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Formation of "Metal Wool" Structures and Dynamics of Catalytic Etching of Platinum Surfaces during Ammonia Oxidation

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Reconstruction of a clean surface of a platinum catalyst and a platinum surface covered with gold during ammonia oxidation was studied by SEM observations. It was found that the process of catalytic etching had two sequential stages in which different crystal structures with different rates of growth formed on the surface. The first stage was the formation of parallel facets, and the second stage was the formation of individual microcrystals with perfect crystal faces. It was also found that the second stage had a threshold character, beginning after some delay from the start of the reaction. A structure resembling metal wool and consisting of interlaced platinum filaments was found to form on the surface of gold-covered platinum catalysts. Characteristic features of this structure's development are reported. The growth of filaments is attributed to the vapor–liquid–solid mechanism of whisker growth. On the basis of the observed platinum whisker formation and behavior during ammonia oxidation, a mechanism of catalyst surface reconstruction that explains observed characteristic features of the process of catalytic etching is proposed.

INTRODUCTION

The phenomenon of rapid etching of the surface of platinum catalysts, and great platinum loss caused by it, in catalytic oxidation reactions has been well known since the beginning of intensive industrial application of these types of reactions. Despite the long history of the problem (1–3), however, there is not yet a common theory of the mechanism of this process. Thus, Flytzani-Stephanopoulos and Schmidt (3–6) attributed the process to gas diffusion of the fluent oxide PtO_2, which forms in the reaction. The rate and equilibrium of this process are considered in Ref. (6). Phillips and co-workers (7, 8) assumed that catalytic etching occurs due to the action of homogeneously formed HO_2 radical on the platinum surface and that clusters of metallic platinum form homogeneously in the boundary layer over the surface and then fall onto the surface, forming a polycrystalline structure on it.

To explain the extremely high rate of surface reconstruction, Barelko, Volodin, Khalzov and co-workers (9–13) used the hypothesis of a nonequilibrium process of catalyst surface activation, as developed in Refs. (14–18). The hypothesis is based on the suggestion of heat activation of the catalyst surface by the reaction occurring on it, i.e., that some of the energy released by chemical coupling does not dissipate into equilibrium heat of the lattice, but creates new active centers on the surface. The role of these active centers is attributed to "adatoms," that is, atoms of platinum which have lost their places in the lattice and have only a weak bond with the surface. Thus, a two-dimensional quasi-gas of adatoms is formed due to the reaction. Such an excited state of the surface provides an increase in the rates both of surface diffusion and of platinum sublimation (by tearing adatoms off the surface) and in this way leads to rapid surface reconstruction.

Another interesting result concerning platinum transport and recondensation properties was reported by Genkin *et al.* (19), who observed growth of platinum whiskers on a cold platinum surface in the vicinity of platinum participating in ammonia oxidation.

In this work catalytic etching was studied by direct SEM observations of local changes on the platinum surface and of species origination and growth during ammonia oxidation. The work consists of two sequential parts. In the first part, reconstruction of the clean surface of pure platinum wire was studied to characterize the process and to determine its peculiar features. The second part was aimed at a more detailed study of the phenomenon of platinum vapor recrystallization on the catalytic surface. To stimulate this process we created artificial passive zones on the platinum surface by depositing gold on it. We expected that, by analogy with (19), these passive zones would act as centers of rapid platinum condensation from the vapor phase and we expected to observe growth of whiskers on them.

EXPERIMENTAL

In the present work, the ammonia oxidation reaction on platinum wire under atmospheric pressure was used

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to study catalytic etching. The ammonia concentration could be varied over a wide range. The gas flow velocity in all experiments was 10 cm/s through a 3-cm^2 reactor cross section and the wire was situated in the reactor perpendicular to the flow. Control of the electric heat supply to the wire, as well as measurement of its temperature and reaction heat, was provided by means of an electrothermographic method (20).

Etching was studied by observation of the surface of the platinum wire during reaction. The installation was the same as described in Refs. (9, 20), but the reaction chamber was modified to allow microscopic observations. A platinum wire length of 3 cm and diameter 100 μm was fixed in a rigid frame. This frame could be placed into the reactor and into the holder of the electron microscope without changing the position of the wire. This allowed the interruption of the reaction at any moment to investigate the surface at any chosen point, after which the wire could be returned to the chamber and the reaction resumed. This cycle could be repeated many times. In this way we obtained a series of micrographs showing the process of catalytic etching at given points on the surface. A Tesla BS-340 scanning electron microscope was used for surface observations.

In the first part of the work, etching of a clean pure platinum surface was studied under 8 and 15% ammonia in pure oxygen. The wire temperature was maintained at 1000–1100°C in all experiments (temperature variations occur because of small oscillations in the ammonia concentration). For 15% ammonia, this wire temperature was due entirely to reaction heat release, while for 8% ammonia additional heating by electric current was provided. Time intervals between observations were chosen, depending on the rate of change of the surface structure, as 30 min for 8% ammonia and 15 min for 15% ammonia.

Measuring the sizes of individual crystal images on the sequential microphotographs allowed us to estimate changes in the particular crystal volume with time and thus to obtain quantitative estimates of the catalytic etching process rate.

In the second part of the work, the experimental procedure was almost the same, except that a platinum surface covered with gold was investigated. All experiments in this part were made under 15% ammonia in oxygen with 30-min intervals between microscopic observations.

As a method of platinum wire passivation, we deposited gold on a region of approximately 1 mm in length in the center of the wire. For this purpose, a drop of gold hydrochloride acid was placed in the middle of the wire, and then, during resistive DC heating under pure oxygen for 30 min, it decomposed, forming gold islands on the platinum surface.

When a sample with a gold-covered region in the middle was placed into the reactor and the reaction was ignited on it, a visible temperature gradient developed along the wire. While the temperature of the clean surface was approximately 1000–1100°C, which is normal for reaction at this concentration without electric heating, the temperature of the covered zone was less than 800°C, and this zone was seen as a dark spot in the middle of the bright wire.

Depending on the amount of gold deposited on the surface of the platinum wire, further behavior of the dark spot varied. When a large amount of gold was deposited on the surface, the spot remained stable during reaction. When, however, only a small amount of gold was deposited, a dark spot was seen in the zone with deposited gold immediately after the reaction was ignited, as in the previous case. During further processing, however, its temperature increased gradually so that after approximately 1.5 h the whole wire had a uniform temperature near 1100°C. We assume that this increase in temperature was caused by disappearance of gold from the surface and gradual incorporation of this zone into the reaction.

RESULTS

1. Dynamics of Catalytic Etching of a Clean Platinum Surface

Figures 1 and 2 are micrographs that illustrate the process of catalytic etching of platinum wire during ammonia oxidation in pure oxygen.[1] The concentration of ammonia in this experiment was 8% and intervals between microscopic observations in this series were 30 min.

Changes in the surface were observed from the very beginning of the process (Fig. 1a). Initially the reaction acted at intergrain boundaries of the original crystal structure of the platinum wire, making the individual crystal grains which were 10–20 μm in size, visible on the previously homogeneous surface of the wire. This phenomenon can be explained using the described hypothesis of nonequilibrium surface activation: boundaries are crystal defects where lattice regularity is strongly disturbed, and so catalytic activity and the rate of platinum sublimation here are much higher than those on surfaces with a regular lattice.

After half an hour of reaction, the grain surfaces are no longer smooth, but are covered with a new type of crystal structure (Fig. 1b). These are rows of "parallel facets," which grow in length and height during the reaction (Figs. 1c, 1d, 1e, 1f). From the series of photos in Fig. 1, one can see that the orientation and the growth

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[1] Small shifts in the wire position occurred from one photograph to another, so one should choose characteristic details on the surface to identify features of relief and to observe their evolution.

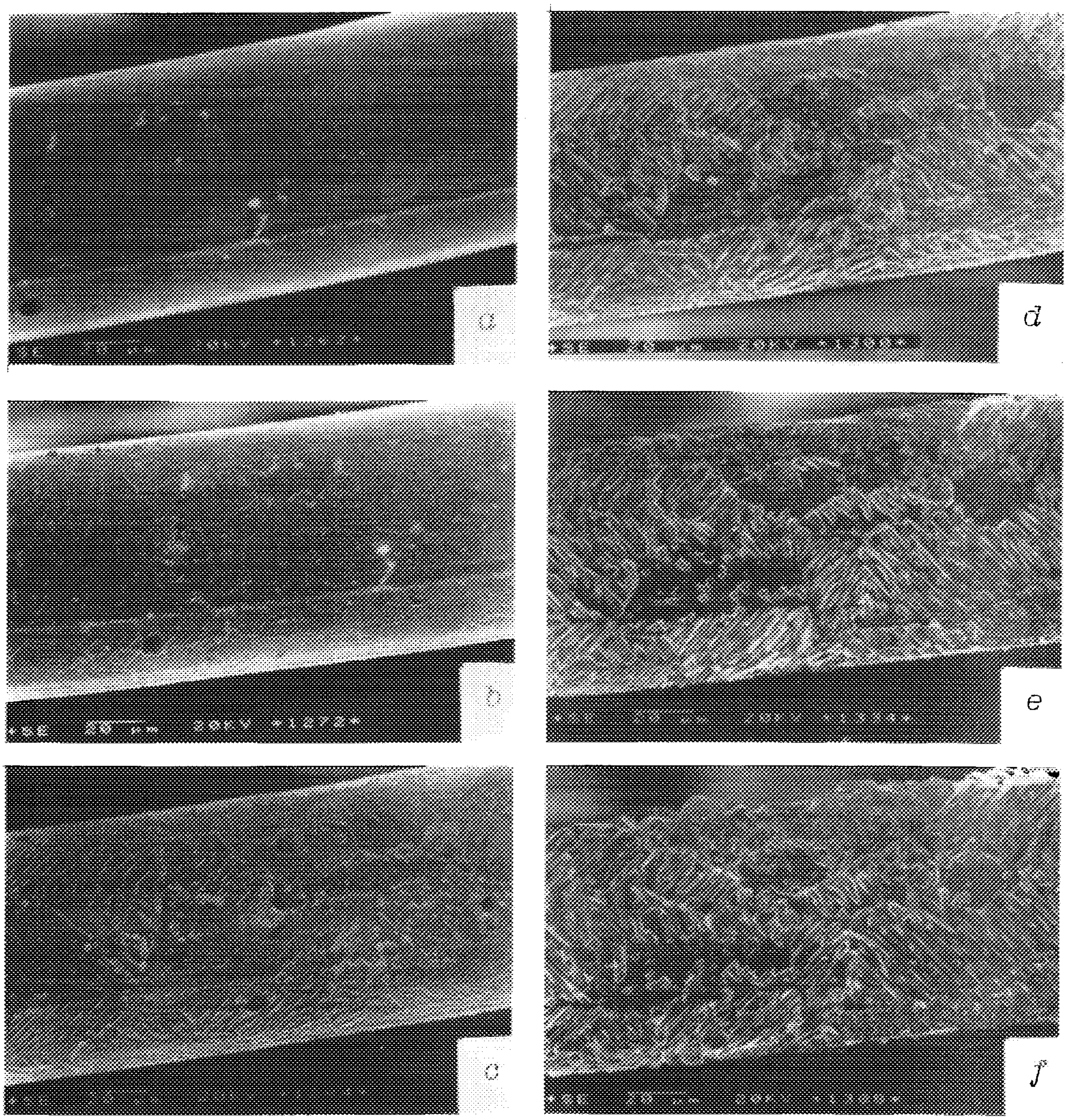

FIG. 1. Catalytic etching of Pt surface in ammonia oxidation reaction (stage of parallel facet formation). 8% ammonia in pure oxygen. (a) 2 min from the beginning of the reaction, (b) 30 min, (c) 120 min, (d) 240 min, (e) 480 min, and (f) 840 min.

rate of parallel facets are different for surfaces of different grains. Probably these parameters depend on the initial orientation (crystallographic index) of the surfaces ofeach individual grain (this question was discussed in detail in Ref. (5)). Furthermore, one can see that the surfaces of some grains remain smooth at all times during the reaction and that parallel facet structures do not form on them. Apparently the surfaces of these grains have the most stable original orientation, and hence minimum catalytic activity.

In Fig. 2, formation of another type of crystal structure, which begins to grow on the surface over the parallel facets after approximately 8 h of reaction, is shown. It consists of individual, randomly situated microcrystals of platinum with well-formed crystal faces, which retain their initial orientation during the entire time of crystal

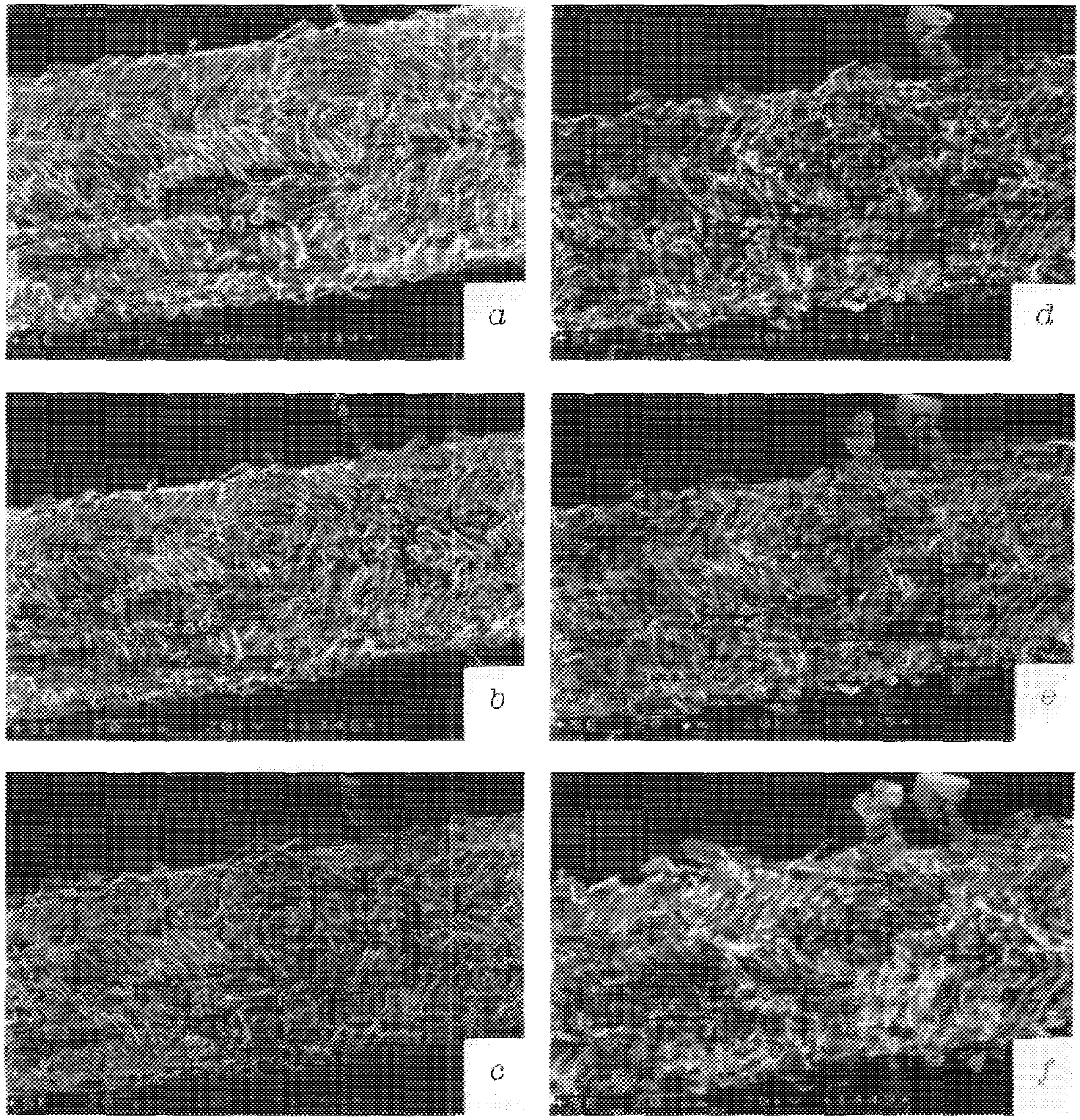

FIG. 2. Catalytic etching of Pt surface in ammonia oxidation reaction (stage of bulk microcrystal formation). 8% ammonia in pure oxygen. (a) 540 min, (b) 570 min, (c) 690 min, (d) 960 min, (e) 990 min, and (f) 1170 min.

growth. In contrast to the parallel facets which lie on the surface, these new crystals for the most part extend into the surrounding volume. To emphasize this difference we will refer to these structures as "bulk crystals." It was found that the process of bulk crystal nucleation has a threshold character; i.e., long and thin crystals spontaneously and rapidly appear on the surface after some delay from the beginning of the process. During further reaction, rather slow growth of these germs occurs (with retention of initial facets). Thus, after 9.5 h of reaction (Fig. 2b) a microcrystal of approximately 30 μm in length appeared, whereas no sign of it had been seen earlier (Fig. 2a).[2] After 16.5 h of reaction (Fig. 2e), another crystal which had not existed 30 min before (Fig. 2d) appeared near the first crystal. Figure 2f presents the picture after 19.5 h of

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[2] Due to the appearance of the crystal, we had to decrease the magnification in Figs. 2b–2f.

reaction. The surface of the platinum wire now resembles one of gauze from a real industrial ammonia oxidation reactor, so we can conclude that real processes in catalytic reactors develop in the same way as those observed here.

Dependence of parallel facets and bulk microcrystal volumes on reaction time obtained by estimation of individual crystal sizes in the series of micrographs in Figs. 1 and 2 is shown in Fig. 3. Velocities of growth of structure volumes were obtained from the plot. For the parallel facet structures, this velocity is 60 μm^3/h, and for bulk microcrystals it is 300 μm^3/h.

However, estimation of the velocity of volume growth for bulk microcrystals at the moment of their origination (assuming that crystals in Figs. 2b and 2e were formed in 30 min, while this process could be faster) gives values of 1050 and 1300 μm^3/h, respectively. Although rather rough estimates, these results confirm that the nucleation of bulk crystals occurs at a much higher rate than the following growth of this structure.

Figure 4 shows a series of photos obtained under an ammonia concentration of 15%. The time intervals between microscope observations were 15 min in this case.

From Fig. 4 it can be seen that the process of catalytic etching passes through the same stages as those in the previous case of 8% ammonia. First, parallel facet structures form on the surface of the previously smooth platinum wire, and then, after some delay, rapid formation of bulk microcrystals begins. There are, however, some differences as well. The process is now significantly faster. The rate of parallel facet growth is 3–4 times higher and the time delay before the beginning of bulk crystal formation is approximately 2 h instead of 8 h for 8% ammonia. Also, not only the rate and delay of formation for bulk crystals are changed, but their shape differs as well. In general, large (30–50 μm) polycrystals form at 8% ammonia (Figs. 2d, 2e), but in 15% ammonia only small (up to 10 μm) microcrystals (their shape and perfect facets suggest that they are generally monocrystals) appear on the surfaces. Furthermore, the "leg" connecting a crystal with the surface becomes very thin, often less than 1 μm (a typical example is shown in Fig. 4f). This results in very rapid disappearance of these crystals due to mechanical failure. It was, therefore, possible to see them in only 4–5 observations after formation.

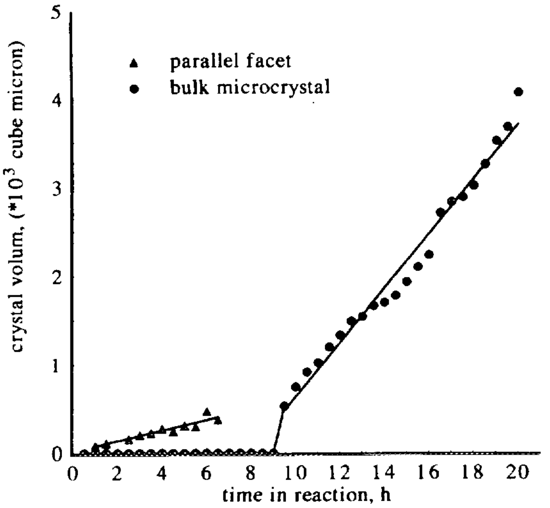

FIG. 3. Dependence of crystal structure volume on reaction time. 8% ammonia in pure oxygen.

II. Formation and Properties of "Platinum Wool" on the Platinum Surface Covered with Gold

The process of crystal growth occurring in a zone covered with gold is shown in Fig. 5. As expected, platinum crystallizes on the gold-covered surface in the form of whiskers. In contrast to the results in previous work (19), where only individual, accidental whiskers were found on the surface, now we observe a whole structure which looks like dense wool surrounding the wire. We will refer to this structure as metal or platinum wool. Figure 5f shows this structure at higher magnification. One can see that it consists of interlaced individual filaments with lengths up to 20 μm and diameters less than 100–300 nm.

An X-ray microprobe analysis of the platinum wool was made. The primary electron beam did not strike the surface of the wire, but passed tangentially through the metal wool structure. The obtained X-ray spectrum represents an averaged composition of the filaments and is not affected by platinum and gold from the surface of the wire. Analysis at 10 different points showed that the structure consisted of both platinum and gold, which varied in content from 2 to 15%.

Results of the X-ray analysis indicate that not only the temperature difference but also the presence of a third phase (gold in our experiment) is important for metal wool structure formation. This is also supported by observations presented in Fig. 6, which shows the growth of an individual "bush" distinct from the main platinum wool on a separate gold island. As the distance between the island and the main passive spot is only ~70 μm, the temperature difference between them should be very small; despite this, however, formation of the metal wool structure occurs only on the gold island, while the platinum surface around it remains clean throughout the process. One can see the same results in Fig. 6e. Bushes of metal wool have grown on two gold islands situated 50 μm from one another, and at the same time, the platinum surface between them remains clean throughout the process.

The platinum wool formations shown in Figs. 5 and 6 were obtained when a large amount of gold was deposited. In this case, the structure remains unchanged during the

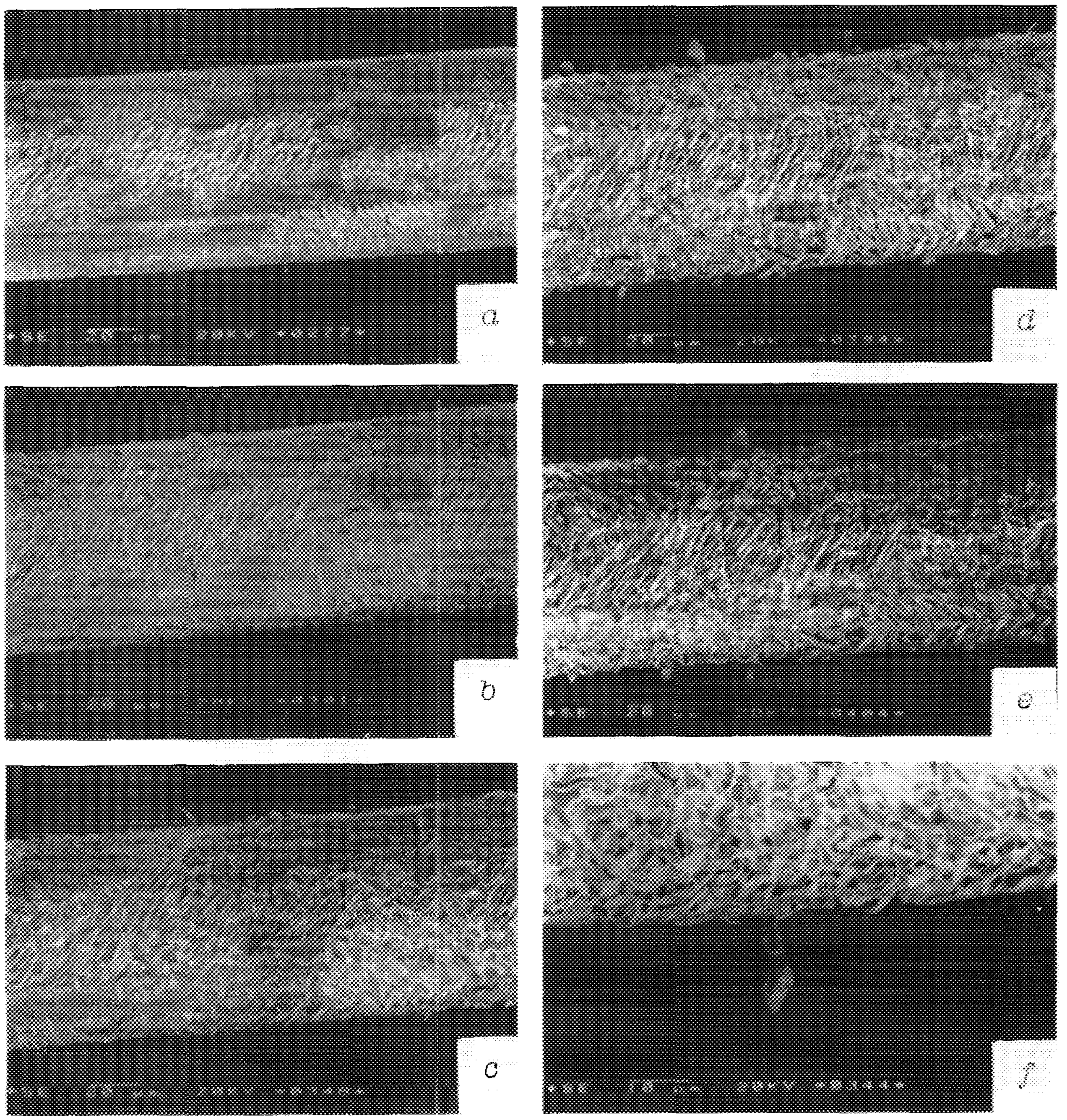

FIG. 4. Catalytic etching of Pt surface in ammonia oxidation reaction. 15% ammonia in pure oxygen. (a) 60 min, (b) 150 min, (c) 180 min, (d) 255 min, (e) 270 min, and (f) 165 min.

entire further observation period. In the case where only a small amount of gold was deposited, different behavior was found. As was mentioned, in this case the temperature of the spot is not constant but increases gradually and reaches that of the clean platinum surface in approximately an hour and a half. This leads to the following changes in metal wool formation (Fig. 7). After the first 30 min of reaction, when the temperature of the spot is rather low, the beginnings of a platinum wool structure, similar to that observed in the previous experiment (Figs. 5 and 6), were found (Figs. 7a, 7b). However, as the temperature of the spot increased, the development of these structures differed significantly from that in the previous case. In contrast to the process in Fig. 5, where individual regions of platinum wool grew in size and formed a "fur coat" around the spot, now the initial zones

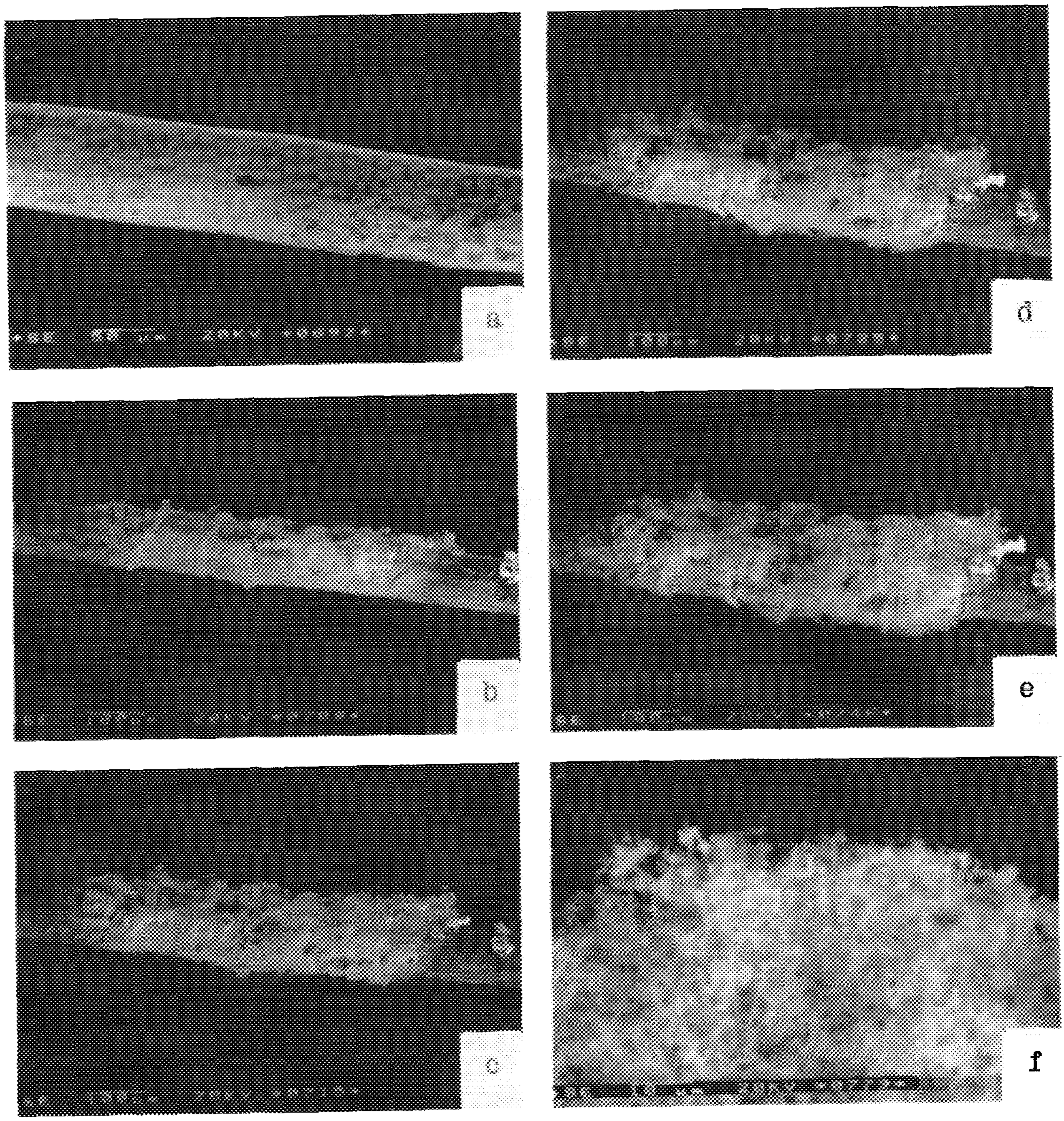

FIG. 5. Formation during ammonia oxidation of platinum wool on the surface of a platinum catalyst wire passivated by deposition of gold. Gas mixture—15% NH_3 in pure oxygen. (a) Left end of gold-covered spot before beginning of reaction; view of the entire spot after reaction times of (b) 1 h, (c) 1.5 h, (d) 2 h, (e) 2.5 h, and (f) central region of platinum wool at higher magnification after 2.5 h.

did not increase, but the whiskers of which they consisted became thicker (Figs. 7c, 7d). Finally, as the temperature of the spot reached the temperature of the whole wire, they degenerated into common bulk polycrystal structures (Figs. 7e, 7f) like those observed in the first part of the work during ammonia oxidation on clean platinum wire.

DISCUSSION

The form and dynamics of formation of crystal structures observed in the experiment (especially of bulk microcrystals which form at high ammonia concentrations; see Fig. 2f, for example) suggest that the mechanism of platinum transition in the process of catalytic etching is

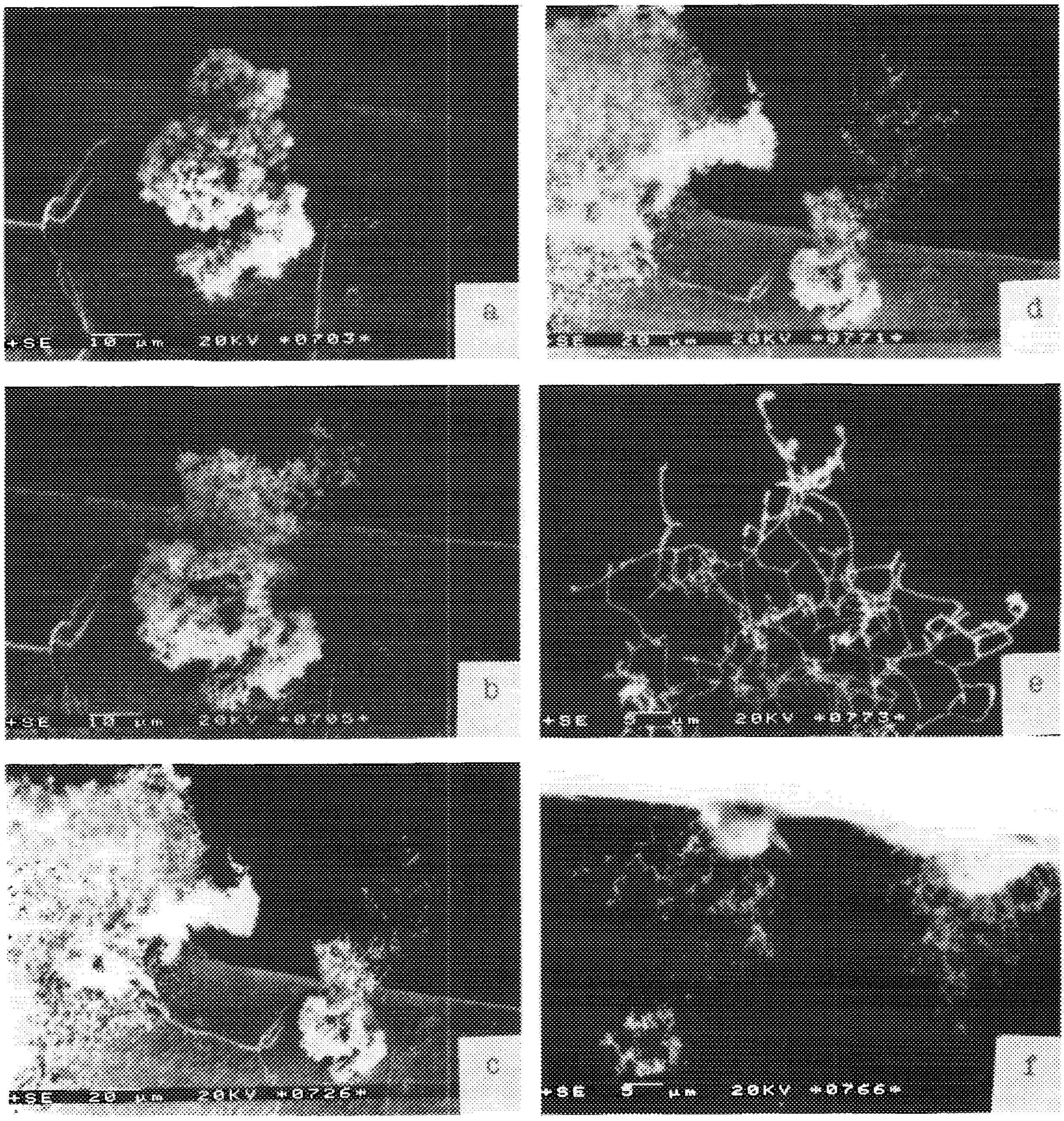

FIG. 6. Growth of individual "bushes" of platinum wool on separate gold islands. (a) Individual island to the right of the main spot at beginning of wool structure formation, 0.5 h in reaction; the same place after (b) 1 h, (c) 2 h, (d) 2.5 h, (e) fragment of (d), and (f) "bushes" on two separate islands to the left of the main spot, 2.5 h in reaction.

gas diffusion of platinum in the boundary layer over the surface.

Mechanisms which can cause sublimation of platinum, and hence make possible its rapid transition through the gas phase, were described above. Observations made in this work do not allow us to deduce the particular mechanism, but some arguments can be made here. In Refs. (9, 11) it was shown that as the rate of catalytic etching during ammonia oxidation is much higher than that in pure oxygen at the same surface temperature, it can hardly be the result of a thermodynamic equilibrium process of platinum oxidation such as was considered in Ref. (6). Also, the assumption of PtO_2 formation cannot explain the occurrence of catalytic etching in reactions which take place in the absence of oxygen (for example, radical recombination on metal surfaces or catalytic decomposi-

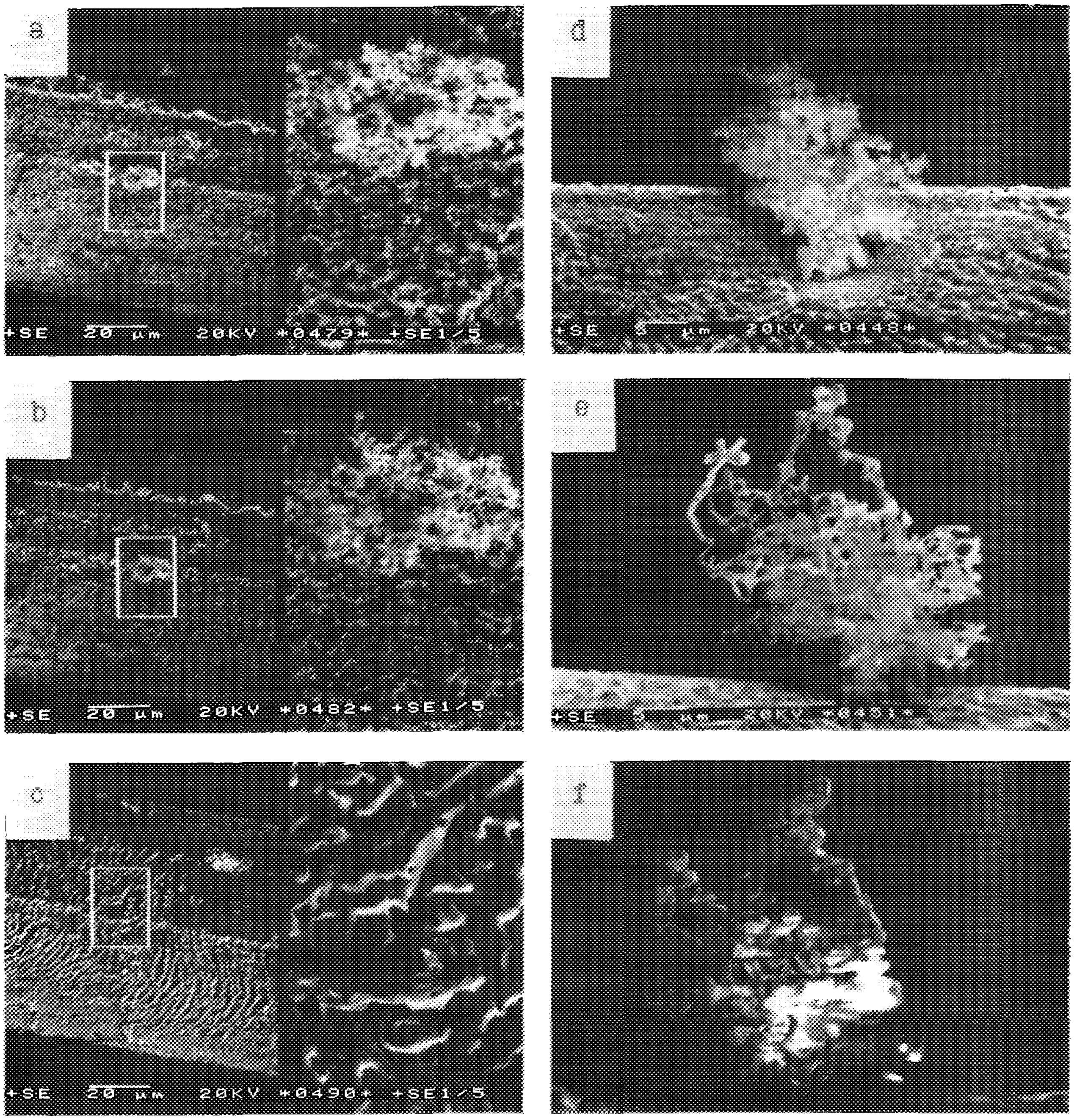

FIG. 7. Degeneration of platinum wool. Two different spots after reaction times of (a) and (d) 0.5 h in reaction, (b) and (e) 1 h, (c) and (f) 1.5 h.

tion of ammonia on platinum). On the contrary, the high rate of crystal growth suggests that an above-equilibrium concentration of platinum exists in the boundary layer, which causes a fast process of platinum condensation back on the surface. We suggest, therefore, that heterogeneous reaction causes rapid sublimation of platinum from the surface and its high concentration in the gas phase, over equilibrium for a particular surface temperature, and that recrystallization of this platinum back onto the surface is the reason for the observed morphology changes.

The suggested mechanism of catalytic etching makes it possible to explain the difference between rates of parallel facet and bulk microcrystal growth (60 and 300 μm^3/h, respectively). From the above description, we see that because structures of the second type are more perfect crystals, i.e., their faces have minimum surface energy and activity, the rate of platinum condensation on their surfaces will therefore be higher than that for surfaces of parallel facets. Also, bulk crystals in general are oriented perpendicular to the wire and have only a small bonding surface to it, and so their temperature should be less than that of parallel facets, which lie on the surface. This also increases the rate of bulk crystal growth. (In Fig. 2 one can see that the fastest growth occurs on the regions of bulk crystals which are farthest from the surface, and hence have minimum temperature.)

The observed acceleration of catalytic etching with increasing ammonia concentration supports the conclusion of nonequilibrium platinum sublimation due to chemical reaction. In fact, with increased ammonia in the mixture, the oxygen concentration decreases, and thus, as the surface temperature remains the same, the rate of volatile oxide formation cannot increase. Therefore, the increase in catalytic etching rate can be explained only by an increase in platinum sublimation from the surface due to a higher reaction rate.

The study of the dynamics of reconstruction of a clean platinum surface in the first part of the work shows that the process of catalytic etching has two sequential stages in which different types of crystal structures form on the surface: parallel facets and bulk microcrystals. These structures not only have different shapes and rates of growth, but also have different characteristics of nucleation. Parallel facets begin to form from the very beginning of the reaction and gradually increase in size, starting from the smooth surface, which can be explained as due to recondensation of platinum with formation of planes with minimum free energy (Ref. (5)). On the contrary, bulk microcrystals start growing with some delay from the beginning of the reaction and at the very first moment appear as long, narrow, sufficiently large crystals. While the following growth of these structures can also be attributed to plane platinum recondensation from the gas phase onto crystal surfaces, this peculiar manner of nucleation forces us to look for some special mechanism to explain the described properties.

The observed phenomenon of platinum wool formation during ammonia oxidation on a platinum catalyst with deposited gold islands also strongly supports the hypothesis of platinum diffusion and recrystallization from the gas phase as a mechanism of catalytic etching. It hardly seems possible to imagine another transition mechanism which could lead to whisker formation. Deposition of particles of sufficient size cannot provide the observed features. At the same time, mechanisms of whisker crystallization from the gas phase are well known in crystallography. One of them is the so-called "vapor–liquid–solid" mechanism (21, 22), in which small drops of liquid (approximately 1 μm or less in size) are deposited on the crystal surface on which whisker growth is to be stimulated. Because of its less regular structure, molecules should be collected from the vapor much faster on the liquid than on the clean crystal surface around the drop. If saturated vapor is over the surface and the process of condensation takes place, then molecules captured by the liquid pass through the drop and are incorporated into the lattice of the crystal base on the other side of it. In this way, a column with a drop of liquid on its end grows. Crystal whiskers, which may be as long as 50–100 μm and which have diameters equal to that of the initial drop, can be obtained by this method. Also, they can branch (if the drop splits), change in diameter (if the diameter of the drop changes), change direction of growth, etc.

A review of the works of Baker and co-workers devoted to the formation of filamentous carbon in various chemical systems was made in Ref. (23). Direct observations using a controlled atmosphere electron microscopy technique, made in these works, showed how various metals and alloys catalyze the growth of this type of structures.

As was seen from the experiment, the metal wool structure has the following features. It consists of thin filaments that branch, twist, and interlace to form the whole structure. Growth of filaments takes place on gold islands but not on clean surfaces, and some amount of gold was detected in the wool. These features are very similar to those described above for the vapor–liquid–solid mechanism of whisker growth. This suggests that in this case we have the same process of filament formation. Apparently, after ignition of the reaction, gold islands partially melt, forming drops of the liquid phase on the platinum surface. At the same time, the reaction creates an above-equilibrium concentration of platinum vapor over the surface. Thus, conditions similar to those required in the vapor–liquid–solid method arise, and platinum atoms captured by liquid gold produce whiskers, which then form platinum wool. The nonuniform initial distribution of gold on the surface of the spot allows the chaotic character of filament growth and leads to formation of the complicated interlaced structure.

The suggested mechanism of metal wool formation also makes it possible to explain the phenomenon of wool degeneration observed in the experiment. It was found that degeneration took place when only a small amount of gold had been deposited on the platinum surface and when the temperature of the spot had increased. As was mentioned, we connect the increase in temperature with a decrease in the amount of gold on the surface; i.e., part of the gold islands gradually disappears and more and more areas become active in the reaction. As follows from the vapor–liquid–solid mechanism, if for some reason the drop of liquid disappears from the end of the growing whisker, its further growth in length will stop. If there are other drops and growing columns around it which actively absorb vapor from the boundary layer, then the column will remain unchanged in time. If, however, all the liquid phase has disappeared from this area, then no preferable sites of vapor condensation will exist and molecules from the oversaturated gas phase will adsorb uniformly along the entire length of the whisker, which will thereby begin growing in width. Obviously, during this growth (which will be much slower than the initial whisker growth) crystal faces with minimum free energy will form and they will retain their orientation throughout the process. Also, the fastest increase in width will be found in the coldest region of the whisker. Thus, one can see that all the features described were experimentally observed in the process of platinum wool degeneration into a bulk polycrystal structure (Fig. 7).

Accepting the vapor–liquid–solid mechanism of whisker formation, we can estimate the concentration of platinum in the boundary layer over the surface from the rate of whisker growth.

From the experimental results one can see that during a time interval of $t \sim 500$ sec, a whisker with length $l \sim 20\ \mu\text{m}$ and width $2r \sim 0.2\ \mu\text{m}$ grows on the surface. This means that the flow of platinum atoms that passed through the drop on its end was

$$j = \frac{V * n_s}{\tau} = \frac{\pi r^2 * l * n_s}{\tau},$$

where $V = \pi r^2 * l$ is the volume of the whisker and n_s is the density of atoms in crystal platinum ($n_s \sim 6.6 \times 10^{22}\ \text{cm}^{-3}$).

Assuming that all atoms from the gas that strike the surface of the liquid drop are adsorbed by it, and estimating the mean free path of platinum atoms in air as $\lambda \sim 2\ \mu\text{m}$ (that is, much greater than the whisker diameter), we can estimate the flow of atoms from the gas into the crystal as

$$j = \frac{v_T^* S}{4} * C = \frac{v_T^* 2\pi r^2}{4} * C,$$

where $S = 2\pi r^2$ is the outer area of the liquid drop on the top of the whisker, v_T is the thermal velocity of platinum atoms ($v_T \sim 4 \times 10^4$ cm/s), and C is the concentration of platinum atoms in the boundary layer.

Equating these flows, we find the concentration of platinum atoms in the boundary layer to be

$$C = \frac{2 * l * n_s}{v_T^* \tau} \sim 10^{13}\ \text{cm}^{-3}$$

Converting to pressure units, $P \sim 10^{-3}$ Torr.

This value is many orders of magnitude higher than the equilibrium pressure for saturated platinum vapor at the temperature of the reacting wire. Thus, as was suggested above, we see that the reaction causes an enormous increase in platinum sublimation from the surface.

The experimentally observed phenomena of platinum wool formation on the surface of a platinum catalyst covered with gold and of its degeneration into a bulk crystal structure provides the basis for suggesting a hypothesis for the mechanism of bulk poly- and monocrystals nucleation during catalytic etching of clean surfaces. As was seen in the first part of this work, a characteristic feature of these crystals was their rapid and random initial appearance in the form of long and rather thin columns, with further growth in width while length remained constant. On the basis of the observed platinum wool formation and degeneration and the above discussion, it is natural to suggest that individual whiskers or pieces of platinum wool are the nuclei of bulk crystals; i.e., we assume that during the reaction, drops of liquid phase may accidentally form on the surface of the catalyst. This may happen due to impurities and dust in the gas flow which melt when they fall on the hot surface of the catalyst, due to NH_4NO_3 formation on it, or possibly to some other reasons. Then by the mechanism described above, a platinum whisker or "bush" of platinum wool rapidly grows from the drop. After the drop evaporates, the structure degenerates into a bulk mono- or polycrystal, respectively. This mechanism explains the random character of bulk crystal nucleation, the initial rapid growth of the crystal in length (only during the short period when the drop exists on its end), and its slow increase in width during further processing (when the drop disappears and platinum absorbs directly from the gas phase). To support this hypothesis, photographs obtained in observations of catalytic etching of clean platinum wire in an ammonia oxidation reaction with 15% ammonia in pure oxygen are shown in Fig. 8. Figure 8a shows a platinum whisker which grew on an impurity spot on the surface of the wire (the characteristic shining of the spot under the electron beam indicates its nonmetallic nature). Figures 4b–4f show the process of bulk crystal growth. In this series, one can see a thin initial column (it appeared within 15 min of the previous observation) and its further increase in width while retaining the initial orientation of its faces. Also, more rapid growth of the region of the crystal which is farther from the surface of the wire is well seen.

In addition, we would like to make some practical notes based on the results of this work. The first conclusion concerns the decrease of the activity of catalytic platinum gauzes in industrial ammonia oxidation reactors after some time of service. This phenomenon is usually attributed to the existence of some poisons in the gas mixture or to transformation of platinum or rhodium to their oxides. In accordance with the proposed mechanism, another possible cause exists. Decrease in activity can be attributed to formation of perfectly shaped and hence less active crystal structures on the surface of platinum gauzes. This conclusion is in accordance with the theoretical concepts developed in Refs. (24, 25) concerning peculiarities of the diffusive regime of catalytic reaction on catalytic surfaces with nonuniform activity.

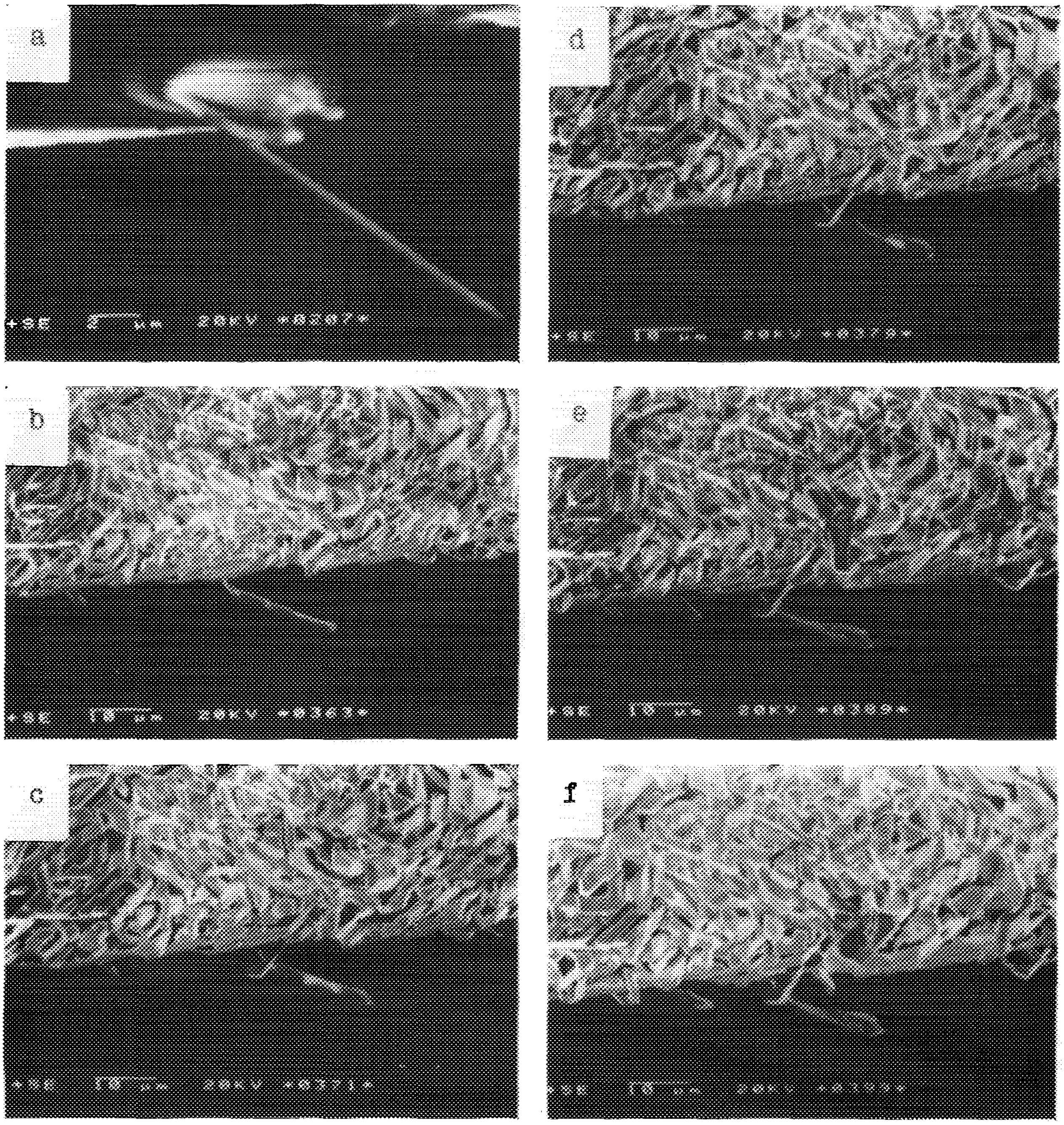

FIG. 8. Formation of bulk microcrystals on the clean surface of platinum catalyst during ammonia oxidation. 15% NH_3 in pure oxygen. (a) Growth of platinum whisker on an impurity island, 30 min in reaction. (b–f) Another place. Appearance of a bulk crystal after (b) 195 min in reraction, (c) 210 min, (d) 225 min, (e) 240 min, and (f) 255 min.

Another note concerns the Degussa method of decreasing platinum loss in industrial ammonia oxidation reactors, in which palladium–gold alloy gauzes are used to trap platinum from the gas mixture stream after the catalyst package. We think that these gauzes may have the same mechanism of platinum absorption as we observed in experiments with gold-covered platinum wire.

SUMMARY

Observations made in this work showed that the process of catalytic etching consists of two sequential stages. First, immediately after the reaction begins, a regular "parallel facet" structure consisting of parallel "furrows" of approximately 5 μm in depth begins to form on the surface. After several hours of reaction (depending on concentration and temperature) another type of structure, a "bulk crystal" structure, begins to form over the first one. It consists of individual poly- or monocrystals with well-defined crystal faces, a small area of bonding with the surface, and sizes up to 30–50 μm.

We attribute the process of surface reconstruction to the gas phase diffusion and recondensation of platinum intensively sublimated from the surface due to chemical reaction.

The following characteristics of the process of bulk crystal nucleation were found. Crystals of this type first suddenly appear as long narrow columns, which then grow, retaining the initial shape and orientation of their facets. During growth these columns increase mainly in width, and only slightly in length.

During ammonia oxidation the appearance on the surface of a platinum catalyst covered with gold and a structure resembling metal wool and consisting of interlaced crystal whiskers of platinum with lengths up to 20 μm and diameters 0.1–0.3 μm was experimentally observed. Formation of this structure was attributed to the mechanism known in crystallography as the vapor–liquid–solid method. Deposited gold provides liquid drops on the surface and the catalytic reaction provides saturated platinum vapor in the boundary layer.

The rate of whisker growth allows estimation of the platinum vapor pressure over the catalytic surface as $P \sim 10^{-3}$ Torr. This value is many orders of magnitude higher than the equilibrium value at the temperature of the platinum wire.

Degeneration of platinum wool into a bulk crystal structure after disappearance of gold from the surface was observed. These observations suggest that platinum whiskers are the nuclei for bulk crystal formation on platinum catalysts during ammonia oxidation. This hypothesis can explain the observed characteristic features of bulk crystal formation.

On the basis of the study of the dynamics of surface reconstruction, the observed formation and degeneration of platinum wool structure, and the hypothesis of above-equilibrium platinum sublimation from the surface caused by heterogeneous reaction, we assume the mechanism of the whole process of catalytic etching as follows. After ignition of the reaction, a large increase in the rate of platinum sublimation from the surface occurs. This leads to platinum concentration in the boundary layer which is much higher than the equilibrium value (at the temperature of the reacting platinum wire), and hence causes the thermodynamically opposite process of platinum condensation on the surface from the gas phase. Evidently, during recrystallization, faces with minimum free energy will most likely form on the surface of the catalyst, and so grain surfaces with initial orientation different from the stable one will split into facets. In this way, the parallel facet structure forms on the catalyst. As these parallel facets consist of the most stable, and hence the least active and the coldest surfaces, after some delay, when they become large enough, conditions favorable for the appearance of liquid drops on the surface occur. These accidental drops will rapidly absorb platinum vapor and enable growth of platinum whiskers or "bushes" of platinum wool, which rapidly degenerate into bulk microcrystals after evaporation of the liquid. As the surfaces of bulk microcrystals are larger and colder than those of the parallel facets, the rate of their growth is much higher. Thus, as more and more bulk crystals appear on the surface, they become the main trap for the vapor atoms and soon the whole surface of the catalyst acquires a chaotic cover of crystals of various sizes and shapes.

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REFERENCES

1. Parsons, C. L., *Ind. Eng. Chem.* **11,** 540 (1919).
2. Handforth, S. L., and Tilley, J. N., *Ind. Eng. Chem.* **26,** 1287 (1934).
3. Schmidt, L. D., and Luss, D., *J. Catal.* **22,** 269 (1971).
4. McCabe, R. W., Pignet, T., and Schmidt, L. D., *J. Catal.* **32,** 114 (1974).
5. Flytzani-Stephanopoulos, M., Wong, S., and Schmidt, L. D., *J. Catal.* **49,** 51 (1977).
6. Flytzani-Stephanopoulos, M., and Schmidt, L. D., *Chem. Eng. Sci.* **34,** 365 (1979).
7. Dean, V. W., Frenklach, M., and Phillips, J., *J. Phys. Chem.* **92,** 731 (1988).
8. Hess, J. M., and Phillips, J., *J. Catal.* **136,** 149 (1992).
9. Barelko, V. V., *et al. Dokl. Akad. Nauk SSSR* **231**(5), 1143 (1976).
10. Khalzov, P. I., and Barelko, V. V., *Dokl. Acad. Nauk* **246**(6), 1420 (1979).
11. Barelko, V. V., Khalzov, P. I., and Doronin, V. N., *Poverkhnost* **6,** 91 (1982).
12. Khalzov, P. I., and Barelko, V. V., *Poverkhnost* **5,** 132 (1982).
13. Genkin, E. S., *et al. Dokl. Acad. Nauk* **316**(3), 658 (1991).
14. Barelko, V. V., and Volodin, Yu. E., *Kinet. Katal.* **17** (3), 683 (1976).
15. Barelko, V. V., *et al. Dokl. Acad. Nauk SSSR* **223**(1), 112 (1975).
16. Barelko, V. V., *et al. Chem. Eng. Sci.* **33,** 805 (1978).
17. Barelko, V. V., *Probl. Kinet. Katal.* **18,** 61 (1982).
18. Volodin, Yu. E., Barelko, V. V., and Khalzov, P. I., *Chem. Eng. Comm.* **18**(5,6), 271 (1982).
19. Genkin, E. S., *et al. Dokl. Acad. Nauk* **316**(3), 658 (1991).
20. Barelko, V. V., and Volodin, Yu. E., *Kinet. Katal.* **17**(1), 112 (1976).
21. E. I. Givargizov, "Growth of Crystal Whiskers and Thin Layers from Vapor." Nauka, Moscow, 1977. [In Russian]
22. R. S. Wagner, *in* "Whisker Technology" (A. P. Levitt, Ed.) p. 47. Wiley, New York, 1970.
23. Baker, R. T. K., *Carbon* **27**(3), 315 (1989).
24. Pechatnikov, E. L., and Barelko, V. V., *Khim. Fiz.* **8**(6), 816 (1989).
25. Barelko, V. V., Khalzov, P. I., and Chernishov, V. I., *Khim. Prom.* **8,** 506 (1987).