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# The Effect of Surface Protrusions on Self-Sustained Thermal Oscillations during Hydrogen Oxidation on a Nickel Foil

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The effects of surface pretreatment on ignition instabilities leading to self-sustained oscillations during hydrogen oxidation on a nickel foil are examined. Nickel foil samples were subjected to a series of pretreatments then put in a reactor and run under conditions where oscillations were expected. A rapid ignition to a high-temperature state was observed with some of the catalysts, while under the same conditions others produced oscillations. Some of the oscillations occurred with a regular pattern, while others were chaotic. Examination of the catalysts revealed that in all the cases where oscillations were observed there were protrusions of 5–20 $\mu$m on the surface of the catalyst, while no such protrusions were seen for the samples that did not catalyze the oscillations. The regular oscillations occurred when the protrusions all looked similar while chaotic oscillations were seen when there were protrusions of many different sizes and shapes. There were no significant differences between the surface compositions of the various catalysts. These results are discussed in the context of the fuzzy wire model of Jensen and Ray (*Chem. Eng. Sci.* **35**, 2439 (1980)).

## INTRODUCTION

Observations of self-sustained oscillations during catalytic oxidation reactions are becoming increasingly common (see (*1, 2*) for an overview). A wide variety of ignition and extinction phenomena have been observed in systems that exhibit multiple steady states. Oscillations have been reported during the oxidation of hydrogen on an unsupported nickel catalyst by Belyaev *et al.* (*3–5*), Schmitz *et al.* (*6, 7*), and Kurtanjek *et al.* (*8, 9*). Belyaev *et al.* (*3–5*) did experiments where the catalyst temperature and the inlet flow rate and composition were held constant and reaction rate was monitored. They found that when the inlet temperature was between 180 and 300°C and the inlet oxygen concentration was below 0.3%, the rate fluctuated in a regular pattern. Schmitz *et al.* (*6, 7*) did experiments where the feed temperature, flow rate, and composition were held constant, and the catalyst temperature was allowed to vary. They found that the catalyst temperature oscillates when the feed temperature was between 230 and 250°C and the inlet oxygen concentration was below 5%. Initially, the oscillation appeared to follow a regular pattern, but after a few hours the regular patterns broke down; the temperature fluctuations became increasingly chaotic with time. At higher oxygen concentrations, two stable steady states were reported. Kurtanjek *et al.* (*8, 9*) did experiments where the inlet temperature, flow rate, and composition were held constant and the catalyst temperature was allowed to vary. They measured the contact potential of the surface and the outlet composition as well as the catalyst temperature. They found that the contact potential, outlet composition, and temperature all oscillate at feed temperatures between 160 and 400°C and oxygen concentrations below 1%. At low flow rates all of these components vary in a synchronized, regular pattern. However, at high flow rates, the syn-

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chronization is less evident, and often chaotic patterns are seen. Interestingly, no oscillations were observed above 2.6% oxygen, while Schmitz *et al.* observed them at oxygen concentration up to 5%.

Over the years, there have been many mechanisms proposed to explain the oscillatory phenomena. It has been found that processes such as periodic oxidation/reduction of the catalyst (*6*), reversible adsorption of an inhibitor (*10*), coverage-dependent activation energies (*4, 11, 12*), changes in the mechanism of the reaction with coverage (*13*), hot spots due to protrusions on the surface (*14*), or amplification of concentration fluctuations in the gas phase (*15, 16*) could cause the reaction rate to oscillate. Changes in the form of the oscillations are normally thought to occur due to slow changes in the composition or structure of the catalyst.

Presented here are the results of a study of the effect of surface structure and composition on the self-sustained thermal fluctuations produced during hydrogen oxidation on a polycrystalline nickel foil. Catalysts were prepared using a variety of different procedures. The catalysts were placed in a reactor similar to that used by Schmitz *et al.* (*6, 7*) and reactants were introduced under conditions where self-sustained fluctuations in the temperature of the catalyst were observed by Schmitz *et al.* (*6, 7*) but none were observed by Kurtanjek *et al.* (*8, 9*). The temperature of the catalyst was recorded as a function of time. Periodically the catalyst was removed from the reactor and its surface structure and composition were examined with a scanning Auger microprobe. It was found that it was possible to correlate changes in the surface structure with changes in the oscillatory phenomena.

## APPARATUS

A schematic diagram of the apparatus is shown in Fig. 1. Air products H. P. Grade hydrogen (99.95%) and oxygen (99.5%) flow from gas cylinders through a 1-ft-long, ½-in. copper tube filled with anhydrous calcium sulfate, through calibrated flowmeters, and into check valves. The gases are then mixed at a tee, passed through a third check valve, and admitted to the reactor through a ½-in. copper tube.

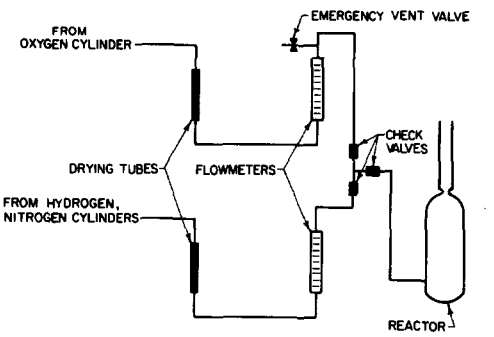


FIG. 1. Schematic of the apparatus.

The reactor was modeled after the one used by Schmitz *et al.* (*6, 7*). It was constructed entirely of glass, and consisted of a bottom section, a top section, and a connection between the two. The bottom section of the reactor was a 43-cm-long tube with a diameter of 4.95 cm. The top section of the reactor was 23 cm long with a diameter of 2.19 cm. A constriction with a diameter of 0.6 cm connected the two sections. Reactants entered the bottom of the reactor through a ¼-in. ball joint. The bottom section of the reactor was filled with glass wool up to the level of the gas inlet. A mixture of 3-, 4-, and 5-mm glass beads was then used to fill the reactor approximately two-thirds full. A glass wool plug was placed just above the constriction, and more glass beads were used to fill the top section of the reactor to within 6 cm of the outlet. Two 8-ft Cal Cords were wrapped around the reactor in order to preheat the reactants, and the entire reactor was insulated with asbestos tape. The voltage to the heating tapes was controlled using two Variacs.

Although a similar reactor was reported previously (*7*) to provide a uniform gas flow, it was found here that the gas temperature decreased with distance from the center of the reactor. The reactor outlet was

covered with glass wool in an attempt to alleviate this problem, but the success of this measure is doubtful.

The nickel catalysts used in this study were disks with diameters of $\frac{3}{8}$-in. These disks were cut from a sheet of nickel foil with a thickness of $\frac{5}{1000}$ in. The temperature of the catalyst was measured using a $\frac{3}{1000}$ in. chromel–alumel thermocouple. A ceramic insulator kept the thermocouple wires separated. The thermocouple was attached to a recorder which was calibrated with an Omegatemp digital thermometer.

## PROCEDURE

### A. *Experimental*

The procedure varied somewhat from run to run. In general, the catalysts were treated, loaded in the reactor, and activated. Then the reaction was started at conditions which were expected to produce oscillations. The behavior of the catalyst was watched closely, and the reaction was stopped and the catalyst removed for analysis after any significant change in behavior.

Three different treatment procedures, which are labeled I, II, and III, were used to prepare the catalyst. Procedure I was to mechanically polish the face of the catalyst with various sizes of diamond paste down to 1 $\mu$m, spot weld on the thermocouple, and position the catalyst in the reactor about 2 cm above the level of the glass beads. Procedure II was to polish the catalyst as in I, place it in air in a furnace at 500°C for 1 hr, cool the catalyst, spot weld on the thermocouple, and position the catalyst in the reactor. Procedure III was to take a catalyst sample, with no treatment, spot weld on the thermocouples, and position it in the reactor. No steps were taken to poison the back of the catalyst or the thermocouple leads in any run.

The activation procedure was the same in all runs. The oxygen flow rate was adjusted to the highest value allowed by the flowmeter (about 300 ml/min), and the Variac voltages were adjusted to raise the catalyst temperature to between 340 and 370°C. After 1 hr, the oxygen flow was terminated, and the reactor was purged with nitrogen for 5 min. After purging, hydrogen was introduced to the system at a rate of 2100 ml/min, and the Variacs were readjusted to maintain the catalyst temperature at 340 to 370°C. After one-half hour, the oxygen flow was turned on at a rate of 63 ml/min, resulting in a gas mixture of 3% oxygen by volume. For the duration of a given experiment, temperature versus time data were collected by the recorder. The length of the experiments varied from a few minutes to 4 hr. After any significant change in behavior, the oxygen flow and the Variacs were turned off, and the catalyst cooled to 150°C or less in hydrogen. The catalyst was then removed from the reactor, separated from the thermocouple wires, and carried to a scanning Auger spectrometer for analysis.

### B. *Analysis*

A Physical Electronics 595 scanning Auger microprobe with a beam energy of 10 keV, was used for all the analysis. High-resolution photographs of the surface were taken with a beam current of 0.4 NA and a magnification setting of 100,000. Low-resolution photographs of the surface were taken with a beam current of 10–50 NA and a magnification setting of 500. Auger spectra were taken by defocusing the beam with a beam current of 100 NA. Component maps were done by setting the beam current to 100 NA and the magnification to 500, scanning an energy window around the appropriate Auger peak at each point on a 256 × 256 array on the surface of the catalyst, and then computing the difference in the maximum and minimum in the undifferentiated Auger spectrum, and normalizing to the minimum.

## RESULTS

### A. *Catalytic Behavior*

Results for one of the catalysts prepared

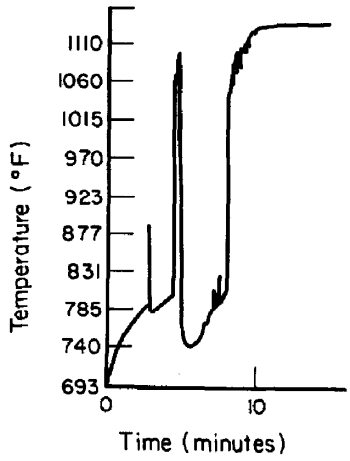


FIG. 2. An example of the temperature jumps seen initially on a catalyst prepared by Procedure I.

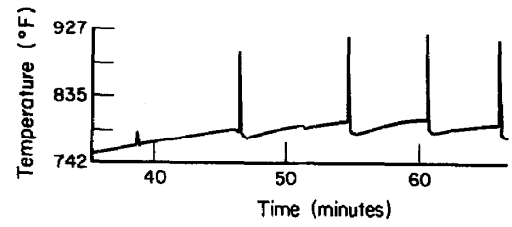


FIG. 3. An example of the initial oscillations of a catalyst prepared by Procedure III.

by Procedure I are shown in Fig. 2. Before the introduction of oxygen the catalyst temperature was 693°F. When the oxygen flow started the temperature rose to 785°F over a period of 3 min and an oscillation with an amplitude of about 100°F occurred. Two minutes later a very large amplitude oscillation occurred which raised the catalyst temperature to 1105°F and then back down to 740°F. The temperature then rose slowly over a period of 4 min with some small oscillations and then the temperature rose quickly to 1135°F and did not return. Turning off the oxygen flow and restarting it

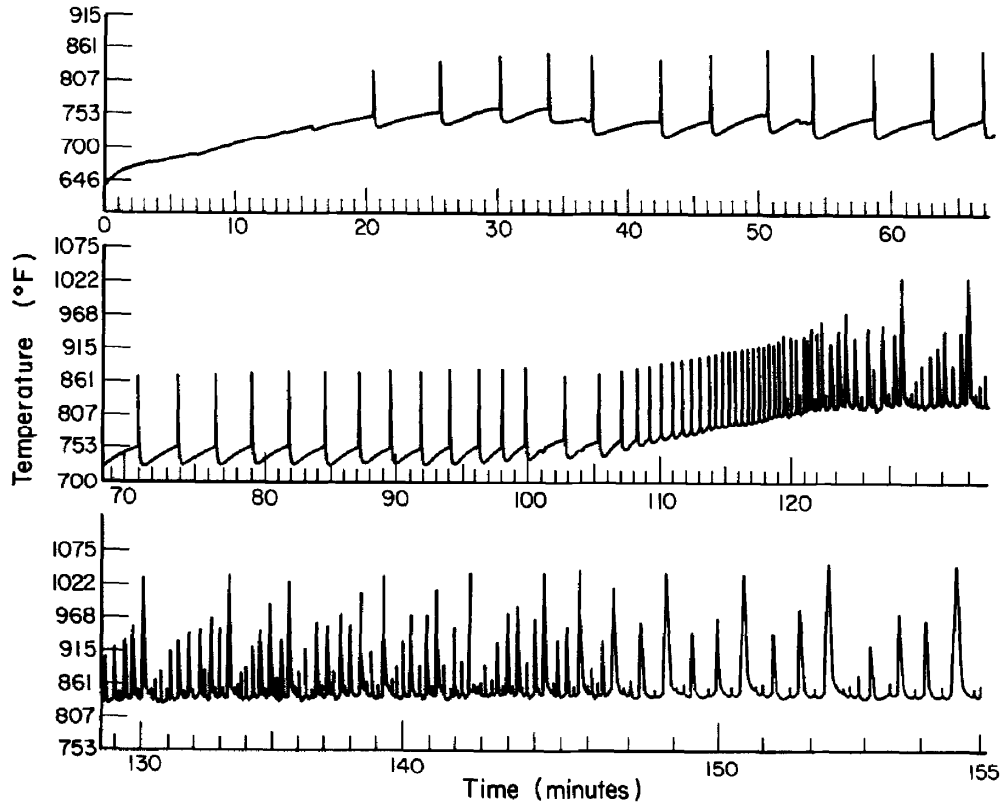


FIG. 4. The behavior of the catalyst in Fig. 3, after being removed from the reactor, and reloaded, oxidized, and reduced. There are time scale changes in the figure at 122 and 147.5 min.

after the catalyst had cooled resulted in a direct jump to the high-temperature state with no oscillations. Similar results were obtained for all catalysts prepared using Procedures I and II. At most, two oscillations occurred before the catalyst went to the high-temperature state.

Catalysts of Type III, which were not polished or calcined, exhibited sustained oscillations. Figures 3 through 6 show the temperature versus time data for a typical catalyst of this type. After the behavior shown in each figure the catalyst was removed from the reactor, analyzed, and placed back in the reactor.

Figure 3 shows the initial behavior of the catalyst. After the oxygen flow was started the temperature rose from 670 to 770°F over a period of 38 min. At this point, a small oscillation with an amplitude of about 20°F occurred. Eight minutes later, the temperature had risen to 770°F, where a second oscillation occurred. During this oscillation, the temperature rose to 900°F, and dropped back down to 780°F. A slow temperature rise to 800°F over the next 8 min resulted in a third oscillation, which increased the temperature to 920°F, and then decreased it to 780°F. Two more oscillations occurred over the next 10 min which were similar to the third one. Peak widths were about 10 sec for all of the oscillations. The sample was then removed for analysis.

Figure 4 shows the second type of behavior exhibited by this catalyst. The temperature rose from 640 to 750°F over a period of 20 min at the beginning of the experiment. Oscillations then began to occur with amplitudes of around 100°F, and periods of 3 to 5 min. A gradual decrease in period and increase in amplitude occurred over the first 100 min of the experiment. These

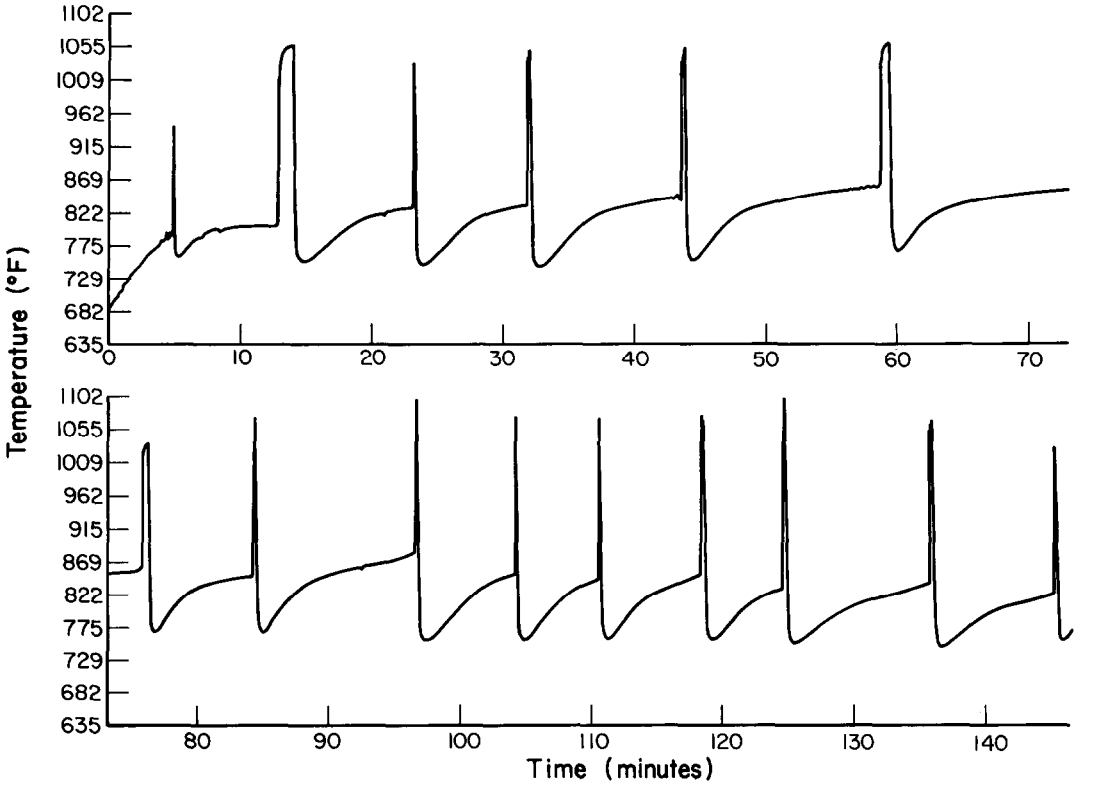


FIG. 5. The behavior of the catalyst in Fig. 4 after being again removed from the reactor, reloaded, and oxidized and reduced.

changes were found to be due to drifting of the hydrogen flow rate. Readjustment of the flow rate resulted in a reproduction of the original behavior. The gas temperature was increased after 105 min in order to induce a behavioral change. As the temperature increased, the periods became smaller, and the lower limit of the oscillations increased. The amplitude of the oscillations remained at about 100°F. Seventeen minutes after the temperature increase began, the lower oscillation limit was at 825°F, and the period of the oscillations was about 30 sec. At this point, the behavior became chaotic with peak amplitudes varying from 15 to 200°F. The lower limit stayed constant at 835°F. The chaotic behavior was allowed to continue for 30 min before the experiment was ended and the sample removed for analysis. It should be noted that the time scale in Fig. 4 changes at 122.5 and 148 min. Also, the small temperature variations at times of 16, 101, and 104 min were caused by oxygen flow rate adjustments, not catalytic behavior.

The third type of behavior exhibited by the catalyst is shown in Fig. 5. Within 5 min of the introduction of oxygen, the temperature had risen from 680 to 785°F. Several small oscillations of 5 to 10°F occurred followed by a larger oscillation in which the temperature rose to 945°F and then fell to 755°F. The temperature rose slowly to 808°F over the next 8 min, followed by another oscillation. This oscillation had a much larger amplitude and peak width than any previously observed oscillation. The maximum temperature reached was 1055°F, and the peak width was about 80 sec. Subsequent oscillations also had unusually large amplitudes and peak widths. The upper temperature limit varied from 1040 to 1100°F, while the lower limit remained essentially constant at around 755°F. The peak widths varied from 20 to 60 sec. Several of the oscillations were preceded by some small-amplitude (2–5°F), small-period (20 sec) oscillations. The amplitude of these oscillations gradually increased for 1 to 2 min before the large oscillation occurred. For the 4th, and 12th, and 14th peaks, three to four small-amplitude oscillations were superimposed on the large oscillation at the top of the peak. The period between the large oscillations varied from 6 to 17 min. Some of the variation in period may have been due to drift in the hydrogen flow rate. The experiment was ended after 150 min, and the sample was removed for analysis.

In Fig. 6, the transition to the high-temperature state is shown. For the first 120 min of this experiment, the behavior was very similar to that shown in Fig. 5. Consequently, the gas temperature was increased in an attempt to force the reaction into the high-temperature state. The result of this was an increase in both the upper and lower temperature limits, and a decrease in the period. The lower limit increased to 835°F and the upper limit went from 1080 to 1100°F. The period decreased to 4 min. After four oscillations at the increased temperature, the high-temperature state was reached. The temperature of this state was nearly the same as the upper limit of the preceding oscillations. The catalyst was again removed for analysis.

A fifth experiment was also done with this catalyst. In this experiment, the catalyst was brought to the high-temperature state and left there for 5 hr and then removed. No oscillations were observed after the system was restarted.

These experiments were repeated for

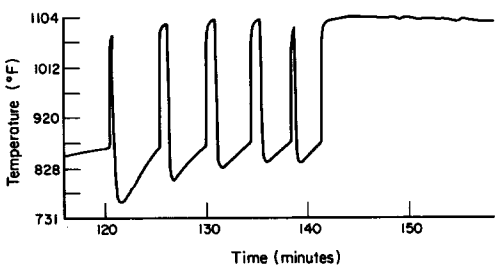


FIG. 6. The behavior of the catalyst in Fig. 5 after being removed from the reactor, reloaded, and oxidized and reduced.

three other catalysts prepared in Procedure III. In general, the results looked similar to those in Figs. 2 through 6. Oscillations were observed with a range of periods of 20 to 1000 sec, and a range of amplitudes of 5 to 350°F.

*B. Auger Analysis*

Figure 7 is a low-magnification picture of the catalyst whose behavior was shown in Fig. 2. The surface shows some small scratches which were caused by polishing, but no large ridges or valleys. At a higher magnification, shown in Fig. 8, small peaks and valleys with a size on the order of 200 Å can be seen, but no gross features exist. All catalysts prepared by Procedures I and II looked qualitatively similar. The catalysts looked relatively flat on the scale of 10 $\mu$m, but there were some small features on the order of 2–300 Å in diameter.

An Auger scan of one of the catalysts prepared by Procedure I is shown in Fig. 9. The analysis shows large amounts of oxygen (483 and 513 eV) and nickel (716, 783, 848 eV), with a small amount of carbon (272 eV) and trace impurities. Sputtering with Argon for 3½ min at a voltage of 2 kV, a current of 0.1 NA, and an Argon pressure of $4 \times 10^{-7}$ Torr resulted in the spectrum shown in Fig. 10. Most of the impurities have been removed along with a fraction of the oxygen. Auger analysis of all the other catalysts prepared by Procedures I and II showed similar features. The surfaces contained large amounts of nickel and oxygen, small amounts of carbon, and trace amounts of other components. There was a

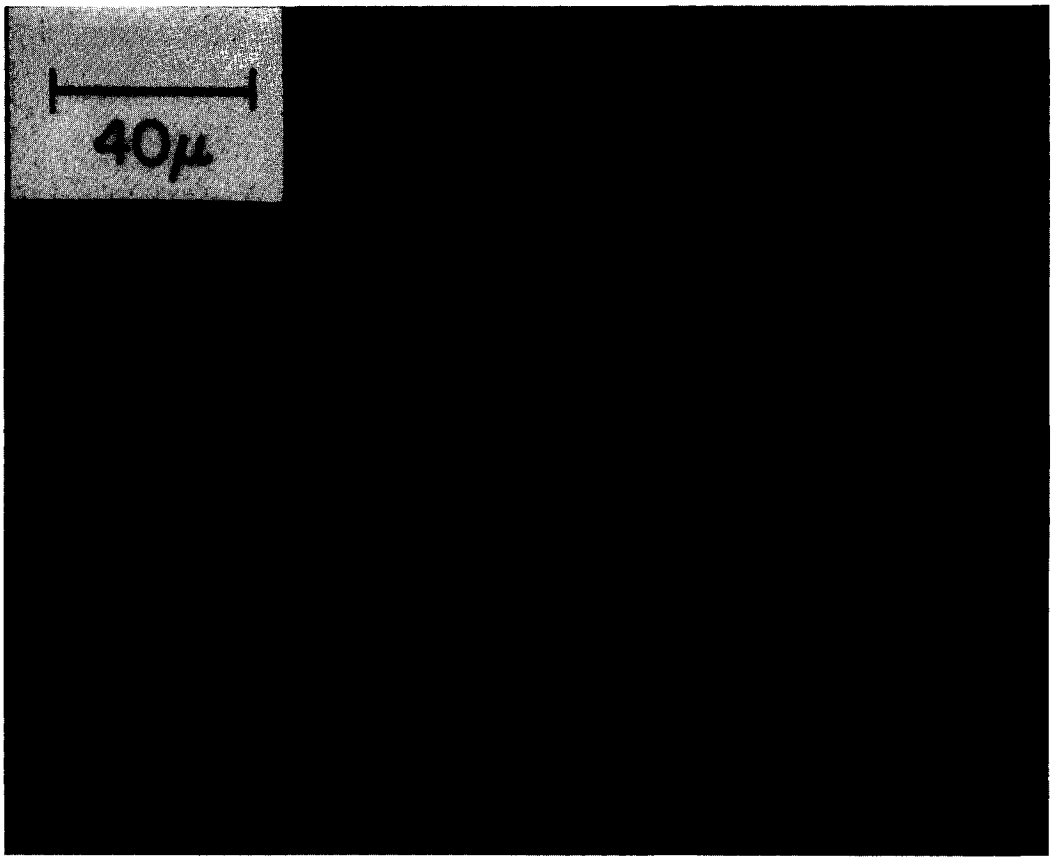


FIG. 7. Low-magnification SAM pictures of the catalyst at the end of the experiment in Fig. 2.

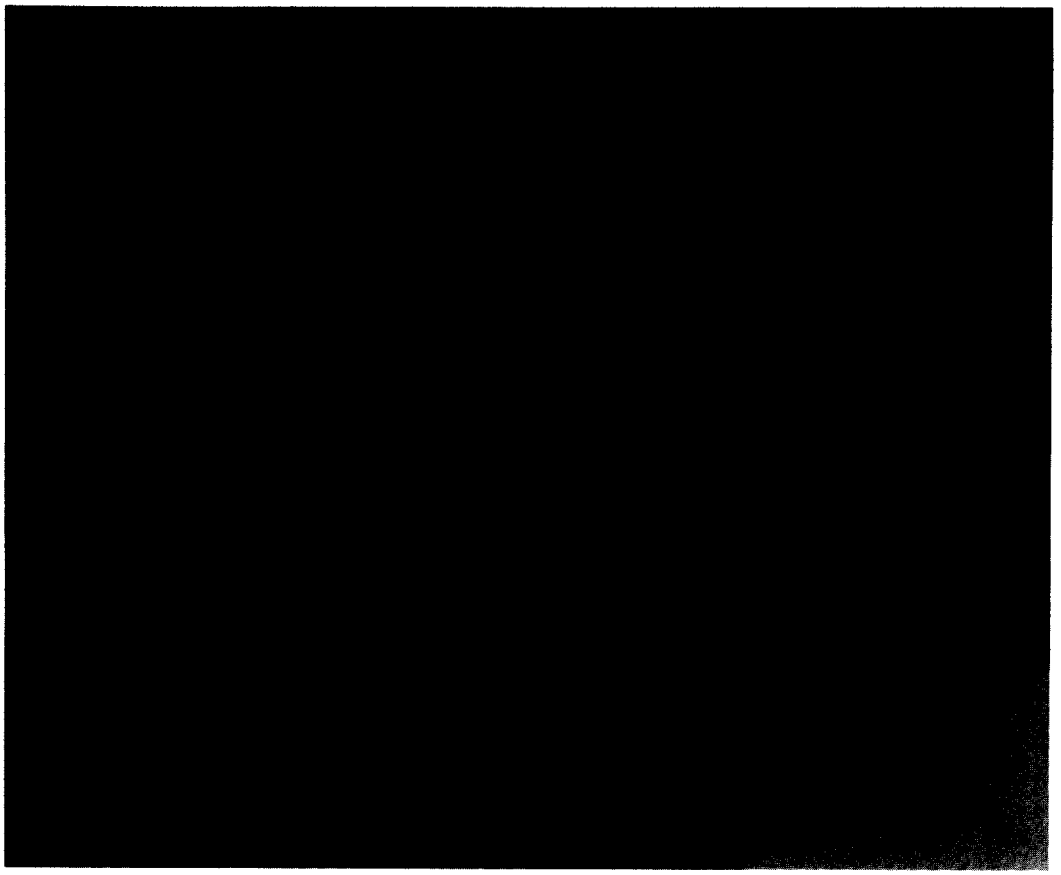

FIG. 8. High-magnification SAM pictures of the catalyst in Fig. 7.

30% variation in oxygen/nickel ratio from catalyst to catalyst, with the catalysts of type II averaging a somewhat higher oxygen content. Not shown are oxygen and carbon maps, which indicated that the oxygen and carbon concentrations are essentially constant over the surface.

Low-magnification pictures of the catalyst whose behavior was shown in Figs. 3 through 6 are given in Figs. 11 through 14. After the simple periodic oscillations in Fig. 3, the surface exhibited mountains and ridges with an average width of about 8 $\mu$m with some relatively flat areas as shown in Fig. 11. After the chaotic behavior shown in Fig. 4, the surface still had some large ridges as before, but the previous flat areas were covered by small pits and spots as shown in Fig. 12. The very large amplitude oscillations in Fig. 5 occurred when the surface had smaller mountains, and some very tiny cracks as shown in Fig. 13. Just after the catalyst went to the high-temperature state, the surface was much smoother than originally, with few large mountains as shown in Fig. 14.

Higher-magnification pictures of the oscillating catalysts were very similar to those in Fig. 8. There were small peaks and valleys with a size on the order of 300 Å. The density of peaks and valleys was the same, within experimental error, as those in the figure. We searched for a submicron difference that could account for the difference in activity between the catalysts with micron size profusions, and those without protrusions, but none was found.

The Auger analysis of the oscillating cat-

alysts was also very similar to those seen for nonoscillating catalysts. An unsputtered sample showed large oxygen and nickel peaks, a much smaller carbon peak, and some trace impurities. The ratio of oxygen and nickel peaks was within the variation seen for catalysts prepared by Procedure I and II. Sputtering at the same conditions as before, again removed the impurities and some of the oxygen. In one case, sputtering appeared to increase the carbon content, but this occurred on a day when the Auger system was dirty and depositing carbon.

## DISCUSSION

The data in the last section illustrate the large effect that the pretreatment and aging of the catalyst has on the presence and form of the thermal oscillations during hydrogen oxidation on a nickel foil. No sustained oscillations were observed when the catalysts were highly polished, while the catalysts that were loaded without pretreatment exhibited self-sustained oscillations under the same conditions. Kurtanjek *et al.* (*8, 9*) annealed their samples in hydrogen and did not observe sustained oscillations at the oxygen concentration used in this study, while Schmitz *et al.* (*6, 7*) heated their samples with a butane torch and found oscillations. In most cases, Schmitz *et al.* observed oscillations in which the catalyst spent most of its time at a high temperature, but every so often the temperature dropped rapidly, and then rose back to the high temperature again. Here oscillations were seen in which the catalyst spent most of its time at a low temperature, but every so often the

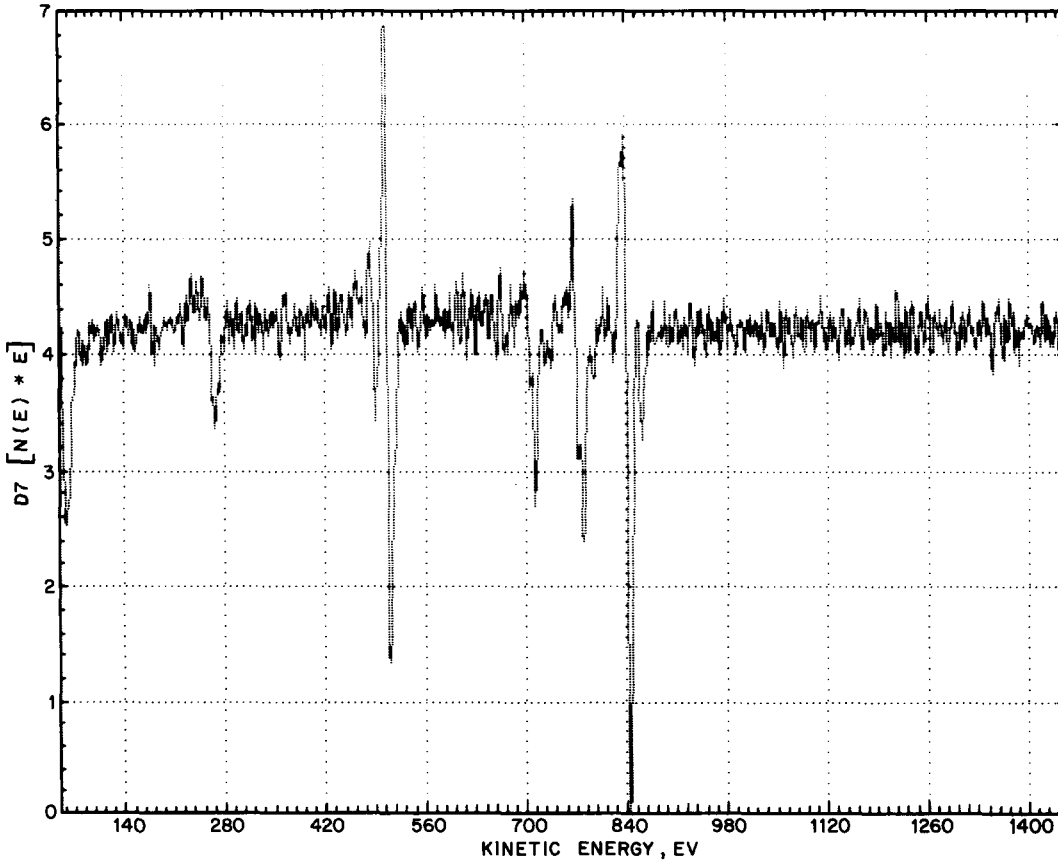


FIG. 9. Differentiated Auger spectrum of the catalyst in Fig. 7.

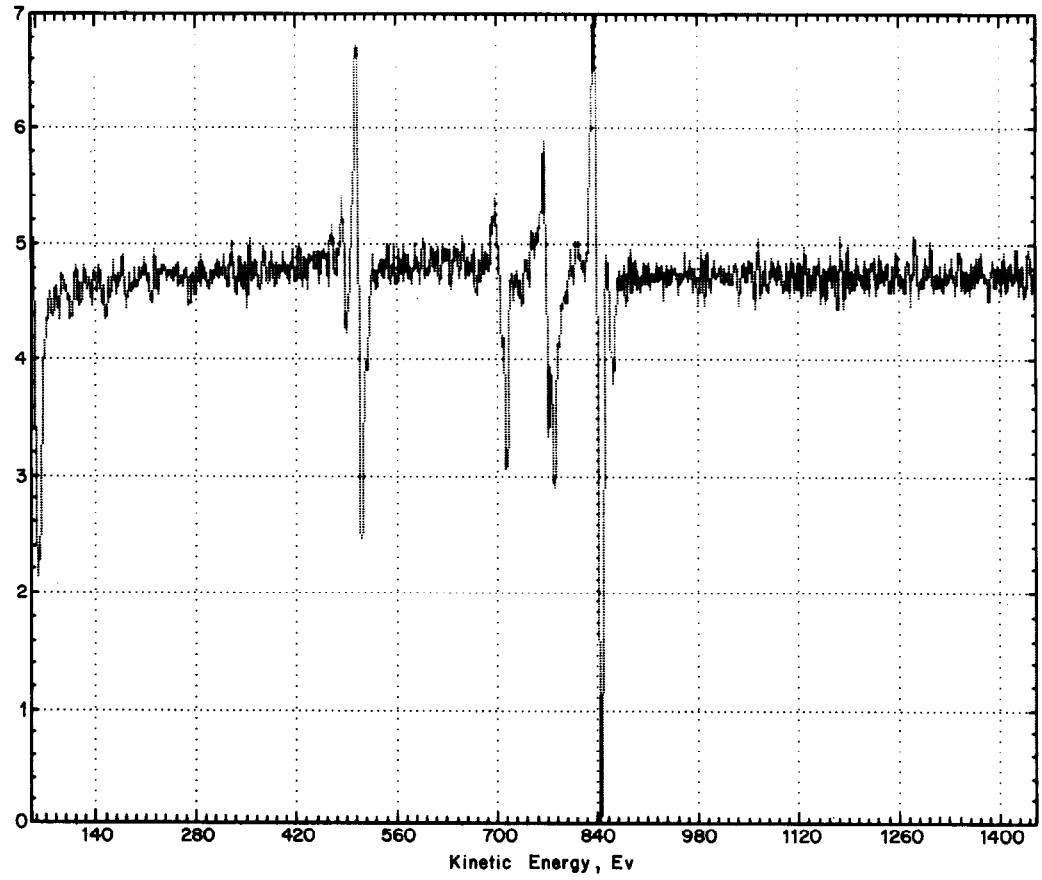


FIG. 10. Differentiated Auger spectrum of the catalyst in Fig. 8 after being sputtered by 3.5 mins at 5 "NA."

catalyst temperature rose rapidly, and then quickly dropped. Of course, the pretreatment procedure used by Schmitz *et al.* was much different from the one used here. From the data it is clear that the pretreatment of the catalyst can have a major effect on the presence and form of the oscillations.

The data in the last section indicate that the pretreatment procedure used here (i.e., polishing) had a large effect on the morphology of the surfaces of the catalysts, but little effect on the surface composition. The Auger spectra taken in this study indicated that the surfaces of all of the catalysts were covered by a thick layer of nickel and oxygen. The proportion of these two components varied only slightly from catalyst to catalyst, and while there were some impurities whose concentration varied by a larger amount, there did not appear to be a correlation between the presence of any of the impurities or the surface oxygen concentration and the observation of self-sustained oscillations.

However, a comparison between Figs. 7 and 11 shows that there is a significant difference between the surface morphology of the catalysts that catalyze the oscillations and those that do not. One can observe that at the magnification used to take these pictures, the catalyst in Fig. 7 which is one that did not catalyze oscillations looks flat, while the catalyst in Fig. 11, which is one that did catalyze oscillations looks very rough. The other low-resolution photo-

graphs, Figs. 12–14, show that as the oscillations get more complicated, the surfaces get progressively rougher, while the surfaces appear to get smoother as the oscillations dampen away. High-resolution pictures show that the differences between the various samples are large-scale differences; all of the samples look similar on a scale of tenths to hundredths of microns. This is not surprising since the only difference between the various samples is the degree of polishing, which was done with 1-$\mu$m diamond paste.

There is evidence in Figs. 9 and 10 that there is oxygen dissolved in these samples. The oxygen peak in Fig. 9 is quite large. Figure 10 shows that it persists even after sputtering for 3.5 min at 4 "NA." By comparison the Auger spectrum of a sample which had been cleaned in vacuum and then left out in the room for over a month showed an oxygen peak that was a third as large as the one in Fig. 9. Thirty seconds of sputtering at 0.5 "NA" decreased the peak by roughly a factor of ten. Quinn and Roberts (*17*) report that oxygen will form a suboxide on nickel at room temperature with an equivalent coverage of two monolayers. We observe much more oxide in the samples used in this study than was observed in the room temperature sample which suggests oxygen dissolution, and/or oxide formation.

Prior work also shows evidence for dissolution of oxygen. Many years ago Larson and Smith (*18*) studied the oxidation of hy-

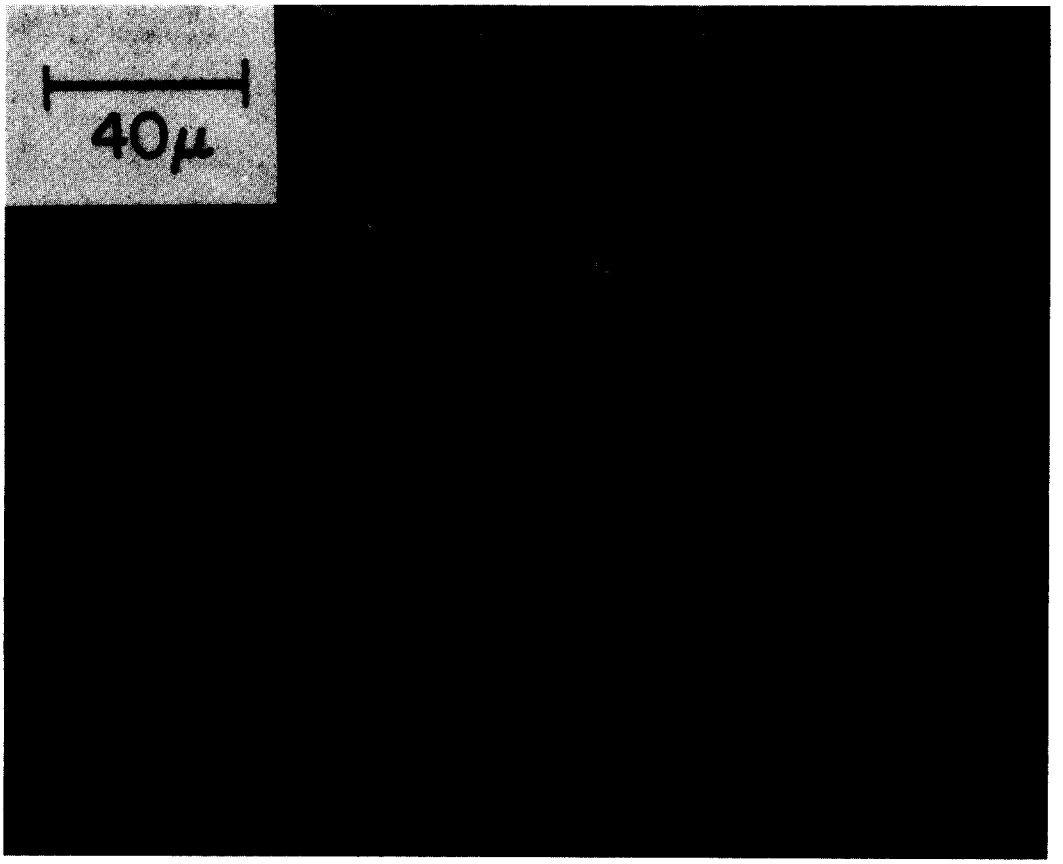


FIG. 11. SAM picture of the catalyst at the end of the experiment in Fig. 3.

FIG. 12. SAM picture of the catalyst at the end of the experiment in Fig. 4.

drogen on a nickel catalyst. They found that the oxidation reaction persists long after the oxygen is turned off. Clearly dissolution of oxygen is occurring. Kurtanjek *et al.* (*8, 9*) measured the work functions of their surfaces during hydrogen oxidation. They observe an unusual hysteresis effect where the contact potential of the surface is higher when the oxygen concentration is decreasing rather than increasing. Again dissolution is suggested.

Taken all together these results imply that the oscillations seen here are caused by a physical rather than a chemical mechanism. There was not any significant difference observed between the composition of those samples that catalyze the oscillatory states and those that do not, and while there were some large-scale differences in the morphology of the various catalysts, no small-scale, i.e., submicron, differences were observed; at the maximum resolution of our microprobe the density of all of the submicron features on the surface of the catalyst are all approximately the same. There remains a small possibility that some feature, too small to resolve, is formed and destroyed at the same time the protrusions are formed and destroyed, and this feature changes the chemistry. However, barring this unlikely possibility, we would conclude that the oscillations seen here are caused by a physical rather than a chemical mechanism.

One physical model that can be used to explain a major portion of the data is the

fuzzy wire model of Jensen and Ray (*14*). Jensen and Ray considered the effect of surface protrusions on oscillating reactions. They noted that if the diffusional resistances are large, then there could be a significant difference between the temperature and fuel concentration on the protrusions and that on the rest of the wire. This gives at least four dynamic variables (at least two temperatures and two concentrations), which are coupled through an Arrhenius rate law. Several previous investigators have shown that such a system of differential equations can lead to oscillations for some values of the parameters. If we plug in parameters characteristic of our system, then one finds, from Fig. 9 in Jensen and Ray (*14*) that oscillations are expected. We have done numerical simulations to confirm this.

In order to use Jensen and Ray's model one has to know something about the protrusions. If, for example, all of the protrusions are about the same size and shape, then it is reasonable to assume that the temperature and fuel concentration on all of the protrusions is about the same (the temperature spikes should synchronize the oscillations on the various parts of the catalyst). This reduces the problem to four dynamic variables; Jensen and Ray show that regular oscillations could occur in such a system. Alternately if there were many different sizes and shapes of protrusions, then one would have to include the individual temperatures and concentrations in the

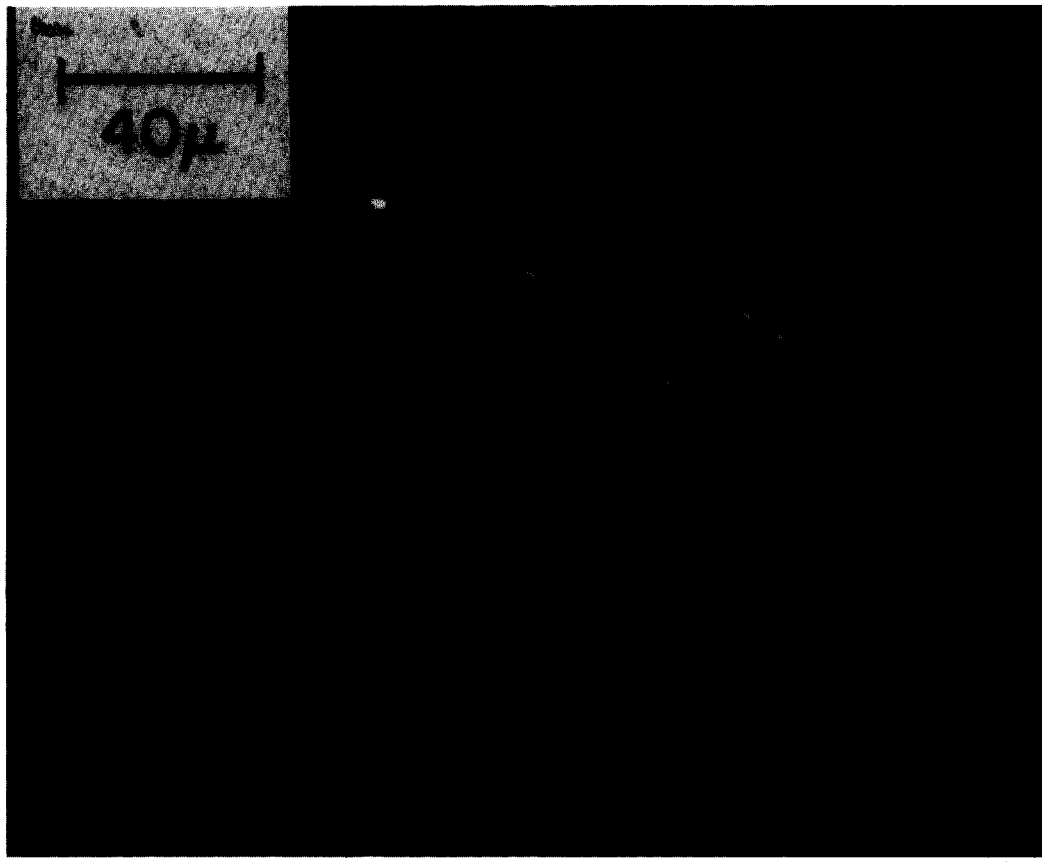


FIG. 13. SAM picture of the catalyst at the end of the experiment in Fig. 5.

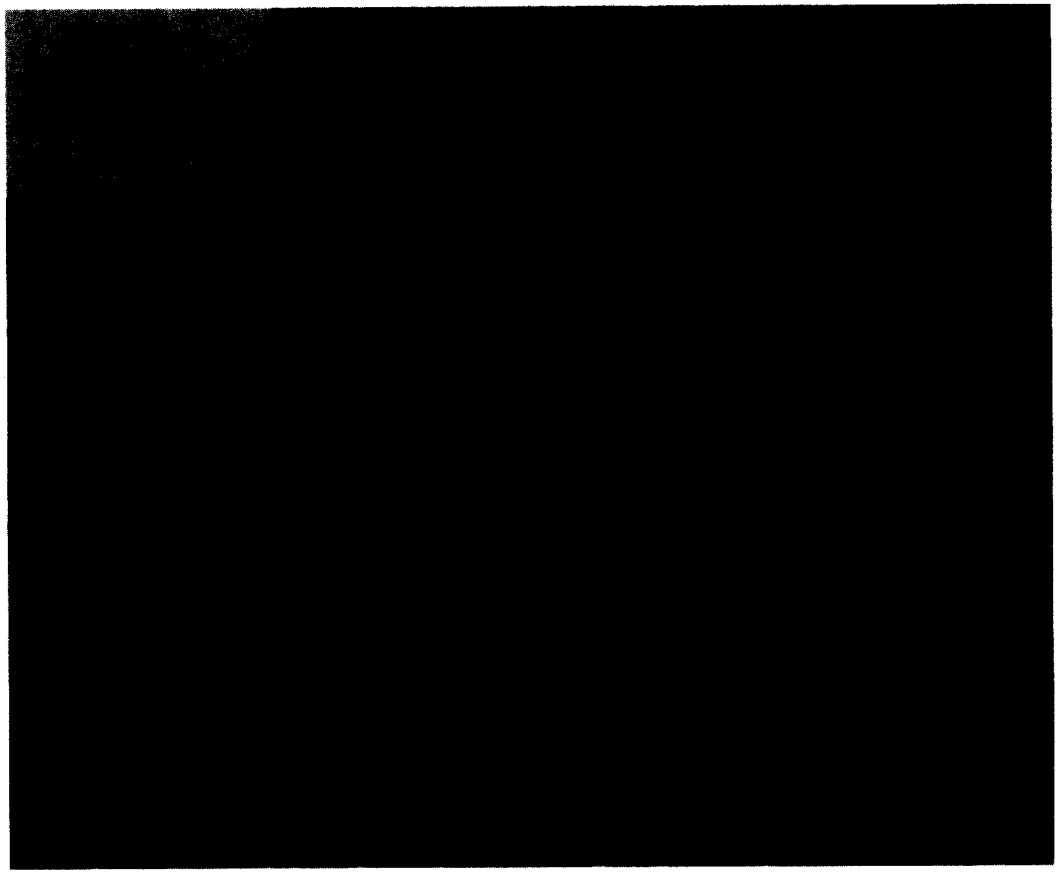

FIG. 14. SAM picture of the catalyst at the end of the experiment in Fig. 6.

calculation. Jensen and Ray predict chaotic oscillations under these circumstances.

Generally the predictions in the last paragraph agree with our observations for most of the runs done on the catalysts prepared by Procedure III. The protrusions in Fig. 12 all seem to have similar sizes and shapes and as predicted, regular oscillations were seen. The protrusions in Fig. 13 have many different sizes and shapes, and as predicted the oscillations were chaotic.

## CONCLUSIONS

We have observed a multiplicity of states during hydrogen oxidation on a nickel foil. A stable high-temperature state, simple harmonic oscillations, and chaotic oscillations are all seen at the same reaction conditions. The high-temperature state is seen when the catalyst surface is flat on the scale of microns, while oscillations are seen when the surface is covered by protrusions of 5–20 $\mu$m. The oscillations are chaotic when the protrusions have a large variation in sizes and shapes. Interestingly, the protrusions sometimes grow and shrink spontaneously under the reaction conditions. These results can be interpreted in terms of the fuzzy wire model of Jensen and Ray (*14*).

## ACKNOWLEDGMENT

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