

6 The Surface Acoustic Waves (SAW)*

“In a general sense, chemistry is the study of the interaction of energy and matter. Chemical reactions require energy, in one form or another, to proceed and, in large part, the properties of a specific energy source determine the course of a chemical reaction. Ultrasonic irradiation is a unique means of interacting energy and matter.” K.S. Suslick, *Science* **247**, 1439 (1990).

One of the central problems in chemistry is the development of methods for controlling the outcome of a chemical reaction [1], e.g., to maximize the yield of the products or to suppress unwanted sideproducts, or to allow the synthesis of new materials. This control can be applied in a variety of means. For instance, by varying control parameters such as pressures and temperature, by selecting a suitable catalyst to lower the activation barrier, by preparing *ad hoc* the energetic state of the reactants [2], photochemically (see next chapter) or by stereodynamic control [3].

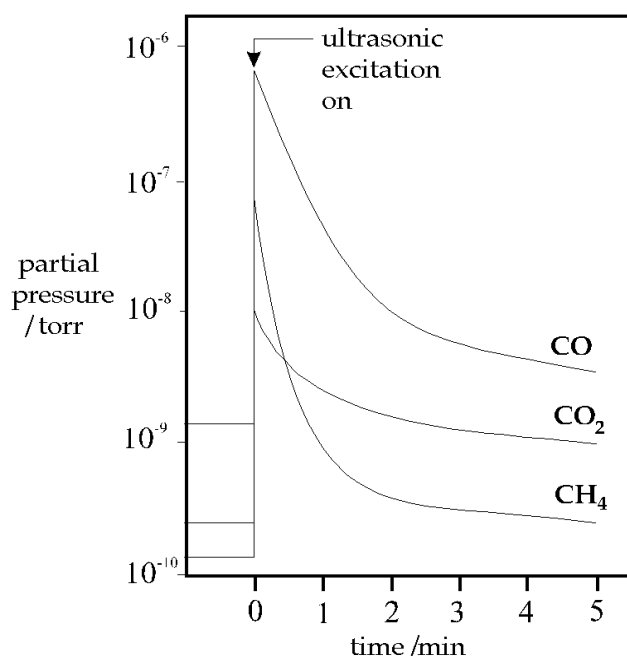


Fig. 6.1 Ultrasonic-induced desorption at 40 kHz and about 1 W transferred power. After Denison, 1969.

* References at page 62

Ultrasound has been reported [4] to increase reaction rates in a number of liquid and liquid-solid systems. The first effect of surface acoustic waves at gas-solid interfaces was found by Denison [5], aiming to improve the base pressure of a vacuum chamber. Once the system had reached a steady pressure, he switched on an ultrasonic transducer connected to the chamber. A short and drastic increase of the monitored CO_2 , CO , and CH_4 partial pressures, as shown in Fig. 6.1, was recorded.

Krischer and Lichtman [6] investigated desorption phenomena of residual gases from a quartz single crystal surface under UHV. The data showed a sharp increase in the desorption with increasing acoustic power. Brezhnev and coworkers [7] connected a quartz plate to the edge of a Pt(100) crystal to study the influence of acoustic excitation on the CO oxidation under UHV conditions. They concluded that, in certain regimes, rate oscillations can be influenced by acoustic excitation.

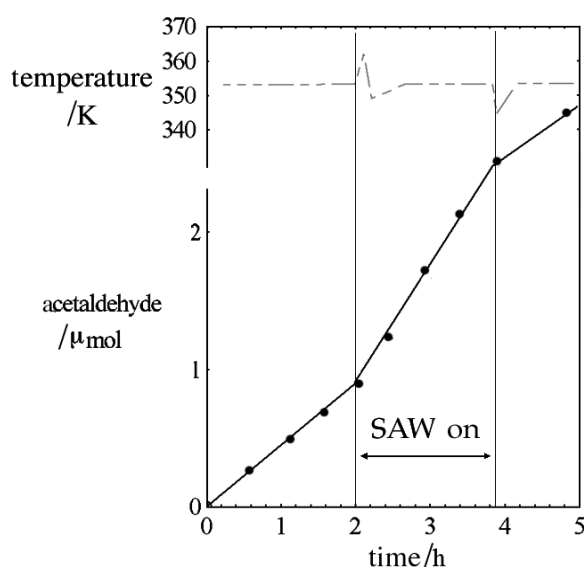


Fig. 6.2 The effect of SAW on catalytic activity and temperature of the Pd catalyst during the formation of acetaldehyde from $\text{C}_2\text{H}_5\text{OH}$ and O_2 .

The potential of using acoustic waves for substantial improvements in the rates of catalytic processes was for the first time recognized by Inoue and coworkers. They reported a remarkable increase (Fig. 6.2 after ref. [8]) in the rates of several catalytic reactions at the gas-solid interface upon acoustic waves excitation of the catalyst surface. These studies, reviewed by Gruyters and coworkers [9], were performed in a gas circulating apparatus operating at around 30 torr with polycrystalline metal films as catalysts. Reactants and products were analyzed, typically at intervals of 10 min, by a gas chromatograph connected to the reaction system.

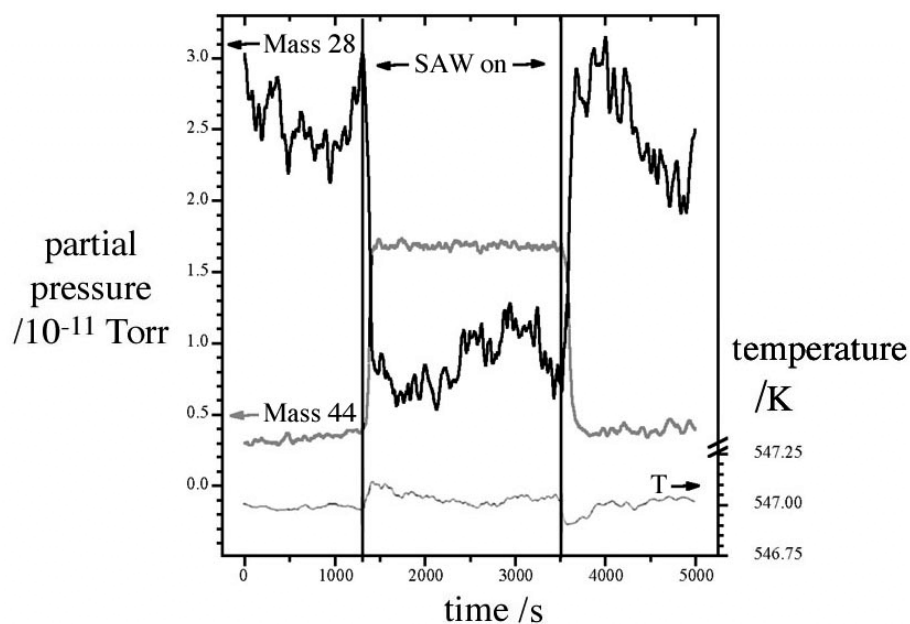


Fig. 6.3 The effect of SAW on the rate of the CO oxidation on Pt(110). The curves represent the CO and CO₂ partial pressures and the temperature.

With the aim to understand under well-characterized conditions the physical mechanisms of the rate enhancement effect driven by acoustic excitation, the group of D.A. King in Cambridge started a UHV investigation of the catalytic CO oxidation on Pt single crystals. Their results, in Fig. 6.3 from Kelling and coworkers [10], present evidence for a non-thermal acoustic enhancement of the reaction rate. In order to disentangle the physical nature of this enhancement, in collaboration with Sven Kelling of the Department of Chemistry of the University of Cambridge a PEEM investigation has been performed in our laboratory. In the course of the experiment the adsorbate coverage changes caused by the propagation of the SAW on the Pt(110) have been recorded simultaneously with the CO₂ production.

6.1 Experimental

The 300 nm x 10 mm x 10 mm Pt(110) single crystal film was grown by Jacques Chevallier, at the Aarhus University [11] Denmark, by evaporating the metal onto dissolvable single crystal supports with a suitable lattice size.

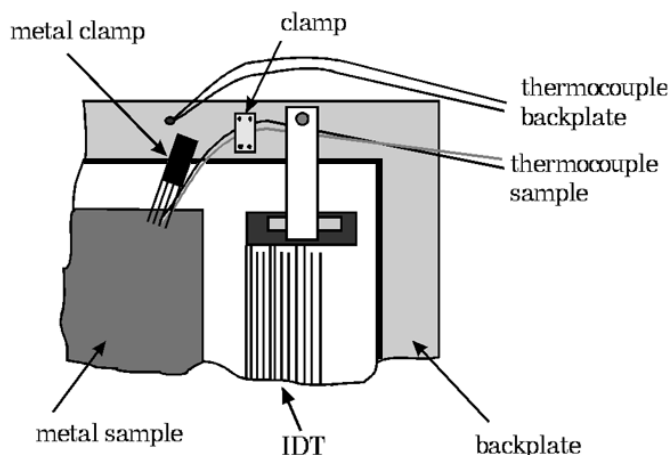


Fig. 6.4 Sample, connectors, and thermocouple mounting.

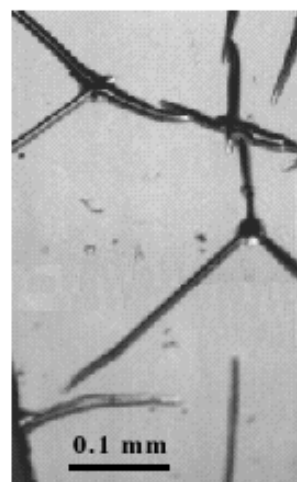


Fig. 6.5 Optical micrograph of the Pt film corrugations.

The description of the film preparation is given in the following. Provided that the lattice mismatch between the required metal and the support is not larger than a few percent, the film grows epitaxially on the substrate. Ionic salts meet the requirements since they are single crystals and can be dissolved in water. In particular sodium chloride, prepared by cleavage and radiation hardening, is used to grow low-index platinum surfaces. The surface orientation is controlled by X-ray diffraction. By electron beam vapor deposition the platinum metal film is grown at a rate of 10 Å/s. A layer-by-layer growth is achieved by heating the substrate at 700 K, allowing fast diffusion. After that, the Pt film is removed from its support by dissolving sodium chloride in ultra pure water, which in turn relieves the stress due to epitaxial mismatch, and eventually cold welded on the Pt/LiNbO₃ substrate (Fig. 6.4). Despite some folds (apparent in Fig. 6.5), a flat platinum single crystal with a fairly good adhesion to the piezo substrate is eventually attained.

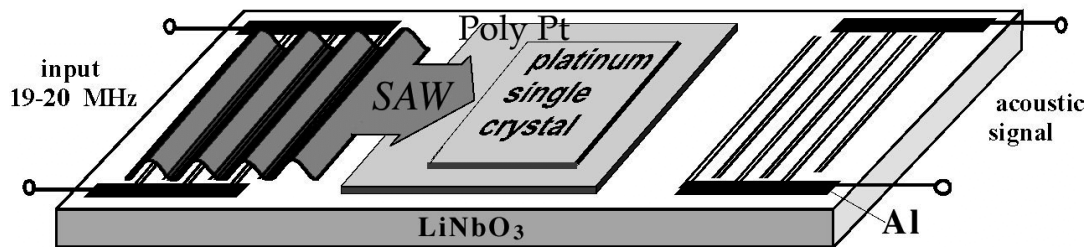


Fig. 6.6 An IDT device.

To generate Surface Acoustic Waves (SAW), an interdigital transducer (IDT), shown in Fig. 6.6, has been employed. The device consists of a poled Y-cut ($10\bar{1}$) LiNbO_3 substrate. Lithium niobate crystals display a number of remarkable properties like ferroelectricity, piezoelectricity, and pyroelectricity, besides having nonlinear optical coefficients, and are nowadays widely used in optical and acoustic devices. The catalytically inert, thin (to prevent signal damping) aluminum electrodes with a length of 7 mm are fabricated in the form of a comb with $200\ \mu\text{m}$ periodicity. A 30-nm-thick Pt film was interposed between the single crystal and the piezo substrate to increase the adhesion.

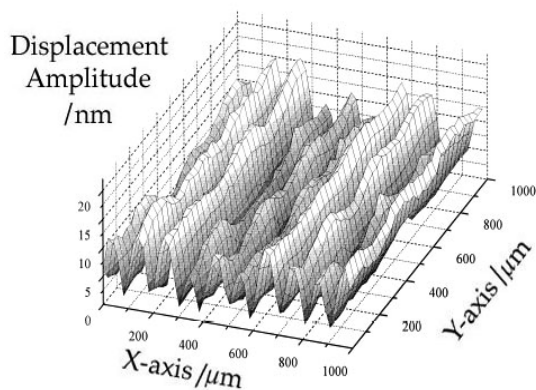


Fig. 6.7 Doppler displacement plot of a bare LiNbO_3 -IDT upon SAW excitation at 0.6 W, in air, at room temperature.

An AC voltage is applied to the input electrodes. At the resonant frequency, i.e., when the wavelength of the induced electromagnetic signal matches the comb periodicity, a stationary field of vertical displacement is established on the surface of the piezo. The center frequency of these oscillations is 19.5 MHz and the power transferred is about 1 W. These (Rayleigh) waves can be imaged, as in Fig. 6.7, after

Kelling and coworkers [12], with the laser Doppler displacement method.

Prior to experiments, the sample was prepared by some gentle argon ion sputtering, oxygen treatment, and annealing at 700 K until a sharp (1×2) LEED pattern, a mark of the clean surface, was achieved.

6.2 Results

The experiments to investigate the influence of acoustic waves on adsorbate structures and the rate of CO_2 formation under reaction conditions were performed at a sample temperature of 485 K. During these experiments the O_2 pressure was kept constant, typically at 2.0×10^{-4} mbar, whereas the CO was varied in the 10^{-5} mbar range. Starting from an oxygen-covered surface in the reactive branch of the reaction, the CO pressure was slightly increased. As a result, CO islands started forming on the surface, causing the system to drift into the non reactive, CO-poisoned regime. These are the conditions in which a reaction rate increase upon acoustic excitation has been reported [13].

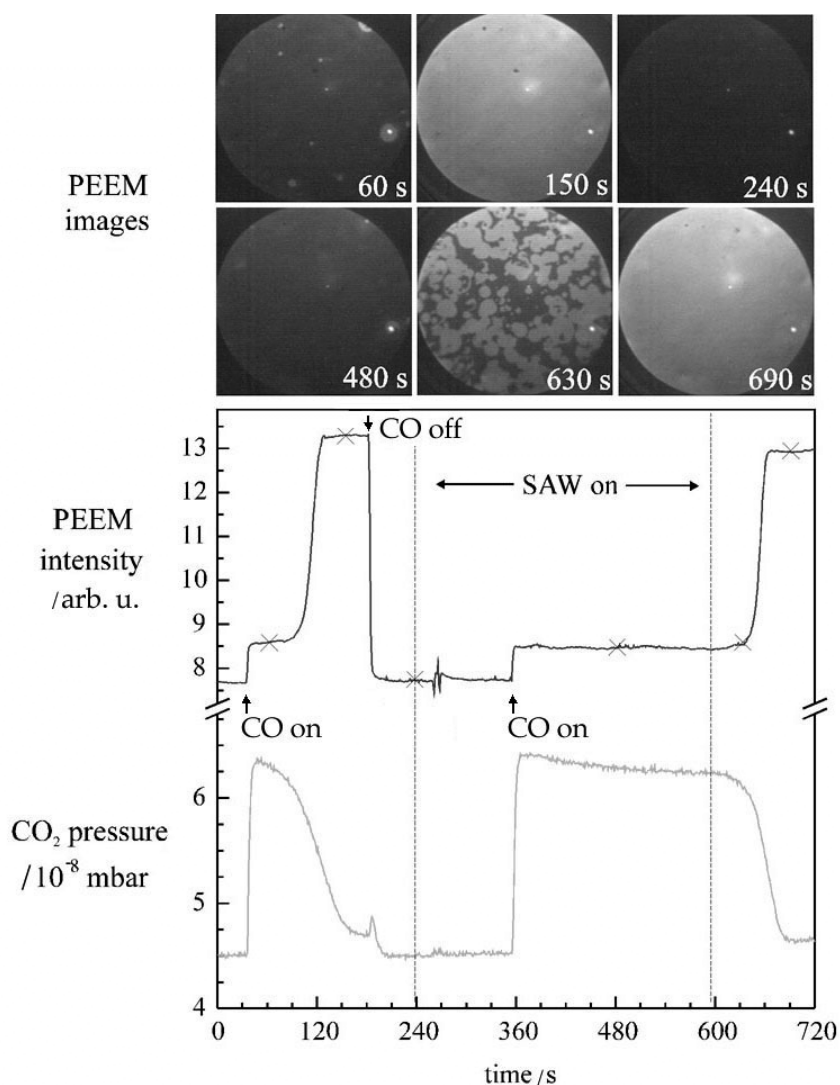


Fig. 6.8 PEEM images, PEEM intensity, and CO partial pressures. SAW were generated at a frequency of 19.52 MHz and a RF power of 1.7 W, $p(\text{CO}) = 1.6 \cdot 10^{-5}$ mbar, $p(\text{O}_2) = 1.7 \cdot 10^{-4}$ mbar, $T = 500$ K.

The first experimental results are presented in Fig. 6.8, where a sequence of PEEM images, a graph representing the PEEM intensity integrated over the whole observed area, and the amount of CO₂ produced are presented. The integrated PEEM intensity is inversely related to the work function of a given area. On the left-hand side of Fig. 6.8 the behavior of the system is shown with a constant oxygen pressure of $1.7 \cdot 10^{-4}$ mbar upon admitting $1.6 \cdot 10^{-5}$ mbar CO. The PEEM image brightens up due to the adsorption of CO on the homogeneously oxygen precovered surface. The CO₂ production rapidly reaches the maximum value obtainable at the given oxygen pressure and sample temperature.

After remaining in the highly reactive branch for a few seconds, the reaction rate starts to decrease due to the shortage of adsorbed oxygen. Patches of CO, visible as brighter islands in the PEEM images, start to grow on the surface causing a further drastic drop in the CO₂ production. By switching off the CO supply, an oxygen-covered surface is obtained, as shown in the dark PEEM image at 240 s. We have then repeated this experiment on the acoustically excited surface by generating SAW at a frequency of 19.5 MHz and a power of 1.8 W. Letting the CO in the chamber caused the system to establish a longer lasting reactive regime. Even after 4 min, an exposure that would already have caused CO poisoning, no CO patches were observed on the crystal. Moreover, only after turning off the acoustic excitation, the CO islands started to nucleate on the surface causing a drastic decline of the activity.

Having found suppression of CO island formation on a SAW propagating surface, we examined whether the reactive state of the surface could be regenerated from the CO-poisoned state using acoustic excitation. The state was prepared by using the same pressures and temperature as in the previous experiment and waiting about 2 min to get an inert CO-covered surface.

Fig. 6.9 shows the integrated PEEM intensity and the CO_2 production measured during this experiment. After 2 min, acoustic waves were first excited on the surface of the prepared catalyst. Following an induction time of 1 min, the reaction rate started slowly to increase. The PEEM shows the appearance of dark-gray patches, assigned to the reactive oxygen and CO coadsorbed state, which grow and eventually cover the whole surface. As already noticed in the previous experiment, turning off the SAW causes the system to drop back into the nonreactive, CO-poisoned regime. To check the reproducibility of the reactivation, also data of a second cycle of a 4-min acoustic wave excitation are shown in Fig. 6.9. During these experiments no acoustically induced change in shape or typical size of adsorbate islands or spirals has been observed.

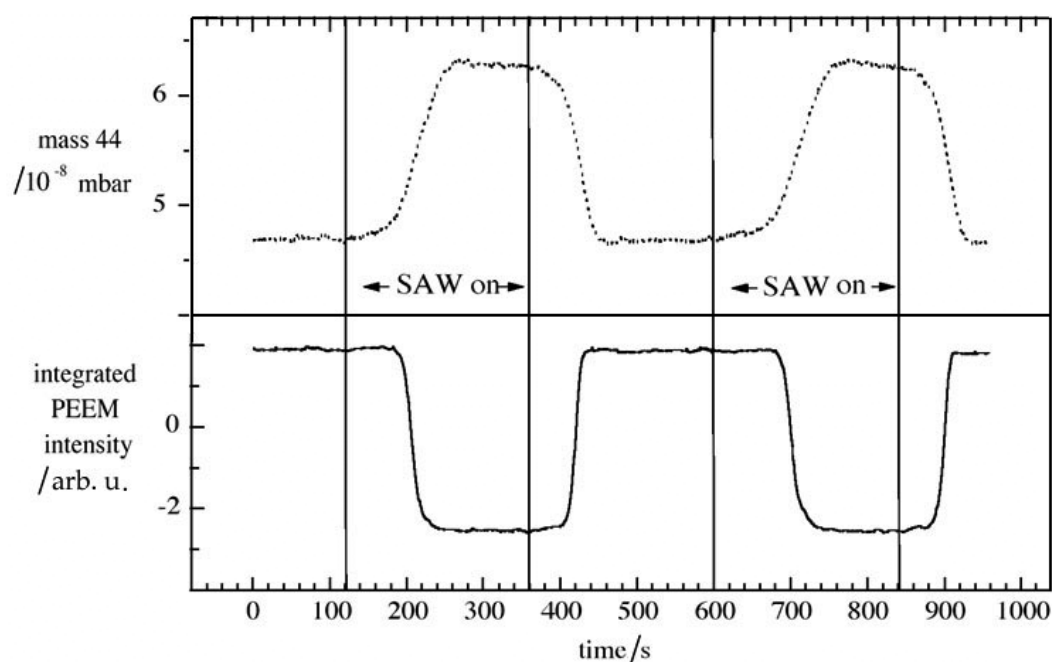


Fig. 6.9 The influence of SAW excitation on the rate of CO_2 formation (dotted line) and on the PEEM intensity (straight line) in conditions where the catalyst surface is CO-poisoned.

The described experiments allow us to conclude that the transformation between the reactive and the CO-poisoned surface state can, depending on partial pressures and temperature, be slowed down, prevented, or reversed by exciting the surface with acoustic waves. However, if the $\text{CO}:\text{O}_2$ ratio exceeds a certain threshold, surface poisoning cannot be prevented.

To gain more information about SAW effects on adsorbates, we investigated surfaces covered with only one reactant. We started exciting a freshly cleaned crystal with acoustic waves. No change in PEEM intensity, which means no change in the work function, was observed. Exposing the crystal to constant oxygen pressures between 10^{-9} and 10^{-5} mbar at the typical reaction temperature of 500 K and applying SAW, no work function change was measured by PEEM, nor oxygen partial pressure change was observed. However, exposing a clean crystal to $1 \cdot 10^{-8}$ mbar CO and applying SAW did produce changes in the PEEM intensity. As shown in the upper curve in Fig. 6.10, turning on the acoustic power leads to a sudden decrease in the work function.

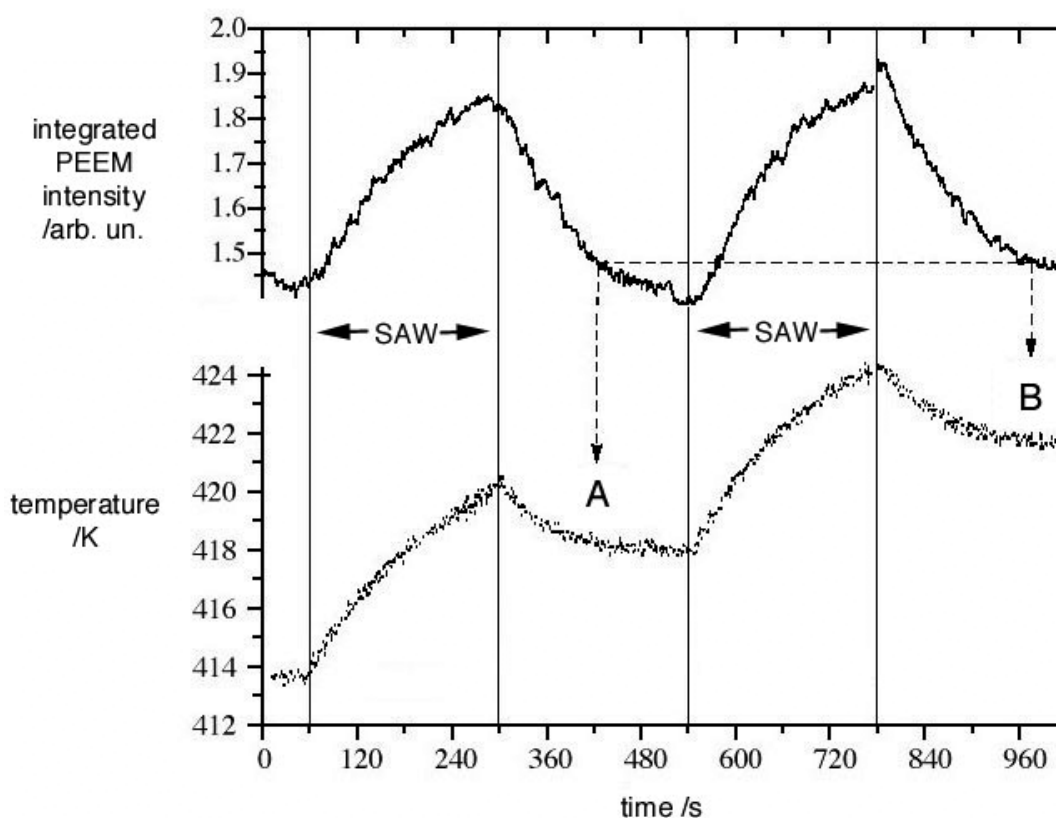


Fig. 6.10 PEEM intensity and sample temperature recorded during two 4-min SAW cycles. A and B mark points of equal PEEM intensity at different temperatures; $p(\text{CO}) = 1 \cdot 10^{-8}$ mbar.

A 4-min SAW excitation caused a 0.5 units increase in photoelectron intensity, which corresponds to 40% of the PEEM integrated intensity variation between CO-covered and clean surfaces found in the present experiment (1.2 units).

The temperature of the region imaged by PEEM was simultaneously monitored using an IR camera. In Fig. 6.10 it can be seen that a 4-min SAW treatment produced a temperature rise of 7 K. After 4 min without acoustic excitation the work function rose back to the starting value, whereas the sample temperature decreased by only 2 K. At this point, a second cycle of 4 min acoustic excitation was performed. The fact that the same PEEM integrated intensity (A and B labels in Fig. 6.10) is obtained at two different temperatures implies that temperature changes of a couple of degrees do not have any influence on the PEEM intensity. The conclusion is that the increase in the PEEM intensity in the said temperature range is not attributable to thermal desorption. In a further series of experiments the temperature and pressure range in which SAW propagation influences the CO coverage were investigated. We found the effect to be dominant at high temperatures and low CO pressures. At pressures higher than $5 \cdot 10^{-6}$ mbar and temperatures lower than 375 K the influence of acoustic excitation was negligible. At that point, we simulated the observed effect on the rate of CO oxidation by raising the sample temperature. In agreement with earlier results [10], the same reaction rate enhancement induced by acoustic excitation could always be reproduced by increasing the crystal temperature by about 45 K. The analysis of the IR temperature images during SAW propagation did not reveal the presence of any hot spots on the surface of the sample.

We have shown that PEEM is a suitable technique to study the influence of SAW on the behavior of mesoscopic-scale adsorbate structures during catalytic reactions. Under reaction conditions that normally cause CO poisoning, exciting the catalyst with acoustic waves can inhibit, slow down and even reverse the process of CO covering the surface. Therefore, a larger CO:O₂ ratio is required to poison the acoustically excited catalyst for a given temperature. The reaction can then be run at a higher CO partial pressure, giving a larger reaction rate than on the non-excited catalyst. Conversely, to achieve the same reactivity for a fixed partial pressure ratio, the acoustically excited catalyst can be operated at lower temperature. These observations on Pt(110) are in good agreement with previous studies of King and coworkers concerning pressure and temperature dependence [10]. Furthermore, the present results show that acoustic excitation does not alter the reaction mechanism or the adsorbate mesoscopic structures formed during CO oxidation.

From our observations it can be concluded that acoustic wave generation shifts the adsorption-desorption equilibrium for CO towards the desorption. Although a rise in the CO partial pressure could not be measured with the QMS, we conclude that, in the early stage of the CO poisoning, SAW excitation promotes CO desorption, restoring the CO oxidation reaction. This conclusion is supported by several experimental facts. Firstly, the reaction-rate-enhancing effect can be simulated by increasing the rate of CO desorption via a rise of the sample temperature. Secondly, no effect can be observed below the CO desorption temperature. Finally, the work function decrease of the CO-covered surface with acoustic excitation can be explained by desorption, a conclusion which is in agreement with above mentioned findings of Denison and Krisher.

6.3 Discussion

The present results bring us to the main question. What are the underlying physical mechanisms by which surface waves cause a change in the rate of desorption? Evidence for a non-thermal enhancement of the reaction rate upon acoustic excitation of the catalyst was already presented in a work by Kelling and coworkers [10] where a *resonance effect* of specific acoustic frequencies was ruled out too. Two of the mechanisms that could account for the observed effects are presented in the next sections.

Is there any chance SAW that can induce desorption of weak chemisorbed CO molecules via phonon interaction? The answer is “possibly no”. In fact, the energy of a vibration quantum for the 10^7 Hz SAW (10^{-12} eV) is orders of magnitude smaller than the desorption barrier (1 eV). One could be tempted to invoke the cavitation [14] as a means of concentrating in *hot spots* the phonon energy via the formation, growth, and implosive collapse of bubbles. Although observed in liquid and liquid-solid systems, no cavitation effects have been reported for gas-solid systems in the range of pressures of the present work, where laminar flow is expected to dominate.

A central aspect is that the *fresh* Pt crystal surface displays evident signs of degradation upon SAW treatment. The structures in Fig. 6.11a exploit approximately the periodicity of the SAW. Tiny Pt particles are ejected several mm from the surface (Fig. 6.11b). Moreover, spikes in the vertical displacement appear in the Doppler plots [12].

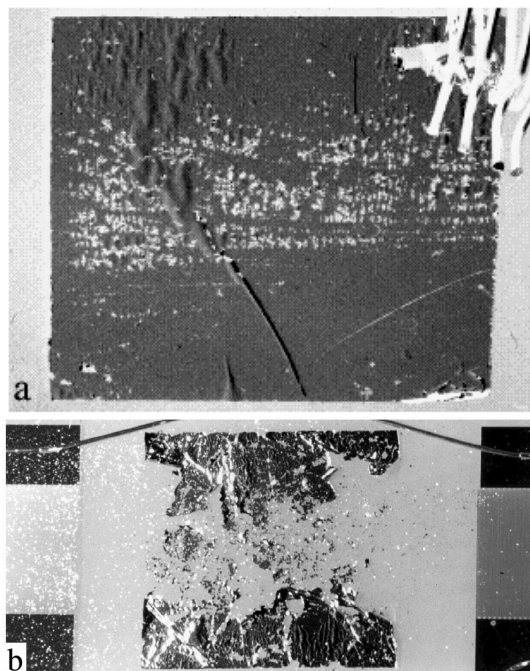


Fig. 6.11 Morphological changes of a 500 nm thick Pt(111) upon 1 W SAW excitation after 1 (a) and 7 hours (b).

For polycrystalline platinum films, on the contrary, S. Kelling found no enhancement of the rate in the CO oxidation and no surface damage whatsoever upon acoustic excitation [15]. This raises the suspicion that the damaging process itself may account for the dramatic change of CO desorption and overall reactivity!

Before discussing viable mechanisms for the SAW to produce damages in the thin Pt film, we shall note that an increase in reactivity upon acoustic excitation without damaging was found on polycrystalline films for the ethanol oxidation on Pd [16] and the ethanol decomposition on Cu [17]. Clearly a different mechanism must account for that. We will consider a further possibility later in section 6.3.2.

6.3.1 Mechanical effects

The question is whether SAW are able to release enough energy to destroy a Pt film. Let us assume that in order to break a bond the stretch of two adjacent Pt atoms must exceed 5 times the thermal fluctuation of 2 pm [18]. For a perfectly flat surface with an interatomic distance (c) of 277 pm the maximal displacement (D) upon 1 W, 10 nm amplitude (A), and 200 μm wavelength (λ) SAW excitation estimated by

$$D \approx 2 \pi A c / \lambda$$

is three orders of magnitude smaller than the critical value.

Nevertheless, using a similar derivation it can be shown that, if a fold is present along the wave path, the resulting phase difference of the stationary SAW at the fold location may cause a displacement large enough to tear atomic bonds apart. In fact, for a cylindrical fold with diameter d , the path difference is $0.57 \times d$ and the maximum displacement

$$D \approx A \sin(2\pi 0.57 d / \lambda)$$

of about 1nm, well surpasses the threshold!

Is it then possible to explain the features of the rate enhancement, such as the reversibility, with the SAW-induced fracturing of the catalyst film? A possibility is to regard the crack propagation as a reaction promoter, since the release of elastic strain energy at the tip of the crack produces a drastic increase of the temperature. At the tip the "local" non-equilibrium temperature, the so-called equivalent temperature, has been estimated [19] to reach some thousand K. The resulting heating may substantially influence the catalytic activity. However, no traveling hot spots have been detected in the present experiments by infrared imaging (IR).

A second hypothesis is that in the course of fracturing new fresh Pt surfaces are constantly created on the border of the cracks. At the cracks, catalytically active surfaces can also originate on the backside of the catalyst in the case of a non-perfect adhesion with the substrate. It is even possible that the flapping of the film may mechanically strip molecules from the exposed part of the backside. Therefore, even in a regime where CO blocks most of the oxygen adsorption sites on the surface, no poisoning takes place.

6.3.2 Electronic effects

Is it possible that the electric field, closely related in a piezoelectric material to the displacements, plays a role in enhancing the reactivity? It has been observed [20] that applying a 10^4 V cm^{-1} electrostatic field causes a shift in the CO vibrational frequency on a Ni substrate via the modification of the electron density. This shift, named vibrational Stark effect, is linearly proportional to the electric field with a proportionality constant, the *tuning* rate, of $5 \cdot 10^{-7} \text{ V}$. The change in the electron density may in turn modify the back-donation and, consequently, the strength of the CO–metal bond.

The electric field associated with a transverse SAW has the following form:

$$\mathbf{E} = \mathbf{E}_0 \exp(-z/\delta) \cos(z/\delta - \omega t),$$

Here z represents the coordinate perpendicular to the surface, $\delta = (2/\omega \mu_0 \sigma)^{0.5}$ the penetration depth, μ_0 the vacuum permeability, and σ the conductivity. For a 20 MHz SAW the penetration depth is about 20 μm , which causes an electric field [21] of about 10^4 V cm^{-1} at the outer catalyst surface, and a work function change

$$\Delta\phi = (e^4 E / 4 \pi \epsilon_0)^{0.5}$$

of about 40 meV. Incidentally, the fact that no work function changes were observed in the course of our PEEM experiments is not conclusive, since the time response of the imaging device is inadequate to follow the 20 MHz oscillations in the work function. The time needed for a 90 to 10% intensity decay of the phosphor screen is, in fact, 4 ms.

Using the above-mentioned tuning rate, a CO vibrational frequency shift of the order of 10^{-3} cm^{-1} can be expected in our case, which is negligibly small even compared with the 40 cm^{-1} shift caused by CO coverage variations [22]. The result is that the electric field at the surface is not sufficient to influence the CO desorption significantly. However, it may not necessarily be true that the tuning rate for the SAW is of the same order as the one reported for an electrostatic field.

6.4 Overall Conclusions

As a result of our CO oxidation investigations on a Pt single crystal catalyst under UHV we found an increase in the activity upon acoustic excitation, via a CO desorption enhancement as detected by PEEM. Since a mere thermal effect has been ruled out as possible mechanism explaining the enhancement, we have considered other alternatives, bearing in mind the observed correlation between catalyst film morphological change and reactivity. Neither the mechanical nor the electric mechanisms, however, turned out to convincingly explain the SAW effects.

Regardless of the underlying mechanism, the results presented in this work demonstrate acoustic excitation is a viable route to increase the activity of a catalytic reaction at the gas-solid interface. It can therefore be inferred that SAW may be relevant for the design of improved controllable catalysts, with, in principle, a relevant impact on industrial applications.

- [1] F. Crim, *Selective excitation studies of unimolecular reaction dynamics*, Annu. Rev. Phys. Chem. **35**, 657 (1984).
- [2] A. J. R. Heck and D. W. Chandler, *Imaging techniques for the study of chemical reaction dynamics*, Annu. Rev. Phys. Chem **46**, 335 (1995).
- [3] R. J. Gordon and S. A. Rice, *Active control of the dynamics of atoms and molecules*, Annu. Rev. Phys. Chem. **48**, (1997).
- [4] T. J. Mason and J. P. Lorimer, *Practical Sonochemistry* (Ellis, Horwood, 1991).
- [5] D. R. Denison, *Phonic desorption*, J. Vac. Sci. Technol. **6**, 214 (1969).
- [6] C. Krischer and D. Lichtman, *Observation of desorption from quartz induced by surface acoustic-waves*, Phys. Lett. **44 A**, 99 (1973).
- [7] V. Brezhnev, A. Boronin, V. Ostanin, V. Tupikov, and A. Belyaev, *Observation of surface acoustic phonon resonances - applications to the CO+O₂ oscillatory reaction on Pt(100)*, Chem. Phys. Lett. **191**, 379 (1992).
- [8] Y. Inoue, Y. Matsukawa, and K. Sato, *Effect of surface acoustic-wave generated on ferroelectric support upon catalysis*, J. Am. Chem. Soc. **111**, 8965 (1989).
- [9] M. Gruyters, T. Mitrelias, and D. King, *Effect of surface acoustic-waves on activity in heterogeneous catalysis*, Appl. Phys. A **61**, 243 (1995).
- [10] S. Kelling, T. Mitrelias, Y. Matsumoto, V. P. Ostanin, and D. A. King, *Acoustic wave enhancement of the catalytic oxidation of carbon monoxide over Pt{110}*, J. Chem. Phys. **107**, 5609 (1997).
- [11] F. Besenbacher, I. Stensgaard, and K. Mortensen, *Adsorption position of Deuterium on the Pd{110} surface determined with transmission channeling*, Surf. Sci. **191**, 288 (1987).
- [12] S. Kelling, N. Saito, Y. Inoue, and D. A. King, *Surface morphological changes induced in catalysts by acoustic waves*, Appl. Surf. Sci. **150**, 47–57 (1999).
- [13] S. Kelling and D. A. King, *Platinum Met. Rev.* **42**, 8 (1998).
- [14] K. S. Suslick, *Sonochemistry*, Science **247**, 1439 (1990).
- [15] S. Kelling, *Enhancing CO oxidation over Pt single crystals by SAW*, Ph.D. thesis, Cambridge, UK, 1998.
- [16] N. Saito, Y. Ohkawara, Y. Watanabe, and Y. Inoue, *Appl. Surf. Sci.* **121/122**, 343 (1997).
- [17] H. Nishiyama, N. Saito, T. Yashima, K. Sato, and Y. Inoue, *Effect of shear horizontal leaky surface acoustic wave on selectivity for ethanol decomposition of a copper thin-film catalyst deposited on a positively polarized ferroelectric LiTaO₃ single crystal*, Surf. Sci. **427-428**, 152 (1999).
- [18] G. A. Somorjai, *Introduction to Surface Chemistry and Catalysis* (John Wiley & S, New York, 1994).
- [19] P. G. Fox and J. Soria-Ruiz, *Fracture-induced thermal decomposition in brittle crystalline solids*, Proc. Roy. Soc. Lon. **A 317**, 79 (1970).
- [20] D. K. Lambert, *Vibrational Stark effect of CO on Ni{100}, and CO in aqueous double layer: Experiments, theory and models*, J. Chem. Phys. **89**, 3847 (1988).
- [21] Y. Inoue, M. Matsukawa, and K. Sato, *Effect of Surface Acoustic Wave Propagated on Ferroelectric LiNbO₃ on Catalytic Activity of a Deposited Pd Thin Film*, J. Phys. Chem. **96**, 2222 (1992).
- [22] R. Bare, P. Hofmann, and D. A. King, *Vibrational studies of the surface phases of CO on Pt{110} at 300 K*, Surf. Sci. **144**, 347 (1984).