Surface morphological changes induced in catalysts by acoustic waves

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Abstract

An interdigital transducer device equipped with a metal catalyst sample that can be used to enhance catalytic activity by acoustic excitation is investigated. It was found that the propagation of 20 MHz surface acoustic waves of the Rayleigh type on Pt thin film single crystals causes drastic changes in surface morphology. The process of film breaking is observed and it is concluded that a phase shift in the acoustic wave induced by folds and cavities in the sample is responsible for the appearance of cracks. The influence of the change in morphology on catalytic activity and the acoustically induced rate enhancement effect is studied, and it is concluded that these changes are not a significant factor in the observed enhancement. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Inoue et al. have repeatedly reported remarkable increases in the rates of catalytic reactions at the gas–solid interface upon excitation with surface acoustic waves (SAWs) and resonance oscillation of bulk acoustic waves. Switching the acoustic excitation off is found to cause the reaction rate to decrease and stabilise at the original value [1–4]. These studies were performed in a gas circulating apparatus at pressures around 30 Torr using polycrystalline films as catalysts. Experiments performed in an UHV environment by Kelling et al. [5,6] demonstrated that the acoustically induced rate enhancement is a true surface effect that cannot be completely assigned to a thermal effect. More recently it was found that SAW propagation affects the rate of adsorption and desorption [7,8] and it is proposed that SAW-induced changes in the electronic structure at the surface are responsible for the observed phenomena.

In this paper an additional effect of SAW propagation is reported. It was observed that the excitation of thin metal film single crystals with long wavelength (200 µm), low amplitude (15 nm) SAWs results in the appearance and propagation of cracks which eventually lead to a drastic morphological change of the single crystal film surface along the wave propagation path. The drastic morphological changes were significant for the single crystal films which were weakly bound to the ferroelectric substrate and have voids, folds and cavities, but not for...
the polycrystalline film. It is interesting to investigate the origin of this effect, and also to establish whether these acoustically induced morphological changes are a possible pathway for influencing the rates of catalytic reactions at the gas–solid interface. These changes were therefore monitored by optically imaging the surface, studying the influence of surface damage on the SAW displacement pattern, and relating the degree of surface damage to the magnitude of the catalytic rate enhancement. It is emphasized that the acoustically induced rate enhancements reported by Inoue et al. [1–4] for the polycrystalline films are not attributable to morphological changes. Based on these observations various mechanisms leading to an increased reactivity are discussed.

2. Experimental

SAWs were generated and detected by an inter-digital transducer coated with the Pt sample on the propagation path of the SAW. The IDT consists of a poled 128° Y-cut LiNbO₃ single crystal substrate with an input and output aluminium electrode array capable of exciting Rayleigh waves at 20 MHz. It is described in more detail elsewhere [1,2,9]. Two kinds of Pt catalyst samples have been employed: thin film single crystal and polycrystalline films. For the latter pure Pt metal was evaporated and deposited directly on the propagation path, with a thickness of 100–300 nm. The metal single crystal films, however are deposited on the IDT substrate by a cold welding technique explained in more detail elsewhere [10,11]. The platinum thin film single crystals are lifted from a water surface onto the cleaned piezo substrate. Gentle squeezing of the film removes the excess water trapped between the crystal and its support resulting in a permanent cold-weld with good adhesion. The application of radio frequency power to the IDT crystals was made in a manner similar to the methods described previously [1,3,6].

The catalytic oxidation of carbon monoxide was carried out in a closed circulation vacuum apparatus at a base pressure of 3 × 10⁻⁵ Torr. The total pressure of CO and oxygen with a ratio of 1:10 was 40 Torr. The reactant and products were analysed by a gas chromatograph directly connected to the apparatus.

Vertical lattice displacements induced by the propagation of a Rayleigh-SAW propagating on the catalyst surface were measured by a laser Doppler displacement method. The sample was irradiated with a He–Ne laser and the Doppler shift between original and reflected beam measured. In all the experiments presented here, a 1-mm² area was scanned with a step width of 10 μm.

3. Results

3.1. Optical imaging of surface changes

Careful observation of the surface of a new single crystal film reveals that, in contrast to polycrystalline catalyst films, the crystal surface is not perfectly flat but exhibits folds running across it. With an optical microscope the average width of the folds was determined to be 50 μm. These single crystal films start to disintegrate after only a few minutes of SAW generation. After 1 h of acoustic excitation with 1 W power at room temperature (RT) under UHV conditions major changes in the surface morphology occur. A photograph of a sample at this stage of destruction is shown in Fig. 1. The input IDT electrode array (not shown in this picture) is located on the right side. As can be seen in the upper left corner of the sample most folds develop into cavities. Along

Fig. 1. First stage of SAW induced morphological changes. The sample shown here (10 mm²) was excited with acoustic waves at 1 W for approximately 1 h in UHV at RT. The input electrode array is located on the right side.
the wave propagation path bits of the catalyst film are missing; the underlying LiNbO$_3$ can be seen through the holes (dark patches). The damage is greatest in the centre region of the sample and shows a symmetry that can be related to the spread of the acoustic waves. Despite this morphology the LEED pattern obtained from this sample is sharp, indicating that areas of ordered crystal surface remain.

Applying acoustic wave excitation to the sample for a few more hours leads to even more drastic morphological changes. A photograph of a sample after about 7 h of SAW generation with 1 W power is presented in Fig. 2. The catalyst film has nearly completely disappeared along the wave propagation path. The most damage is found on the side of the sample facing the input electrode array. On areas not directly exposed to acoustic waves the catalyst film is partly detached from the substrate and shows significant folds. Furthermore, small platinum particles can be seen to be dispersed over the IDT sample and as far as 1 cm away from the single crystal. This suggests that during acoustic excitation these particles could be kicked relatively large distances away from the surface into the vacuum. To test this possibility the damaged sample was observed in air while acoustic waves were generated with approximately 0.5 W power. It was indeed possible to observe micro-size particles jumping up to 5–10 mm from the horizontally positioned sample surface with the naked eye.

3.2. Laser doppler displacement measurement

A SAW is in the first instance an induced lattice displacement. Although the lattice displacement itself is not sufficient to explain the observed influence on catalytic reactions reported in Refs. [1–6], studying this basic property might help to understand the variety of effects caused by acoustic wave propagation including film destruction.

As described in Section 2 a laser Doppler method was used to measure the vertical lattice displacement. Since one complete scan takes 12 h, acoustic power was applied at only 0.6 W to prevent surface damage during the measurement. To understand the displacement diagrams, it should be noted that they are not snap shots, but display the maximum displacement for each point measured. Therefore, consecutive maxima in the displacement curve correspond to an inward and an outward displacement at one moment in time.

The first measurement was performed on a bare IDT sample on which Rayleigh waves were excited with 0.6 W at 19.63 MHz in air. A 1-mm$^2$ area in the centre of the sample was scanned. Fig. 3 shows a plot of this measurement. Ten displacement maxima, corresponding to 5 wavelengths of 200 μm, can be seen. The pattern is very regular, the wave fronts being parallel. The surface plot Fig. 3b shows that the lattice displacement at wave maxima lies between 10 and 15 nm. Further measurements at points closer and further away from the input electrode array gave the same displacement amplitude.

The next sample to be examined was the same type of IDT-device as used before, but with a 500-nm thick Pt(100) crystal cold welded onto the wave propagation path. The sample was measured as prepared with no acoustic excitation prior to the laser Doppler displacement experiment. SAWs were again excited with 0.6 W at 19.58 MHz in air at RT, and the resulting displacement map is presented in Fig. 4. It can be seen that the lattice displacement on the single crystal film is with an average wave amplitude of 5 nm, which is significantly smaller than for the bare IDT surface. Fig. 4a shows a disturbed wave pattern; superimposed on the Rayleigh wave are spots with a much larger displacement. All areas with an amplitude larger than 8 nm are marked as black islands in the image plot. From the surface plot
Fig. 3. Image plot (a) and surface plot (b) obtained from a laser Doppler displacement measurement on a bare 20 MHz Rayleigh wave generating LiNbO₃ SAW device. The acoustic waves were excited with 0.6 W at 19.63 MHz in air at room temperature. A qualitatively identical displacement field is obtained for polycrystalline films evaporated on top of the IDT device.
Fig. 4. Image plot (a) and surface plot (b) of the vertical lattice displacement measured on 20-MHz SAW device carrying a 500-nm thick Pt(100) crystal film. The sample was measured as prepared with no acoustic excitation or reaction experiment prior to this measurement. SAWs were applied at 19.58 MHz with 0.6 W power, in air, at room temperature. Black islands in (a) correspond to displacement values larger than 8 nm.
Fig. 4b) it can be seen that these spots are sharp spikes with a displacement of up to 20 nm. These spikes have not been observed on polycrystalline materials, but a series of measurements on different Pt single crystal surfaces [(100), (110), and (111) plane] showed that these spikes are characteristic of the single crystal films used in our experiments. Although the crystal shown in Fig. 4 has not previously been excited with acoustic waves, it might be that the as-prepared surface does not exhibit spikes but that the generation of SAWs with 0.6 W power is sufficient to cause spikes to evolve during the displacement measurement. Therefore, the measurement was repeated twice under the same conditions to test if the number of spikes, or the spike amplitude, increases with acoustic excitation time. No significant changes in quantity and quality of spikes were found between the three measurements.

Following these displacement measurement the sample was taken to the gas circulation apparatus for reaction experiments. The crystal was excited with acoustic waves at a power of 0.9 W for 5 h in a O$_2$/CO gas mixture with a total pressure of 40 Torr and a temperature of 180°C. After the reaction experiment, which showed a greater than nine-fold enhancement in the rate of CO$_2$ production upon acoustic excitation, large areas of the crystal surface were found to be damaged. Measuring the lattice displacement again showed an enormous increase in the number of spikes. The Rayleigh wave pattern could now only be seen in about 25% of the 1-mm$^2$ area.

An intermediate state of destruction was measured on a 300 nm thick Pt(110) sample. After 2 h of SAW generation at 0.9 W, the particle displacement pattern shown in Fig. 5 was measured. Areas with a macroscopically rough surface could be identified as domains with the highest spike density by comparing the image plot with the morphology of the spot measured. Furthermore, it can be seen that the amplitude of the Rayleigh wave is about 4 nm larger than on the 200 nm thicker Pt(100) sample. This might explain why it took only two more hours of reaction experiments with 0.9 W SAW excitation on this sample for the regular wave pattern to disappear completely.

The same measurements performed on thin polycrystalline Pt and Pd films evaporated on top of the SAW propagating area resulted in an identical pattern to the one observed on the bare IDT substrate (Fig. 3) except for a lower displacement amplitude due to mass loading. Even long term SAW excitation at 1 W does not result in the film destruction observed on the single crystal films.

### 3.3. Correlation between film destruction and sensitivity to SAW

In the previous sections it has been reported that acoustic excitation causes dramatic changes to the morphology of thin single crystal films. Therefore, it is to examine the possibility that these changes in morphology may be correlated with the acoustic enhancement effect. These experiments were performed in a reactor cell of the gas circulation apparatus at 40 Torr. The gas composition was analysed by gas chromatography every 10 min. The CO oxidation reaction experiments over platinum were run for several hours and consisted of alternating 1 h cycles with SAW off and on. The fresh single crystal catalysts showed only a small, about two-fold, rate enhancement in the first cycle. However, after two cycles of acoustic excitation (2 h at 1 W) a much larger reactivity enhancement upon SAW propagation could be measured. The magnitude of the rate increase varied with every sample and ranged from 5 to 10 times. Once the sample has responded to acoustic excitation with a significant rate enhancement the result is reproducible for about 4–6 cycles of SAW on an off. An example is presented in Fig. 6. The Pt(100) sample had 3 h of acoustic excitation with 1 W power prior to the measurement shown. As can be seen in the left-hand diagram, a notable rate increase is obtained in all three cycles. However, a close look at the rate of CO$_2$ production (right-hand diagram, Fig. 6) reveals a steady decrease in catalytic activity both with and without SAW propagation.

Inspection of the sample after this experiment showed that large spots of platinum were missing from the film along the wave propagation path. Hence, the rate decrease is probably due to a reduction in catalyst surface area. Continuing the experiment resulted in a further decrease of both, the enhancement factor and the reactivities, until the SAW enhancement effect was minor. At the final
stage only isolated islands of platinum film were present along the wave propagation path. The same sequence of low–high–low enhancement effect has been observed on all single crystal films and can be correlated with the surface morphology: a fresh surface corresponding to low sensitivity to SAW in-
duced enhancement and a damaged surface with most of the film still remaining on the IDT device corresponding to large enhancement factors.

Polycrystalline films showed completely different behaviour. In all the experiments performed in this work, and independently by Watanabe et al. [12], no surface damage was caused by acoustic wave propagation and the films did not show a dependence of the enhancement factor on sample age.

4. Discussion

4.1. What causes the damage?

First it is desirable to understand the mechanism that causes the film damage. The destruction can certainly be traced back to the propagation of SAWs. We first check whether the induced particle displacement is large enough for direct bond breaking. The bond stretch during thermal oscillation of a surface atom is about 0.02 Å [13]. Stretching it more than five times further would be required to break the bond. The maximum wave amplitude measured for a single crystal film on a non-damaged surface region is 12 nm (Fig. 5). However, during this measurement the catalyst was excited with only 0.6 W which is 0.4 W lower than the RF power applied in most reaction experiments. To obtain the lattice displacement at 1 W SAW power a calibration curve measured and reported by Nishiyama et al. [14] is used. They found that the extent of lattice displacement enhancement was greater in the lower power range (<0.4 W) and decreased gradually with increasing power. These displacement values are in agreement with the measurements presented here. According to Nishiyama’s calibration curve a 15-nm displacement is expected for an excitation with 1 W. A simple calculation shows that the lattice displacement between two neighbouring atoms during SAW excitation with 1 W is in the order of 10 Å and, hence, far smaller than that required to break bonds between platinum atoms.

Therefore, it is likely that the energy continuously pumped into the film by the acoustic waves creates a stress field which, above a certain threshold, causes the catalyst to break up. It is well known, that mechanical stress at solid surfaces leads to deformation processes by the production and motion of dislocations [15]. Particularly, high dislocation densities are expected to occur in the vicinity of maximum acoustic wave displacement. However, no damage has been observed on polycrystalline samples. The reason for this might be the fact that polycrystalline films consist of several crystal domains which makes them more flexible and less prone to break under stress. Furthermore, the polycrystalline films are evaporated directly onto the...
piezoelectric substrate resulting in a good uniform bonding and a flat sample surface. In contrast to this, platinum single crystal films cold welded onto the LiNbO₃ substrate exhibit folds and cavities at the interface, as mentioned earlier. This indicates that unevenness of the catalytic film is a condition for acoustically induced fragmentation.

The displacement measurements have revealed that large amplitude spikes are characteristic of the single crystal films used in this work. Calculating the displacement between two neighbouring atoms for the maximum measured spike amplitude ($A = 45$ nm) and a spike width of 20 μm gives a value of about $1.2 \times 10^{-12}$ m which is still not large enough for bond breaking. From this calculation together with the observation that spikes can always be found on destroyed areas of the film we conclude that spikes do not cause the film destruction, but are a result of it.

We propose an acoustically induced destruction mechanism that is based on a phase shift of the acoustic waves and requires cavities between film and substrate, or folds in the film. In Section 2 it was explained that the IDT device is such that the distance between input and output electrode arrays precisely matches a multiple of the wave length, in order to generate a standing wave pattern. If folds or cavities are present along the wave propagation path the path length is extended leading to a difference in phase between the displacement waves coming from either side of the IDT. The effect is schematically illustrated in Fig. 7.

For an average fold with a typical dimension of $d = 25$ μm and a wave amplitude of $A = 15$ nm, that is expected for a 300-nm thick Pt film upon excitation with 1 W, the maximum difference in displacement between the two waves at a fixed point is $\Delta D_{\text{max}} = 6.5$ nm. Even for the smallest folds, spanning only 5 μm, the difference $\Delta D_{\text{max}} = 1.3$ nm is still significant. Hence, a phase shift induced by a variation in propagation path length can cause a bond stretch large enough to exceed the fracture threshold. Therefore, the thin metal film will break if a SAW runs across a wide fold or cavity.

4.2. Can the new morphology explain the SAW effect?

Having established that there is indeed a mechanism that can explain how long wavelength SAWs damage a thin film cold welded on top of the wave generating substrate, we will now proceed to investigate if the new film morphology has properties that will help us to explain the reaction rate increase upon SAW excitation.

In heterogeneous systems with reactions between solid and gaseous reactants the reaction rate is proportional to its surface area. As shown in the previous sections, SAW propagation on thin films is a possible way to introduce destructive mechanical energy, and hence produce an increased surface area. However, the surface layer accessible by the surrounding gas is not the only important factor for the efficiency of heterogeneous reactions on solids. Hammer et al. [16] found, in large-scale density-functional theory studies, in agreement with experimental studies [13,17,18] an extremely strong structure sensitivity in the adsorption energy of CO on different flat, stepped, kinked and reconstructed Pt surfaces with variations of up to 1 eV from one

![Fig. 7](image-url)
structure to the next. However, since the surface area variation created by acoustically induced film cracking is irreversible, it seems difficult to explain the observed decrease in reactivity after turning the SAWs off. In the following mechanisms that can cause a reversible rate increase are discussed.

4.2.1. Crack propagation as reaction promoter

The reversibility of the SAW phenomenon can be explained if the process whereby the destruction occurs is itself responsible for it. In solid fracture processes highly excited states occur. There is a high concentration of energy, particularly at the front of a running fracture, which is mostly transformed into thermal energy. To obtain the magnitude of this energy, the thermal decomposition produced by the release of elastic strain energy when a fast cleavage crack runs through a crystalline solid was studied by Fox and Soria-Ruiz [19]. By relating the degree of decomposition to the fracture velocity and the kinetics of thermal decomposition, figures for the crack tip temperature were deduced. However, the physical significance of this temperature is not clear, as this local energy surplus does not represent an equilibrium distribution and is therefore designated as equivalent temperature. The equivalent crack tip temperatures obtained range from 1900 K for magnesium oxide to 15,000 K for calcium carbonate. Since similar temperatures can be expected at cracks running through metal crystals the energy released would be sufficient to influence the local catalytic activity. Crack tips would act like fast moving hot spots. However, in high resolution IR camera experiments performed by us no hot spots could be observed. Furthermore, in high resolution IR camera experiments performed by us no hot spots could be observed. Therefore, the repeated non-thermal, several-fold increase in reactivity observed in our experiments can certainly not be attributed to the constant fracturing of a 1-cm² area of 300–500 nm thick film. Moreover, experiments on polycrystalline Pd catalyst showed an enhancement in CO₂ production upon acoustic wave excitation without the development of cracks [12].

4.2.2. Fresh surface

During the fracture process ‘fresh surfaces’ are continuously being produced which have no adsorbate layer on formation. This enables oxygen to adsorb dissociatively on the surface even in a reaction regime where at steady state all adsorption sites on the surface are blocked by CO. Hence, with continuous film breaking the rate decreasing effect of site blocking is reduced at the catalyst by the constant formation of fresh surface. It is noted that the enhancement effect was found to be dominant in a region were oxygen adsorption is limited due to site blocking [5,6,8].

A very similar effect has been studied by Heinicke and Lischke [20] for the hydrogenation of ethylene on an Armco iron catalyst. They report that the blocking by ethylene is reduced due to mechanical treatment leading to an increase in catalytic activity. However, for this mechanism the reaction rate increase is determined by the mechanical development of fresh surface. Therefore, the ongoing catalyst film destruction will very quickly lead to a decline or standstill of reactivity.

5. Conclusion

The apparent relation between catalyst film destruction and influence of SAW on catalytic reactivity indicates that on SAW devices equipped with a thin film single crystal film a mecanochemical effect contributes to the increase in catalytic activity upon acoustic excitation. However, the mecanochemical SAW effect is not significant since on polycrystalline samples an acoustically induced rate enhancement can be observed without changes in surface morphology. This paper highlights once more, that there is a large variety of effects caused by SAW propagation that might influence catalytic activity. The experimental system used (thin metal single crystal films deposited directly on piezoelectric substrate) has limitation if the effect of SAW on well defined single crystal surfaces should be studied. Due to additional mecanochemical effects it is difficult to single out other SAW related mechanisms that might be more interesting from the view point of surface science. The use of mechanically more stable polycrystalline catalyst films to study the effects further seem advantageous.
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