107. Recombination of Hydrogen Atoms on the Copper Single Crystal Surfaces

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Introduction. One of the difficulties encountered in investigating the heterogeneous catalysis may be attributed to the complexity of surface structures of catalysts. Since the study of a simple reaction taking place on a single crystal of metal, in which some physical properties are precisely defined, is supposed to be very useful to elucidate the mechanism of catalytic reactions, the recombination of hydrogen atoms on single crystal surfaces of copper was adopted here as a typical surface reaction.

It was first predicted by Horiuti et al.\(^1\) that the activities of metallic catalysts might be related to their crystallographic faces; in calculating the activation energy of hydrogen adsorption on nickel, they suggested that the least dense (110) face should be the most active among three principal faces. Afterwards Beeck et al.\(^2\) carried out the hydrogenation of ethylene on evaporated nickel films and found that the (110) oriented film was about five times more active than the unoriented one. In their experiment, however, there remains some ambiguity concerning the geometrical structures of surfaces exposed to the gas phase.\(^3\) As experiments in which a massive single crystal was used, the work of Rhodin\(^4\) and that of Gwathmey et al.\(^5\) are noteworthy. Rhodin studied the adsorption of nitrogen on the single crystal surfaces of copper by use of a microbalance operated in vacuum. Dealing with the hydrogen-oxygen reaction on the surfaces of a single crystal of copper, Gwathmey showed that the activities of principal faces under certain experimental conditions decrease according to the following order: (110), (100), (111).

In regard to the recombination reaction of atomic hydrogen, Suhrmann et al.\(^6\) pointed out about twenty years ago that there was a good linear relationship between the recombination coefficients of some various metals and their work functions. On the other hand, some workers\(^7\) have found the anisotropy of work function of copper by measuring the photoelectric threshold or the contact potential. It may be expected then that the anisotropy of recombination activity will appear even in the case of the different faces of a copper single crystal. The present experiment has been attempted to find any correlation between the catalytic action and the bond
energy of chemisorption, or the work function.

**Experimental.** Hydrogen: Electrolytic hydrogen from a cylinder is purified in the usual manner.

Hydrogen atoms: Atomic hydrogen is produced in a Wood discharge tube. Its concentration is measured by the method of Wrede. Variation in the concentration of atomic hydrogen is attained by changing the water vapour content in hydrogen.

Single crystal of copper: A cylindrical single crystal (12 mm in diameter, 8 cm long) is easily prepared from electrolytic copper by the slow progressive cooling method, utilizing the temperature gradient existing downwards near the middle part of electric carborundum resistance furnace (3 kw, 1300°C). The orientation of the crystal was determined by the light-figure method. The figures of two specimens, No. 1 and No. 2, cut out of a crystal rod are shown in Fig. 1. Each of them has two plane surfaces parallel to the principal crystallographic faces. These surfaces are first mechanically polished with 04 emery paper, then buffed up with chromic oxide powder, and finally electropolished in phosphoric acid (1:1 by volume). Their unused side parts are electrically plated with zinc having a relatively low recombination coefficient. It is ascertained by electron microscopy that these surfaces are extremely flat, but their detailed structures on atomic scale remain indistinct for lack of any efficacious method. Though it was also pointed out that on electrically polished surfaces of copper there exists thin cuprous oxide layer, it seems highly probable that this oxide layer may be reduced to metal by hydrogen atoms included in the reacting gas. In hydrogen-oxygen reaction investigated by Gwathmey the rearrangement of surface atoms occurs during the course of reaction, but in the present recombination reaction the copper surfaces remain almost unchanged in their surface characteristics.

**Apparatus:** The essential part of apparatus, made of hard glass, is shown in Fig. 2. A is a part of Wood tube, and B the reaction chamber connected to a rotary oil pump at right side. The tube, T, with the window, f, is fused to B at the upper part, U, and the innerwall of T was plated with platinum so as to minimize the concentration of atoms diffusing to the back side of the sample. The stem, V, hanging the sample to which a thermocouple (copper-
constantan or chromel-constantan) is attached, is introduced in $T$ through the ground glass part at $U$. The end of the side tube, $S$, is closed by a sintered glass disk for measuring the concentration of atoms by means of the Wrede method. Each of the two faces of the single crystal can be fronted, by turns, towards $f$ by turning the stem $V$. Main experimental conditions are as follows.

- Pressure of hydrogen: 0.2 mmHg
- Flow rate of hydrogen: 0.2 cc sec.$^{-1}$ at N.T.P.
- Potential across electrodes: 2000 V
- Operating current: 290 mA

Procedure and results: The temperature of the sample, raised by the heat of recombination, was followed by measuring the thermoelectric potential by use of a potentiometer. After the start of the discharge, it takes about thirty minutes to reach a steady state temperature. The temperature rise is about 30°C, varying with the concentration of atoms. The change in temperature caused by the exchange of the crystal faces is shown in Fig. 3. The temperature differences between different faces are positively appreciable, but their absolute values are no more than about 1°C. The plots of the temperature difference against the concentration of atomic hydrogen are shown in Fig. 4. The absolute values of the recombination coefficients can not be determined, but their order:

$$\gamma(110) > \gamma(100) > \gamma(111)$$

will be undoubtedly acceptable.

This result is in qualitative agreement with that of Gwathmey,
and will be discussed from the theoretical point of view in the following section.

**Consideration.** Obviously the surface atom densities of the three principal faces (Table II) have no direct connection with the anisotropy of catalytic activity. This is immediately noticed from the fact that the order of these densities is opposite to that of activities. Let us analyse next the present result on the basis of reaction kinetics assuming the following scheme for this surface recombination.

The first step is the chemisorption of hydrogen atom on the bare metal surface

\[ M + H \rightarrow MH, \quad (1) \]

which is followed by the reaction between a chemisorbed hydrogen atom and a gas-phase hydrogen atom (Rideal mechanism)

\[ MH + H \rightarrow M + H_2, \quad (2) \]

or the reaction between the chemisorbed hydrogen atoms sitting side by side (Langmuir-Hinshelwood mechanism)

\[ MH + MH \rightarrow 2M + H_2, \quad (3) \]

where the surface metal atom, M, corresponds to one site. Since it seems likely that the first step requires no activation energy, the process (2) or (3) may be considered to be the rate-determining step. The activation energies for both process (2) and (3) can be readily estimated by Eyring's semi-empirical method. They are shown in Table I.

<table>
<thead>
<tr>
<th>Face index</th>
<th>Activation energy (kcal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Independent of face species</td>
<td></td>
</tr>
<tr>
<td>(110)</td>
<td>(100)</td>
</tr>
<tr>
<td>Original value for three-atom system</td>
<td></td>
</tr>
<tr>
<td>8.8</td>
<td>11.8</td>
</tr>
</tbody>
</table>

Since the activation energy of the Langmuir-Hinshelwood mechanism for the dual sites separated by 3.61\( \text{Å} \) is calculated to be smaller than that for 2.55\( \text{Å} \), it follows naturally that the descending order of the activities for the three principal faces must be (110), (100), (111).\(^{11}\) The order just derived is in good agreement with
the experimental result. On the contrary, the anisotropy of activity
can not be interpreted in terms of the Rideal mechanism, so far as
one deals with the simple three-atom system involving one surface
metal atom and two hydrogen atoms. In order to explain the aniso-
tropy of activity by means of this mechanism, it is necessary to
take into account the repulsion effect of bulk metal on the two
reacting hydrogen atoms. The repulsion potentials are estimated in
the same way as used by Horiuti. These potentials for the three
principal faces are superimposed on the original potential surface
for the three-atom system. The activation energies obtained from
these modified potential surfaces are also shown in Table I. If these
activation energies are adopted, the order of activities becomes
favourably comprehensible.

Recently, in comparing the recombination activity of silver with
that of copper, the authors suggested that the bond energy of
chemisorption is to be the governing factor of this reaction. But
in the present case of copper single crystal, the order of activities
can not be understood by the difference of the bond energy, because
the values of bond energies expected from the surface energies stand in the opposite direction to the order suitable for explaining
the experimental result. This statement, however, should not be
taken as implying the non-existence of anisotropy for the bond energy
of chemisorption. It will be more reasonable to suppose that the
effect coming from the anisotropy of bond energy is negligibly small
as compared with the repulsion effect mentioned above.

Table II. Anisotropy of some physical properties of copper surface

<table>
<thead>
<tr>
<th>Face index</th>
<th>(110)</th>
<th>(100)</th>
<th>(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface atom density (relative ratio)</td>
<td>$1/\sqrt{2}$</td>
<td>1</td>
<td>$2/\sqrt{3}$</td>
</tr>
<tr>
<td>Work function (eV)</td>
<td></td>
<td>5.64</td>
<td>4.89</td>
</tr>
<tr>
<td>Surface energy (erg cm$^{-2}$)</td>
<td>2910</td>
<td>2530</td>
<td></td>
</tr>
</tbody>
</table>

The data on the work function and the surface energy are listed in Table II. As for different metals, it was stated by Suhrmann
that the larger the value of work function, the higher the recombination activity. According to his view, it seems at first sight
that the correspondence of activity to work function holds also in
the present case of the different crystal faces of the same metal.
Though he attaches importance to the polarization of chemisorbed
hydrogen atoms, it is doubtful whether such a view may be ap-
propriate to the present case, because of the non-existence of $d$-hole
in copper.
Due to the lack of sufficiently reliable data for the activation energy and the reaction order, it is not easy to decide which of the two mechanisms in question may predominate. At present we are in favour of the Rideal mechanism, judging from the fact that the calculated activation energies of this mechanism are smaller than those of the Langmuir-Hinshelwood mechanism. Whether the anisotropy of activity may be attributed to the crystal parameter in the usual meaning or to the repulsion effect considered above, there seems to be no doubt that the (110) face has conspicuous nature among these three principal faces, both theoretically and experimentally.

**Summary.** The recombination of hydrogen atoms was carried out on the plane surfaces of a single crystal of copper, and the sequence of recombination activities for the three principal crystal faces was found to be

\[ \gamma(110) > \gamma(100) > \gamma(111). \]

The activation energies of this reaction were estimated by Eyring’s semi-empirical method for both the Rideal and the Langmuir-Hinshelwood mechanism. In the latter case, the correspondence of the order of calculated activation energies to the experimental order of recombination activities is good in a qualitative sense. In order to explain the anisotropy of activity by means of the Rideal mechanism which appears to be more important than the other, it is necessary to take into account the repulsion potential from metal surface acting on the reacting system. This means that the anisotropy of activity does not come from the bond energy of chemisorption but rather from the repulsive potential field near the solid surface.

**References**