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NOTE ON THE MODEL OF METALLIC
ADSORBENT OF HYDROGEN

By

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Summary

The two current models of metallic adsorbent, *i.e.* the crystal plane model[3,4] and that underlying the distribution function method[8] are reviewed with regard to their experimental grounds with special reference to the dissociative adsorption of hydrogen. In the crystal plane model, sites of hydrogen adatoms form lattice planes respectively congruent with the basic lattice planes on the surface of adsorbent metal crystal, the sites on the same lattice plane are practically physically identical with each other and there exist appreciable repulsions between adatoms thus situated near to each other. In the model underlying the distribution function method, sites are distributed over the energy of adatoms on the sites, which is peculiar to each site irrespective of the arrangements of other adatoms.

The latter model leads[9] from the observed adsorption isotherms inevitably to a distribution function, which varies considerably with temperature under the condition, where the rearrangements of basic metal atoms, hence the variation of the distribution function is excluded. The results of the differential isotopic method[12], usually accepted as an exclusive evidence for the model, are shown, on the other hand, equally accounted for on the basis of the crystal plane model[13].

The crystal plane model allowed for the lattice imperfections[15] and the two states of adatom, *i.e.* r- and s-states[15], as deduced from first principles of quantum mechanics[14], is .erified by the experimental results of slow electron diffraction[16], field emission microscope[17], adsorption isotherms[20], heat of adsorption[15~19] and entropy of adatoms[21].

On these grounds the crystal plane model is confirmed, while that underlying the distribution function method disapproved.

There have been two camps in modelling metallic adsorbents atomistically; one has premised the physically identical sites of adsorption as has originated from LANGMUIR[1], while the other has supposed physically different sites especially in heat of adsorption, which have been attributed to the topological difference of surface atoms of adsorbent as initiated by H. S. TAYLOR[2]. The former model has been developed by ROBERTS[3] and OKAMOTO, HORIUTI and HIROTA[4] as follows with reference to the dissociative adsorption of hydrogen gas on metallic adsorbent. According to these authors[3,4] the surface of metallic adsorbent consists of different lattice planes of the metal crystal and each lattice plane

furnishes a congruent lattice plane of adsorption sites of adatom, which are practically physically identical with each other. The parameters of the lattice plane have obliged them[3,4] to allow for the quantum-mechanical repulsive interactions between adatoms in deriving adsorption isotherm on the basis of this model. This model will be provisionally called the crystal plane model. The crystal plane model has enabled the latter group of authors[4] to deduce the Tafel law[5], $\tau \equiv (RT/F)\partial \ln i_c/\partial \eta \sim 0.5$ from the catalytic mechanism*[)] in terms of the generalized theory of reaction rate[4,6], where i_c is the cathodic current density of the hydrogen electrode reaction, η the appropriate overvoltage, F the Faraday and RT is of usual meaning; the catalytic mechanism led, in terms of classical kinetics to $\tau = 2$[5] instead, which appears to have long been taken as a decisive ground to exclude the catalytic mechanism[7].

The model proposed by H. S. Taylor might be taken, on the other hand, to have developed into that underlying the distribution function method of adsorption[8]. According to the latter model the energy of an adatom, *e.g.* that of hydrogen, depends solely upon the site it occupies irrespective of the arrangements of other adatoms, the interaction between them being altogether disregarded. It is now the necessary condition for the distribution function method to be applicable, that the distribution of sites over the energy of adatom is invariably derived from observations at different temperatures, in so far as the rearrangements of surface metal atoms of adsorbent is excluded at the condition of experiments in question. One of the present authors has demonstrated[9] that the distribution function in case of hydrogen adsorption on nickel as well as on tungsten varied markedly with temperature from 0° to 300°C as deduced from the observations of Frankenburg on tungsten[10] and of Kinuyama and Kwan on nickel[11].

The model underlying the distribution function method[12] is based upon the result of the differential isotopic method that the portion of adsorbate later adsorbed is preferentially recovered on desorption, which has been taken as the exclusive evidence for the latter model. One of the present authors[13] has shown, however, that this experimental result does not exclusively verify the latter model but is as well derived from the crystal plane model.

Our only alternative is now the crystal plane model, which is distinguished from that underlying the distribution function method in that the sites themselves form lattice planes respectively congruent with the basic ones of adsorbent metal crystal, those on the same lattice plane are practically physically identical with

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*) The rate of hydrogen electrode reaction $2H^+ + 2e = H_2$ is, according to the catalytic mechanism, governed by the step, $2H(a) \longrightarrow H_2$, where e is metal electron in the electrode and $H(a)$ hydrogen adatom on it, which is formed by neutralization of H^+.

each other and adatoms in the latter sites repulse each other, if close enough. The crystal plane model has been elaborated in the two points as below with reference to the state of adatom. One of the present authors has shown[14] from first principles of quantum mechanics that there exist two distinctly different states of adsorption of hydrogen atom ; one is the adatom of usual sense, which is situated outside the electronic surface of adsorbent metal and the other is a sort of hydrogen atom dissolved in the metal, being situated inside but close to the electronic surface, as called by him r- and s-adatoms respectively[14]. It has thus been concluded that each lattice plane provides a group of physically identical sites for r-adatoms and such for s-adatoms as well, which are each equal in number to metal atoms on the lattice plane[14], that the energy of a single isolated r-adatom as well as that of single isolated s-adatom depends on the kind of the lattice plane, which it rests upon, that r-adatoms repulse each other even stronger than estimated previously by OKAMOTO, HORIUTI and HIROTA as exchange repulsion[4] and that the lattice imperfections, *i.e.* steps, kinks and defects furnish sites of s-adatom of extraordinary low energy or of such high heat of adsorption[14,15].

The sites for r-adatoms and those for s-adatoms will be called s-sites and r-sites respectively and the model thus elaborated termed the crystal plane model in what follows. The present note is concerned with the review of increasing evidences for the latter model.

GERMER *et al.*[16] have observed by means of slow electron diffraction the (110)-, (100)- and (111)-lattice planes of metal atoms each associated with a hydrogen adatom on f.c.c. nickel crystal and estimated from the vanishing temperatures of the diffraction patterns of the respective lattice planes that the heat of dissociative adsorption of hydrogen is about 28 Kcal per mol hydrogen gas on (110)-lattice plane, considerably lower on (100)- and still lower on (111)- lattice plane. GOMER *et al.*[17] have arrived at quite a similar conclusion from their observation of nickel covered by hydrogen by means of field emission microscope, showing, besides, that a few percent of the whole sites are associated with extraordinarily high a heat of adsorption.

These results confirm the crystal plane model and the relative magnitudes of heat of adsorption of the respective lattice planes, which are derived from the model as did previously theoretically by OKAMOTO, HORIUTI and HIROTA[4] or more closely recently by HORIUTI and TOYA[15]. They are on the other hand in conformity with the previous result of KWAN[18], that the heat of adsorption derived from observed isotherm is 26 Kcal per mol hydrogen gas at low coverage and decreases slowly with increase of coverage, as it should according to the crystal plane model due to the repulsive interactions ; the sites of extraordinarily

high heat of adsorption due to lattice imperfections, if any, escaped his measurements[18]. Positive evidences for the extraordinarily high heat of adsorption is provided by the recent observation of RIDEAL and SWEETT[19] on evaporated nickel film. They have found[19] that the heat of adsorption amounts initially to *ca.* 32 Kcal per mol hydrogen gas at extremely low coverage but drops off quite steeply to *ca.* 27 Kcal at *ca.* 2% coverage and then further slowly with increase of coverage.

Present authors have afforded further evidences for the crystal plane model by statistical-mechanical calculations as follows. The adsorption isotherms of hydrogen on nickel[20] at different temperatures have thus been worked out allowing for the repulsive potential greater than that estimated by OKAMOTO, HORIUTI and HIROTA[4] in accordance with the theoretical conclusion mentioned above[14] over the ranges of temperature and pressure, where hydrogen is preferentially adsorbed on (110)-lattice plane as mentioned above. The theoretical isotherms thus obtained[20] have been found in concordance with those observed by KINUYAMA and KWAN[11] and by quantitatively adjusting the former to the latter, the magnitude of the repulsive potential has been fixed at *ca.* 1.2 times as large as that of the previous estimation[4], and the number of r- or s-sites on (110)-lattice plane determined at 0.4×10^{15} per cm^2 of BET-area, which corresponds to *ca.* one third of the unit BET-area. On the basis of this magnitude of the repulsive potential, the present authors have deduced the entropy of adatom on nickel[21], which is found in good agreement with that derived from the isotherms observed by RIDEAL and SWEETT[19].

In conclusion, some comments might be made upon the appearance of (110)-lattice plane, which is verified by the various results mentioned above, nevertheless argued against on the ground of its thermodynamic instability. The adsorbent in question, *i.e.* reduced nickel powder or evaporated film of nickel, is by no means in thermodynamic equilibrium for itself, in which case it should be reduced to a compact block of single crystal. They are actually in a frozen transient state instead, where the appearance of the unstable lattice plane (110) is quite possible.

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