NOTES

A Case of Interference between Catalytic Action and Surface Rearrangement

While studying the catalytic behavior of dispersed or massive nickel in ethylene hydrogenation (1, 2), we discovered that even a small oxygen content of the reacting mixture exerts a large promoting influence upon the catalyst activity. We extended this observation to platinum and copper (3) and then to rhodium (4).

Several observations led us to think that this effect of a *permanent trace* of oxygen in the reacting mixture had to be interpreted by supposing a modification of the surface state of the metal while catalyzing the water synthesis simultaneously with ethylene hydrogenation.

This hypothesis was strengthened by the well-known fact that striking surface rearrangements take place when some metals are used as catalysts for the reaction of H_2 and O_2 (5) and also several other reactions (6–9). As suggested by Weisz (10), *"metal atom rearrangement at the atomic level must occur, of course, before structural changes become visible."* This means dislodged atoms may exist for a period during the course of water synthesis. Previously, we reached the conclusion that some of them generate special configurations which are active sites toward ethylene hydrogenation (at least for the main part in our work).

This conclusion can be related to those reached by several other authors. For instance, a similar conclusion is in some measure suggested by Walker and Thomas (11) in a study on the disproportionation of

CO and by Baddour *et al.* (12) dealing with the oxidation of CO on Pd. We also can notice the recent results of Boreskov *et al.* (13), who observed the production of active centers during the course of CO oxidation. These sites can be utilized to make another reaction ($^{16}O–^{18}O$ exchange) proceed 2 or 3 orders of magnitude more rapidly than on the inactivated surface. Moreover, a conclusion reached by Langmuir (14) may be recalled. After he had observed that Pt surfaces become modified and subsequently more active by treatment with a mixture of $H_2 + O_2$ or $NH_3 + O_2$, he deduced that surface atoms were *"pushed around and made to assume new positions"* so that some of them allow the distances to be *"exactly right for the reaction to occur at the highest possible speed."*

We were thus led to test our hypothesis concerning the origin of the activity of nickel and platinum in our previous experiments by observing whether their surfaces undergo any visible rearrangement under conditions close to those which prevailed in that case, namely, $H_2 + O_2$ mixtures of small oxygen content.

The experimental procedure was as follows. The Ni and Pt samples were first observed with an optical microscope while catalyzing H_2 oxidation. When sufficient surface modifications had been detected they were examined with a scanning electron microscope. The experimental apparatus which allowed observation of the samples during the reaction is identical to

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that previously described (15). The reactor is composed of a heating stage (Leitz, 1750°C type) placed under a Leitz microscope (Panphot type). It has the shape of a metallic cylinder closed at its upper part by a quartz window. An external jacket allows a flow of cool water to be set up and the gas flows through the reactor between two opposite apertures. The samples, which are electrically heated by direct current, are made of Ni or Pt ribbon (Ni from Material Research Corp., 99.99%; Pt from Leico, 99.95%) similar to those previously used in ethylene hydrogenation. They are given a U bolt shape, the horizontal part being 8 mm long and the vertical one 10 mm. The microscope allows observation of the horizontal part which lies parallel to the quartz window.

During a preliminary calibration performed before the experiments, the hot point of a Cu–constantan thermocouple is soldered to the central part of the ribbon and gives the temperature versus the current intensity. Repetition shows a perfect reproducibility. We tried to ensure operational conditions very similar to those of our usual hydrogenation experiments with
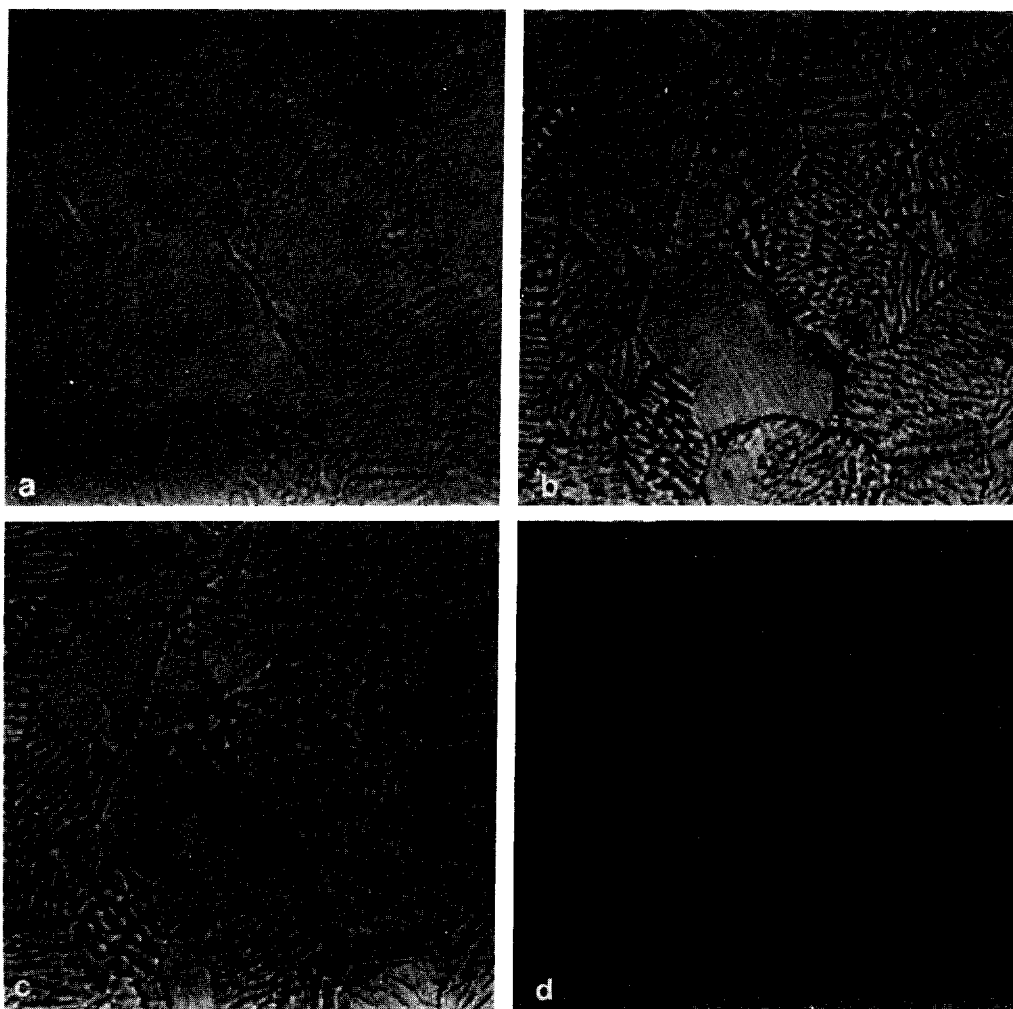

FIG. 1. Electron micrographs of nickel ribbon.

respect to the O_2 content, temperatures and contact times. The reactor is fed with H_2 under 1 atm pressure flowing at 133 ml/min. The oxygen content (15 ppm for instance) is set up using the previously described permeation device (2) in which H_2 flows along a short Teflon tube submitted to some external O_2-pressure. Higher O_2 contents (1000 or 2000 ppm) were obtained by mixing flow rates of N_2 containing 2% O_2 and H_2. Ni samples were electrolytically polished before use, whereas the Pt ribbons were heated in the reactor fed with pure H_2 and until the marks introduced by rolling were eliminated (15 min at 1300°C). A CAMECA MEB 07 scanning electron microscope was used and the samples were at an angle of 28° with the horizontal.

The micrographs show the essential results. They all show that a gross surface rearrangement does occur during the catalytic reaction, whereas the same samples could be submitted to either H_2 or a H_2–N_2 mixture at the same temperature and for a very long time (more than 300 hr) without any change.

Figure 1a ($\times$1300) shows the result obtained on the Ni ribbon, at 260°C, after it had been subjected for 20 hr to a mixture containing 1000 ppm O_2. Figure 1b and 1c ($\times$1300) relate to the same part of the sample and denote the progressive evolution of the surface as the composition remains the same. On the grains which show faceting one can see that this occurs near the grain boundaries and then develops over the whole surface. We can also see that between 100 and 200 hr, some edges disappear in favor of facets (which grow) on the best rearranged grains without any change in the orientation of the remaining edges. We must also point out that some grains do not undergo any modification (at least as far as the magnification we used could show) and preserve their smooth appearance. The same phenomena also occur for lesser O_2 contents, almost the same as those prevailing during the hydrogenation ex-
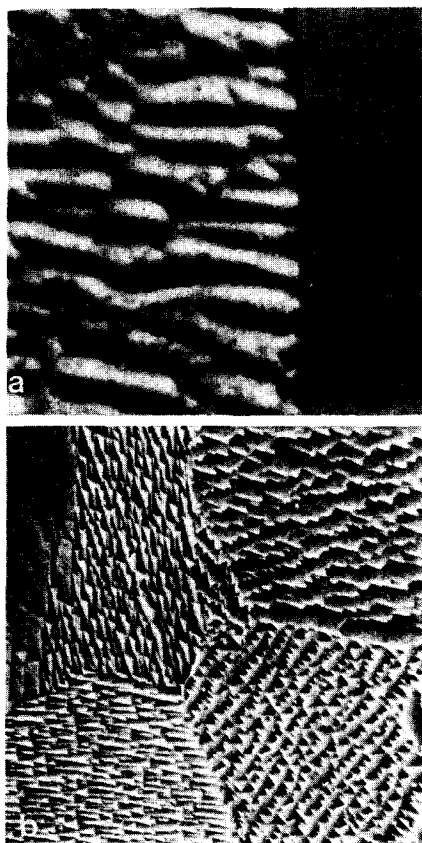

Fig. 2. Electron micrographs of nickel ribbon.

periments previously reported (1, 2). However, the rearrangement occurs less strongly than previously, as indicated on the micrograph 1d obtained after a treatment by H_2 + 15 ppm O_2, at 260°C, for 280 hr. The relief is not more pronounced than in micrograph 1a and this fact leads us to think that the surface rearrangements are related to the number of elementary chemical reactions which occur on the surface. Moreover, a much smaller number of grains is concerned than in the case with a higher O_2 pressure so that faceting seems to grow preferentially from areas that are already undergoing rearrangement.

Figure 2 ($\times$2500) shows two micrographs obtained with the Ni sample by SEM and under the following conditions: (a) H_2 + 2000 ppm O_2, 260°C, 80 hr; (b) H_2 + 2000 ppm O_2, <260°C, 80 hr. The latter

micrograph relates to the vertical part of the same ribbon which remains unobservable by optical microscopy during the reaction and which, being nearer the end, is less heated than the central part. It seems beyond question that the edges are the sharpest and the most numerous upon this part of the sample. On the hotter areas, not only the edges are smoother but the facets are larger. A parallel with the growth of facets with time, which we can see in Fig. 1, leads us to conclude that the extent
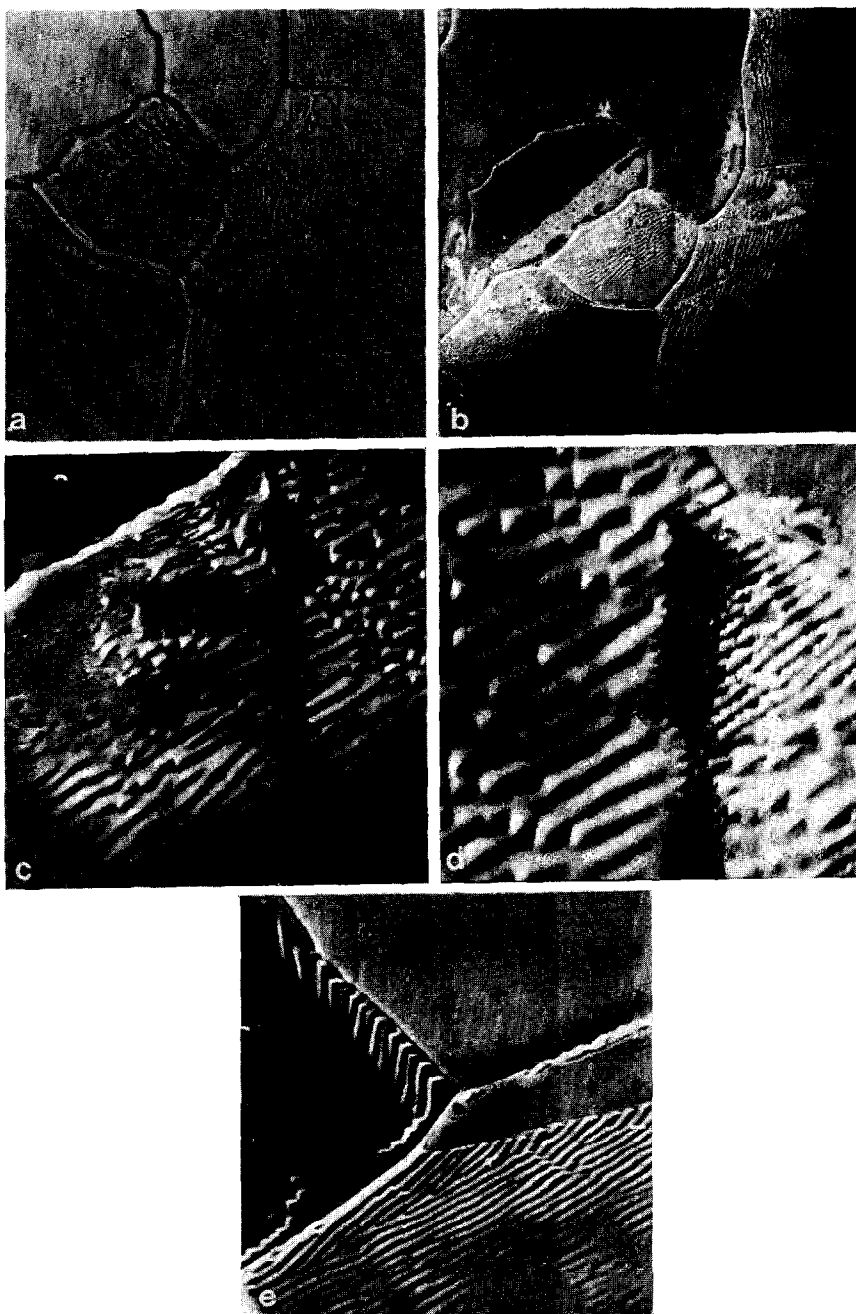

FIG. 3. Electron micrographs of platinum ribbon.

of the rearrangement is related to the number of elementary catalytic reactions.

With regard to the sharpness of the edges, it is worth recalling that Meelheim *et al.* had observed sharp edges when the O_2 content of the O_2/H_2 mixture was increased. It thus seems reasonable to think that the determining factor in the point discussed here is the O_2 coverage of the metal surface. The latter increases when the O_2 content increases as well as when the temperature decreases and so may well be the factor which induces higher differences among the specific surface energies of different crystal faces.

Figure 3 presents the micrographs obtained upon the platinum ribbon submitted to (H_2 + 2000 ppm O_2) for nearly 100 hr at 260°C. Figure 3a and b relate to the same area observed with the optical and the scanning microscope. Figure 3c and d display details inside one of the grains and stress the fact that the surface rearrangement goes forward from favored areas. These areas are often localized at grain boundaries as Fig. 3e shows or are sometimes close to former grain boundaries which were erased during the surface preparation. The only obvious difference with the Ni case consists in a lower rate of rearrangement which can be accounted for by either a lower efficiency in inducing mobility or the fact that water synthesis operates essentially upon areas undergoing rearrangement and at a lower rate upon the inactivated surface which remains.

To sum up, the rearrangements described here occur under conditions of low temperatures and low partial pressures which had never been brought into play until now. However, what is the most important to us is the fact that they have been forecasted by the use of an argument derived from only kinetic observations of different kinds. This prompts us to think that in the case we have studied, the main part of the activity may really originate in a chemical reaction just as it can originate in ion bombardment ([16]) or in cold-working ([17–19]).

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