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Changes in the Catalytic Activity of Cold-worked Platinum during the Oxidation of Carbon Monoxide

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Synopsis. The rate of the oxidation of carbon monoxide was measured on cold-worked platinum to study the influence of annealing on the catalytic behavior. It was found that the presence of lattice defects (dislocations) in the crystal plays a role in initiating the reaction and serves to create new active sites during an acceleration period of the reaction.

Many experiments have been shown that the presence of lattice defects in a metal for various reactions plays an important role in governing the catalytic activity.[1–16] The reactions used in these experiments, in most cases, were hydrogenations and dehydrogenations. There are very few reports about the nature of active sites of metals for oxidation reactions effected by molecular oxygen. Very important contributions to this problem have been carried out by Gwathmey and his colleagues.[17,19] They found that the morphological changes of crystal faces of copper occur during the catalytic oxidation of hydrogen and suggested that these changes are initiated at the special sites of emergence of imperfections in the crystal. The purpose of the present study is to investigate the effects of lattice defects in platinum produced by cold-working on the rate of the catalytic activity change during the oxidation of carbon monoxide. This reaction was chosen as a typical reaction because of the simplicity of the reacting system. The reason for selecting platinum is that this metal is one of the most commonly used catalyst for oxidation reactions and is resistant to bulk oxidation at effective temperatures.

In order to introduce lattice defects, well annealed Pt wire (99.97% purity) with a diamer 0.5 mm was rolled to a thickness of 0.1 mm at room temperature. After being washed with acetone and distilled water, these specimens were annealed again at different temperatures between 300 and 800 °C in hydrogen and under vacuum for 1 hr. The catalytic activity was determined in a static system by measuring the decrease in the total pressure. A stoichiometric mixture of CO and O_2 was used for all experiments at a total pressure of 100 Torr. The product, CO_2, was continuously condensed by a liquid nitrogen trap connected to the reaction vessel. The apparent surface area of specimens used as the catalyst was about 15 cm². The gases, obtained from Takachiho Co., Ltd., were carefully purified by passing through adsorbent traps and fractionating *in vacuo*.

Some typical results at a reaction temperature of 295 °C are given in Fig. 1. Curve (A) shows the course of reaction as a function of time on the fresh specimen annealed at 350 °C (first run). The change in the rate during the reaction is shown as curve (B) obtained from each point in curve (A). It is found that the rate increases at first with the progress of the reaction and attains to a steady limiting value. That is, two periods in the course of reaction can be defined: an acceleration period, and a steady state period, during which the rate of reaction is constant. These two periods are always observed under the conditions of present experiments when the freshly annealed specimens are used as the catalysts. The steady state rate is independent of the annealing temperatures (300—800 °C), however, the length of the acceleration period is strongly dependent on both the annealing temperatures and the reaction temperatures. Curves (C) and (D) are the results of the second run which is obtained with a new dose of the reacting gases after the first run. After an initial decrease, the rate becomes equal to the stationary value and no acceleration period is observed. Such a constant activity is found to remain unchanged even after several reaction runs. These results may suggest that the acceleration period is the process of the production of new active sites by the reaction itself. It is probable that the initial decrease in the rate (curve D) is due to CO poisoning on special active sites which are revealed by the evacuation after the first run. Figure 2(A) indicates the effect of annealing temperature on the catalytic activities in the range of the acceleration process at a reaction temperature of 295 °C. (The activities are expressed as a per cent conversion to CO_2 at a fixed reaction time, 50 min.) The change in the activity is considerable in the range 500—600 °C. According to

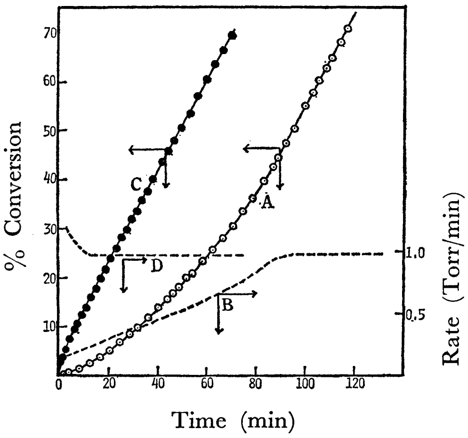

Fig. 1. Oxidation of CO on Pt annealed at 350 °C (reaction temperature 295 °C).
(A) and (B), first run: (C) and (D), second run.

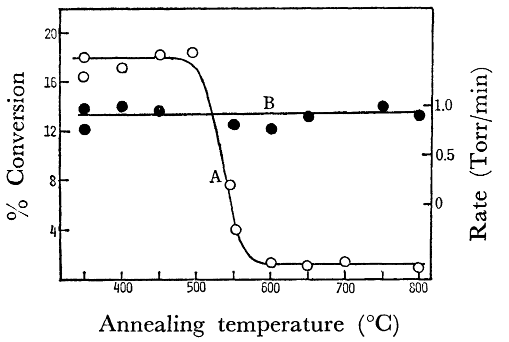

Fig. 2. Dependence of the catalytic activity in the acceleration period (A) and the steady period (B) on the annealing temperatures.
(A) Per cent conversion at a fixed reaction time, 50 min.
(B) Steady state rate, (Torr/min)

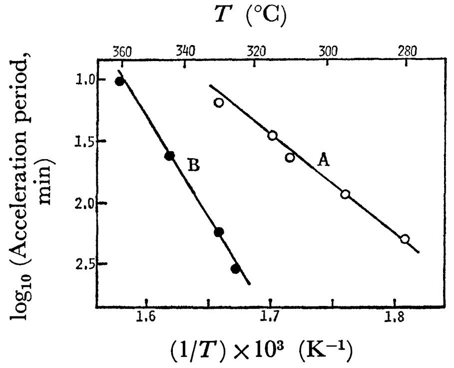

Fig. 3. Dependence of the length of the acceleration period on the reaction temperatures.
(A) Catalysts annealed at 350 °C.
(B) Catalysts annealed at 600 °C.

our previous results, this range approximately corresponds to the recovery temperature range involving the disappearance of dislocations produced by cold-working.[8] Figure 2(B) indicates that the catalytic activities in the stationary state is independent of the annealing temperatures. The dependence of the length of the acceleration period on the reaction temperature is given in Fig. 3. The length of the acceleration period increases with decreasing the reaction temperature, and the Arrhenius plots give the slopes equivalent to the activation energies of 35 and 79 kcal over the range 280—360 °C for the catalysts annealed at 350 and 600 °C, respectively. These results indicate that the activation of the surface by the reaction is very difficult when the catalyst is well annealed. Further, it can be concluded that under the conditions of the present experiments, the surface terminations of dislocations play an important role in initiating the oxidation reaction and serve greatly to create new active sites during the acceleration period. For the nature of these active sites, we have no complete explanation but it seems likely that these sites can be related to a kind of surface defects created by the cyclic oxidation-reduction process of the surface involved in the catalytic reaction. On the other hand, it may be considered that the possible reasons for affecting the catalytic activity on annealing are the decrease in surface area and active lattice planes at the surface, however, these factors do not seem to explain the sudden decrease in the activity in a limiting annealing range (500—600 °C) as discussed in previous papers.[6,7,15,16] Furthermore, it is clear that the annealing at temperatures above 600 °C has direct effects on a length of crystallite boundaries, crystal edges, and angular points at the surface. However, the results also indicate that these factors have no influence on the activity.

A few experiments were also carried out on cold-worked gold at a reaction temperature of 390 °C. It was found that no acceleration period is observed and the activity is not influenced by annealing in the range 400—800 °C. According to the previous paper, the recovery temperature range of cold-worked Au is in the range of 100—200 °C.[15] Accordingly, in this case, dislocations produced by cold-working cannot be responsible for the catalytic activity, since the catalysts are already annealed out at 400 °C before the measurements are made.

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