attempts were made to completely consume the C_2H_4 deposits with either O_2 or H_2. The channel was pretreated with a 200 Torr, 100 s C_2H_4 pulse, a moderate exposure, that would far from completely poison the channel wall. The channel was exposed to a 500 Torr O_2 (H_2) pulse for 3000 s. After pump-down, a 100 Torr H_2 (O_2) pulse was introduced into the gas mixing chamber. In both experiments, the last pulse resulted in significant CO_2 formation. There are, in other words, after a 3000 s exposure of 500 Torr O_2 (H_2) still species present on the surface that readily form CO_2 when exposed to H_2 (O_2). This fact once more demontrates the promoting effect of switching O_2/H_2 gas exposures on the removal of carbon contaminants.

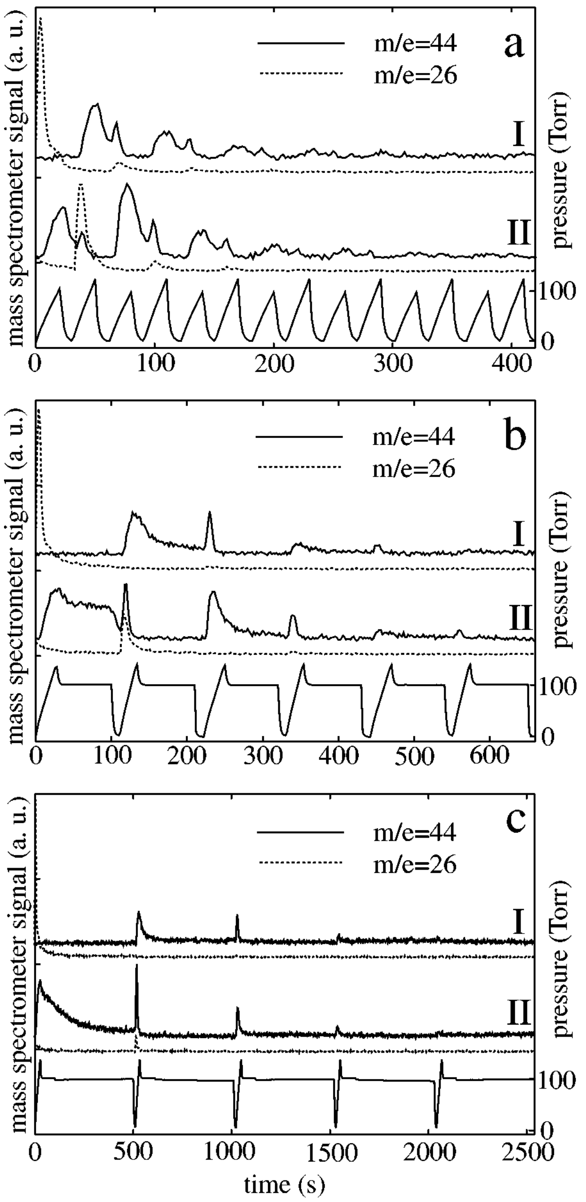

Figure 4. Figures (a)–(c) display six measurements, in which the C_2H_4-pretreated channel is exposed to consecutive O_2 and H_2 pulses. The channel was in all measurements pretreated with a 100 Torr 100 s C_2H_4 exposure. The O_2/H_2 pulse length varies between the figures as (a) 30, (b) 110, and (c) 510 s. Each figure displays two measurements, in which the sequence of exposures starts with H_2 (top) and O_2 (bottom), respectively. (Grey fields indicate O_2 exposures and white fields indicate H_2 exposures.) The pressure in the gas mixing chamber recorded during the respective bottom measurements are presented in the bottom of the figures. This signal is in all essential similar to the corresponding signal for the respective top measurements. (The H_2 flow was slightly larger than the O_2 flow, which results in a somewhat larger rate of pressure increase for H_2.)

To summarize, the following observations were made:

- After a large ethylene exposure (1000 Torr, 2 h) the deposits formed inhibit oxygen adsorption and/or dissociation, while hydrogenation to C_2H_6 during the H_2 exposures readily occurs. There seem to be at least two types of species on the surface, of which one is rapidly hydrogenated, while the other reacts slowly.
- The first hydrogen exposure seems to create free surface sites when hydrogenated surface species desorb as C_2H_6, which enable CO_2 formation during the next O_2 exposure.
- There are two mechanisms for CO_2 formation. Firstly, CO_2 forms when the (not completely poisoned) pretreated surface is exposed to O_2. Secondly, after such oxidation, further CO_2 formation occurs from species accumulated on the surface when exposed to H_2.
- Carbonaceous deposits from C_2H_4 exposure are efficiently removed if exposed to consecutive O_2/H_2 pulses. The higher the switching frequency the faster is the removal of the C_2H_4 contaminants.

4.2. A tentative model for the course of reactions

A possible model for the surface reactions described above is presented in figure 5. CO is suggested to be an intermediate species. The reaction steps are briefly commented on below:

(I) C_2H_4 adsorbs and partly decomposes through dehydrogenation. A C_2H_x layer forms, where at least two kinds of species (possibly with different x-values) are present on the surface. The deposits poison the surface with respect to oxygen adsorption and dissociation.

(II) Hydrogen reacts with some of the surface deposits and all C_2H_6 that would easily form, forms and desorbs. Other species, more resistant to hydrogenation, remains on the channel wall (C_2H_x). The surface is no longer poisoned with respect to oxygen adsorption and dissociation.

(III) Oxygen reacts and forms CO_2 and H_2O. For simplicity, we assume that both species desorb immediately (H_2O interaction with the channel wall is briefly treated in section 3). Oxidation of CO is the rate limiting step in the reaction and accordingly CO accumulates on the surface. The reaction rate decreases with increasing CO coverage, that is oxidation in an O_2 ambient is a self-poisoning process.

(IV) Some accumulated CO is rapidly consumed, forming CO_2 under the influence of H_2. The mechanism of the hydrogen-induced reaction is further discussed below. Removal of the accumulated CO regenerates the surface reaction conditions to the next O_2 exposure.

(V) The two last steps can be repeated several times.

There are several details in the course of reactions that cannot be gathered from our measurements, for which reason the model is a simplified description, which relies only on a few assumptions. The influence of the C_2H_x species on the reactions is restricted to a blocking effect for oxygen adsorption and dissociation. CO is assumed to be an intermediate species. No other intermediate species are taken into account. A mechanism for CO_2 formation when H_2 is

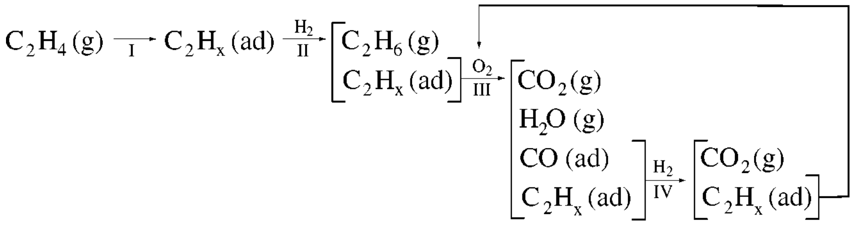

Figure 5. A tentative scheme for the course of reactions when a pretreated Pt surface is exposed to a sequence of H_2 and O_2 pulses. Species denoted (g) and (ad) are gaseous and adsorbed, respectively. The reaction steps I–IV are commented on in the text.

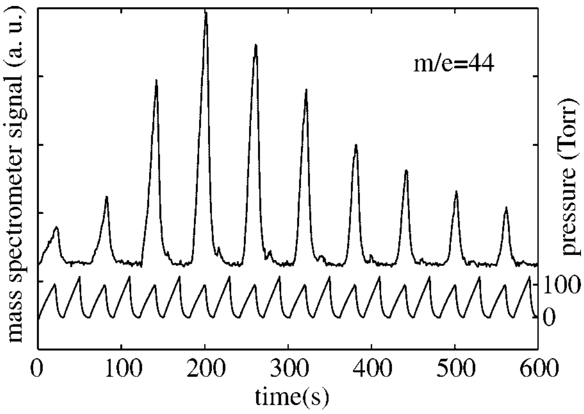

Figure 6. The mass spectrometer $m/e = 44$ (CO_2) signal displayed as a function of time during exposure of the channel to consecutive O_2 and H_2 pulses after a 100 s, 100 Torr CO pulse pretreatment. The pressure in the gas mixing chamber is displayed in the bottom of the figure (scale to the right) and, again, the grey and white fields indicate O_2 and H_2 exposures, respectively.

exposed to a CO/O/C_2H_x-covered Pt surface is presumed, but the nature of this mechanism is not evident. The identification of this mechanism would be an important key to better understand the switching O_2/H_2 pulse conditioning procedure.

4.3. The hydrogen-induced CO_2 formation

To further investigate the hydrogen-induced CO_2 formation, some experiments were performed after pretreatment of the channel with CO. In figure 6 an experiment similar to that in figure 3(b) is shown, where the channel was pretreated with CO instead of C_2H_4. The results are similar to those obtained for the C_2H_4-pretreated channel, but the hydrogen-induced CO_2 formation is small. An indication of hydrogen-induced CO_2 formation is seen from the third H_2 pulse and on, though. It seems, thus, as if the hydrogen-induced CO_2 formation is promoted by the O_2 exposures. A thorough treatment of the observations made in the CO-pretreated channel is beyond the scope of this paper. The most important observation is that hydrogen-induced CO_2 formation was demonstrated in the CO-pretreated channel, but only after O_2 exposures and at much lower rate than in the C_2H_4-pretreated channel. CO is thus a possible intermediate species, as suggested in the model above, and the validity of the experimental results can be extended to several applications, in which CO is likely to form.

The hydrogen-induced CO_2 formation (after either pretreatment) can be due to a reaction between CO and OH groups. This would explain the influence of the O_2 exposures on the hydrogen-induced CO_2 formation seen in figure 6. It is also possible that the presence of hydrogen leads to restructuring of the surface, which in turn enables a reaction between CO and some other species, for instance CO, O, OH or H_2O. Restructuring of similar metal films was reported on by Eriksson et al., who have observed restructuring of 5 nm thick Pd films supported on SiO_2, in a mixture of H_2 and O_2 at atmospheric pressures at 473 K [25].

Hydrogen-induced CO_2 formation from carbonaceous deposits on Pt has, to our knowledge, not been reported on in the literature before. An interesting finding by Dümpelmann et al. [26] should be mentioned, though. They have investigated the conversion of NO and CO mixtures over Al_2O_3-supported Pt and Rh catalysts at temperatures above 150 °C and found that the conversion of NO (to N_2, NO_2 and NH_3) and CO (to CO_2) increases when H_2 is added to the gas mixture. The mechanism behind these phenomena is not clear, but nitrogeneous species may be involved as intermediate species in the conversion.

The mechanism behind the H_2-induced CO_2 formation in this work is still to be determined. It could be due to restructuring of the Pt surface, even though less likely at room temperature, and/or to the formation of a hydrogen-containing intermediate species, for instance OH. A third possibility is that the CO_2 formation takes place on the support, due to oxygen spillover. This is, however, contradicted by the control experiment displayed in figure 6, in which much less hydrogen-induced CO_2 formation occurs, when the surface is pretreated only with CO and not contaminated with hydrocarbon species. Besides, since CO has a large mobility on the surface, it seems not likely that oxygen would accumulate on the surface in presence of CO. The findings made in the CO-pretreated channel indicate, however, that CO is a possible intermediate species and that the results obtained in this work are not only valid for C_2H_4 deposits but that the results can be extended to other common carbonaceous contaminants.

5. Conclusions

We have demonstrated the influence of consecutive O_2 and H_2 exposures on the removal of C_2H_4 deposits on polycrystalline Pt at room temperature. A limited amount of deposits are easily hydrogenated, while the rest are more easily oxidized to CO_2. The oxidation process is promoted by switching O_2 and H_2 exposures and the higher the switching frequency, the faster is the oxidation process. Control experiments in a CO-pretreated channel give similar results, which indicate a validity of the conclusions for common carbonaceous contaminants. We suggest that the oxidation in an O_2 ambient is self-poisoned by adsorbed CO species, which is an intermediate species in the reaction. The H_2 exposures regenerate the reaction conditions by removing the accumulated CO species from the surface as CO_2. The mechanism behind this hydrogen-induced CO_2 formation is assumed to be due to a reaction between CO and either of the following (adsorbed) species: atomic O, CO or OH. This is not very surprising, since these species are reactant/intermediate species in the water–gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$). We do not believe that the water formed in the channel necessarily reacts, but rather that the intermediate O, CO or OH species form due to the O_2/H_2 exposures. Therefore, the CO_2 formation occurs at temperatures well below the temperatures at which the water–gas shift reaction normally occurs.

The measurements were performed in a micromachined long narrow channel and one interesting question is whether the findings made were observed due to the geometrical shape of the channel or not. Langeveld et al. have investigated the temperatures at which C_2H_4 deposits oxidize on a polycrystalline Pt foil [27]. They have observed that deposits from a C_2H_4 exposure at 325 K were oxidized at 410–420 K. The C_2H_4 pretreatments in this work, were performed at 292 K and the deposits formed were oxidized at 292 K, which is far below 410–420 K. The large difference in temperature may indicate that the geometrical shape of the channel is essential for the observations to be made. Since the experimental parameters were not identical, we cannot exclude other possibilities, though. Whether the channel geometry is necessary for the physical manifestation of the phenomenon observed or not, it is a virtue to use a model catalyst, which geometrically is similar to an industrial porous catalyst.

There are many applications, in which deactivation of operating catalysts due to carbonaceous contaminants is a recurrent problem. A commonly used method to regenerate catalyst surfaces is to expose them to a large O_2 pulse (at elevated temperature) followed by a large H_2 pulse. In this work, we have demonstrated that the efficiency of such conditioning procedures could markedly be increased by frequently interrupting the O_2 pulse with H_2 exposures. From practical experience this has been well known to our research group for a long time. The hydrogen-induced CO_2 formation and the regenerating effect of a H_2 pulse on the (O_2)-oxidation reaction conditions have not been demonstrated until now, though.

Several details in the course of reactions are to be further investigated. The temperature dependence of the conditioning procedure has to be characterized and the reaction mechanisms identified. When the conditioning procedure is better understood, it can be tailored for different catalysts in different applications, to yield maximum efficiency.

Acknowledgement

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References

[1] U. Ackelid, *Catalytic Surface Reactions Studied at Near-Atmospheric Pressures: Spatially Resolved Gas Sampling Applied to Oxidation of Ethylene and Hydrogen on Pt and Pd*, Linköping Studies in Science and Technology, Dissertation No. 346 (Linköping University, Linköping, 1995).

[2] W. Steckelmacher, Vacuum 28 (1978) 269.

[3] P. Norberg, U. Ackelid, I. Lundström and L.-G. Petersson, J. Appl. Phys. 81 (1997) 2094.

[4] P. Norberg, L.-G. Petersson and I. Lundström, Vacuum 45 (1994) 139.

[5] I. Lundström, P. Norberg and L.-G. Petersson, J. Appl. Phys. 76 (1994) 142.

[6] P. Norberg, I. Lundström and L.-G. Ekedahl, to be submitted.

[7] P. Norberg, I. Lundström and L.-G. Ekedahl, to be submitted.

[8] P. Norberg, I. Lundström and L.-G. Ekedahl, to be submitted.

[9] A. Spetz, U. Helmersson, F. Enquist, M. Armgarth and I. Lundström, Thin Solid Films 177 (1989) 77.

[10] U. Ackelid, J. Fogelberg and L.-G. Petersson, Vacuum 42 (1991) 889.

[11] L.-G. Petersson, H.M. Dannetun, J. Fogelberg and I. Lundström, J. Appl. Phys. 58 (1985) 404.

[12] E.A. Carter and B.E. Koel, Surf. Sci. 226 (1990) 339.

[13] F. Zaera, Langmuir 12 (1996) 88.

[14] Y.Y. Yeo, A. Stuck, C.E. Wartnaby and D.A. King, Chem. Phys. Lett. 259 (1996) 28.

[15] E. Yagasaki and R.I. Masel, Surf. Sci. 222 (1989) 430.

[16] E. Yagasaki, A.L. Backman and R.I. Masel, J. Vac. Sci. Technol. A 8 (1990) 2610.

[17] E. Yagasaki and R.I. Masel, J. Am. Chem. Soc. 112 (1990) 8746.

[18] A.L. Backman and R.I. Masel, J. Phys. Chem. 94 (1990) 5300.

[19] E. Yagasaki, A.L. Backman and R.I. Masel, J. Phys. Chem. 94 (1990) 1066.

[20] G.H. Hatzikos and R.I. Masel, Surf. Sci. 185 (1987) 479.

[21] A. Stuck, C.E. Wartnaby, Y.Y. Yeo and D.A. King, Phys. Rev. Lett. 74 (1995) 578.

[22] C. de la Cruz and N. Sheppard, J. Chem. Soc. Chem. Commun. (1987).

[23] P. Berlowitz, C. Megiris, J.B. Butt and H.H. Kung, Langmuir 1 (1985) 206.

[24] H. Öfner and F. Zaera, J. Phys. Chem. B 101 (1997) 396.

[25] M. Eriksson, L. Olsson, U. Helmersson, R. Erlandsson and L.-G. Ekedahl, Thin Solid Films, in press.

[26] R. Dümpelmann, N.W. Cant and D.L. Trimm, Catal. Lett. 32 (1995) 357.

[27] A.D. van Langeveld, J.P.F.M. van Hertrooy, J.B.W.P. Loos and J.W. Niemantsverdriet, Vacuum 38 (1988) 393.