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Carbon Deposition on Nickel from a Mixture of Ethylene and Hydrogen

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Synopsis. Two periods (acceleration and steady state period) were defined in the process of carbon deposition on cold-worked nickel from ethylene. From the dependence of the former period on annealing temperature, it was found that lattice defects in the crystal play a role in the creation of carbon nuclei and the separation of nickel atoms from the surface.

Carbon deposition on catalysts has been an important topic in connection with catalytic processes involving hydrocarbons. Recently Lobo *et al.*,[1,2] studying the kinetics of these reactions on nickel foils, have reported that, in general, there are three periods in the course of the reaction: an induction period, an acceleration period, and a steady state period. Furthermore, they suggested that the length of the induction period is strongly dependent on both the mode of pretreatment of the catalyst and the reaction temperature, but the rate of reaction in the steady state is independent of the catalyst history. Many studies[3] have shown that the catalytic activities of metals for various reactions are greatly influenced by pretreatments, such as cold-working, irradiation, and annealing, and that these changes in the activity are mainly ascribed to the generation or the annihilation of active sites during the treatments. It seems probable that a similar situation exists in the case of the reaction of carbon deposition on metals. Shirasaki *et al.*[4] observed the deposit of carbon from C_2H_4 on Ni crystals by an electron microscope and claimed that the boundaries of crystallites were much more active than their plane surfaces. Walker and Thomas[5] have suggested that the deposition of carbon from CO is favored at dislocations in metal catalysts, in agreement with the hypothesis previously presented by Gwathmey *et al.*[6] Emphasis in the present work is placed on the effect of the pretreatments of Ni catalysts on the initial stages of the carbon deposition by the decomposition of C_2H_4.

The reactions were carried out in a static system and a Cahn electrobalance (Venton Instr. Corp.) was used to record the weight change due to the carbon deposition. Well annealed Ni wire (Japan Lamp Industrial Co., Ltd.) with a diameter of 0.5 mm was rolled to a thickness of 0.1 mm at room temperature. Specimens used for the experiment were in the form of ribbons (surface area approximately 10 cm^2). After being carefully washed with solvents, they were suspended from the balance arm and then were annealed at different temperatures between 350 and 800 °C in H_2 for 1 h. After this, the H_2 was pumped out.

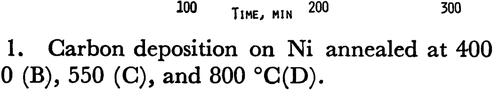

Fig. 1. Carbon deposition on Ni annealed at 400 (A), 450 (B), 550 (C), and 800 °C(D).

C_2H_4 obtained from Takachiho Co., Ltd. was purified by repeated freezing and vacuum distillation. H_2 made by electrolysis was used after passage through hot Cu powder and a molecular sieve column cooled by liquid N_2. A mixture of C_2H_4 and H_2, 1 : 1 molar ratio, was used for all experiments at a total pressure of 13.3 kPa. Under these experimental conditions the reaction occurred at conveniently measureable rates in the temperature range of 360—600 °C. Carbon deposited surfaces were examined by a scanning electron microscope (Japan Electronics LAB-JSM U3 Type).

Figure 1 shows the typical time course of the reaction at 400 °C for the specimens annealed at four different temperatures. The rates increase gradually with the progress of the reaction and attain a steady limiting value (about 4.5 μg/cm^2 min). Thus, two periods are evident: (a) acceleration and (b) steady state period. It is seen that the former is very dependent on the annealing temperature but the latter is not much effected by the treatment. Figure 2(A) shows the effect of the annealing temperature on the catalytic activities in the range of the acceleration period at a reaction temperature of 400 °C. (The activities are expressed as the time to effect equal increment in the amounts of deposition). Although the experimental values are very scattered, the decrease in the activity is apparent in a range of 400—550 °C. It is also shown in Fig. 2(B) that the change in hardness of cold-worked Ni was paralleled

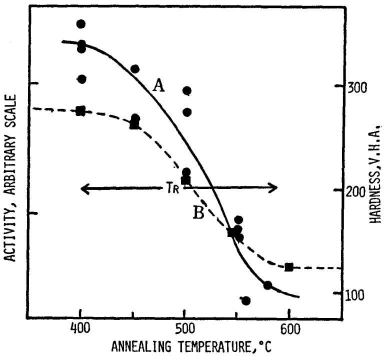

Fig. 2. Dependence of the catalytic activity in the acceleration period (A) and of hardness (B) on the annealing temperature.

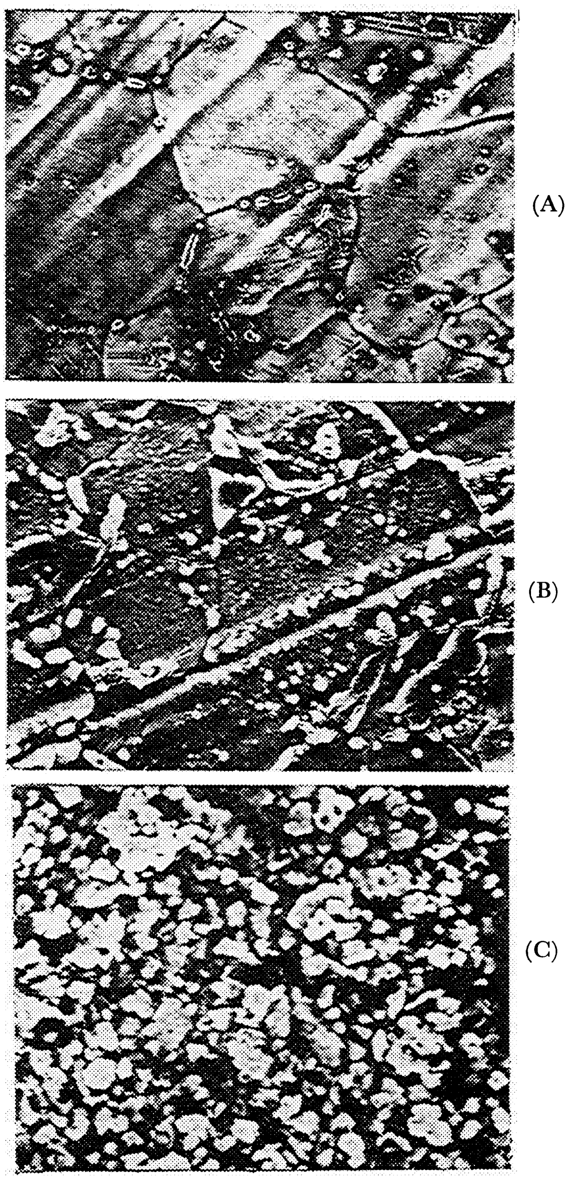

Fig. 3. Scanning electron micrographs (× 1000) of deposited carbon on Ni surfaces annealed at 800 °C.
(A) and (B) showing patterns at point a (10 μg/cm^2) and b (100 μg/cm^2) in Figure 1(D); (C), at a point in the steady state period.

by the change in the activity by annealing. According to our previous results,$^{7)}$ this temperature range approximately corresponds to the recovery range (T_R) involving the migration and the annihilation of lattice defects (mainly dislocations) produced by cold-working. It has been already established that the acceleration period involves the creation of carbon nuclei and a subsequent growth process on the surface, and that the latter process is accompanied by the separation of Ni atoms from the surface.$^{1,8)}$ From the facts presented above, it seems to be right to consider that the defects produced by cold-working in the crystals play a role in these processes in the acceleration period.

On the other hand, as the reaction temperature was raised, the reactions were always accompanied by the reduction in the acceleration period and the rates increased rapidly. At the temperatures above 450 °C, the acceleration periods were hardly discernible and the influence of the pretreatments on the catalytic activity was no longer detectable. These facts indicate that the contributions of normal surfaces to the catalytic activity overwhelm the effects which result from the special active sites responsible for the reactions at low temperatures.

In the case of the catalysts annealed at higher temperatures above 600 °C, the initial processes of deposit were examined with a scanning electron microscope. Figure 3 shows some typical examples observed at a reaction temperature of 400 °C. It is clear that the deposit occurs preferentially at special sites in a crystal face and at grain boundaries. These patterns are approximately similar to those of Shirasaki *et al.*$^{4)}$ In conclusion, the present results suggest that on cold-worked catalysts the reaction is initiated at a large number of evenly distributed active sites formed by the pretreatment, while on the catalysts annealed at higher temperatures it proceeds on a localized region (*e.g.* grain boundaries) and on a small number of special sites which remain after annealing.

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