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STATES OF SURFACE HYDROGEN UNDER REACTION CONDITIONS OF THE FISCHER-TROPSCH SYNTHESIS

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The reaction of hydrogen with Fe surfaces was observed by the ellipsometric method at 77 K to 500 °C under H_2 pressures of 10^{-3} Torr (0.1 Pa) to 500 Torr (7×10^4 Pa). The ellipsometric analysis reveals no existence of adsorbed hydrogen on the surface above 400 °C; hydrogen seems to be alternatively absorbed into the subsurface region of two to three atomic layers. It is concluded that the subsurface hydrogen is specific to the high temperature and the high pressure owing to strained and roughened Fe surfaces as well as the equilibrium with gas phase hydrogen. Absence of adsorbed hydrogen is indicated as well in the ellipsometric response to the hydrogenation reaction of surface carbon species on Fe surfaces.

1. Introduction

The microscopic analysis of the state of hydrogen on catalyst surfaces is a worrying matter at high temperatures under high gas pressures. It has been hence practiced little so far, even though it is of crucial importance to understand the mechanism of hydrogenation reactions. Rapid chemical reactions proceed with fully accommodating molecular structures to the reaction environment to break and form bonds and to transfer energies and momenta. The well-known Eley-Rideal and Langmuir-Hinshelwood mechanisms are limitedly applicable to a part of heterogeneous catalytic reactions. Since hydrogen atom is especially small and known to rest in subsurface sites of metals [1–3] hydrogenation reactions in the FT synthesis may take place in more diverse manners with surface hydrogen under high temperature and high pressure conditions.

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In this paper we intend to characterize the property of surface hydrogen on Fe catalysts on the basis of ellipsometry experiments which were performed from 77 K to 500 ° C under UHV to 500 Torr (7×10^4 Pa) of H_2 gas pressures. Indeed we know very little the state of hydrogen under the FT synthesis. The ellipsometric response to the known states of adsorbed hydrogen [4] at low temperatures and in UHV will be compared with that under high temperature and high pressure conditions. Although the ellipsometry [5,6] is an advantageous optical method to observe thin surface layers without interference with ambient gas phase, it is difficult to interpret the observed effects uniquely. Therefore, comparison of ellipsometric responses under different conditions becomes crucial for the correct interpretation as we will do in what follows. It will become obvious that the known states of surface hydrogen under UHV conditions help little to understand the surface hydrogen in the FT synthesis.

2. Ellipsometry experiments and analysis

We have made two ways of the ellipsometric observation. One is low-pressure and low-temperature experiments with using evaporated Fe films and a manual type ellipsometer installed a He-Ne near infrared laser ($\lambda = 1152$ nm) as the light source. Details of the experimental procedure were reported elsewhere [7,8]. The observation of electrical resistance of the films was made simultaneously. Hydrogen gas was dosed stepwise to the surface within the pressure of 10^{-4} to 10^{-1} Pa and the adsorbed amount was determined by monitoring increments of the film resistance. The heat of adsorption and the work function were measured by using Fe films evaporated on the inner wall of a spherical cell made of pyrex glass. The other ellipsometry measurement was performed at high temperatures and high pressures of hydrogen gas by using an automated rotating analyzer ellipsometer [9,10] with using an Ar laser ($\lambda = 514$ nm). The Fe samples were of plate form which were reduced completely by using dry and wet hydrogen gases of one atmospheric pressure at 800 ° C. The details of the experiments were reported in refs. [11–14].

The ellipsometric response is expressed by two parameters of Δ and ψ, which are defined by $r_p/r_s = \tan \psi \exp(i\Delta)$, where r_p and r_s are the amplitude reflectance of p- and s-polarized light, respectively; ψ is called the amplitude ratio, and Δ, the phase difference [15]. Since the reflectance is a function of the dielectric function ε of solid, Δ and ψ observed from a clean iron surface determine the complex dielectric function of the bulk iron as measured to be $\varepsilon = -7.1-27i$ at $\lambda = 514$ nm. The observed ε is close to literature values [16] which vary depending upon crystallinity, conductivity, surface cleanliness as well as surface roughness. A surface reaction may cause Δ and ψ to vary owing to the formation of a surface layer, i.e., $\delta\Delta = \Delta(\text{clean}) - \Delta(\text{adsorbed})$, and $\delta\psi = \psi(\text{clean}) - \psi(\text{adsorbed})$, from which one can evaluate the dielectric function of the layer formed and its thickness. The methods of the analysis are given in refs. [5, 11, 17 and 18]. We have made the homogeneous one or two layer model analysis [11] but a qualitative explanation of $\delta\Delta$ and $\delta\psi$ is given here. It is a good criterion for an intuitive understanding of adsorption effects that a monolayer physical adsorption of simple gases induces $\delta\Delta = 0.2$–0.3 degree and a negligibly small and negative $\delta\psi$ [19]. $\delta\Delta$ is usually positive for adsorption phenomena meaning piling up of some material on the surface. $\delta\Delta$ is negative only for the cases: (1) An elimination of some surface layers from the substrate; (2) Absorption of simple gases such as hydrogen into metals; and (3) Adsorption of small molecules on defect sites of a metal surface to smooth the surface. The meaning of $\delta\psi$ is complicated but it is usually much smaller than $\delta\Delta$ for adsorption phenomena. When a strongly light-absorptive surface layer is formed, or when a metal surface is strongly modified by a reaction, $\delta\psi$ varies positively and negatively depending upon the dielectric functions of the surface layer and the substrate. If a subsurface hydrogen is produced on Fe surfaces and if the surface lattice structure is conserved with the subsurface hydrogen, the induced $\delta\Delta$ is expected to be negative and as small as 0.2° per one subsurface layer, and the induced $\delta\psi$ will be negligibly small due to absence of core electrons in H atom.

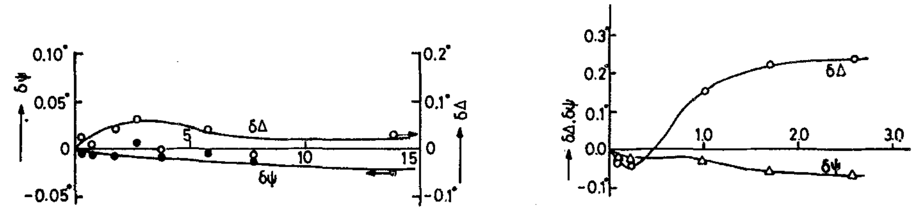
The dielectric function of transition metals is determined by $\varepsilon = \varepsilon_f + \varepsilon_d + \varepsilon_c$, where ε_f is the contribution from free electrons, and ε_d and ε_c, from d- and core-electrons, respectively. The observed dielectric function of Fe $\varepsilon = -7.1-27i$, at $\lambda = 514$ nm is primarily determined by ε_f as expressed by the Drude equation,

$$\varepsilon_f = \left[1 - \left(\frac{\omega_p}{\omega}\right)^2\right] - i\left(\frac{1}{\omega\tau}\right)\left(\frac{\omega_p}{\omega}\right)^2 \tag{1}$$

where $\omega_p^2 = 4\pi N e^2/m^*$ is the plasma frequency and ω, the frequency of the incident light, τ, the mean life time of conduction electrons. When hydrogen is protonic in metal, the real part of ε becomes negatively large due to increase in the number N of free electrons as expected from eq. (1) [20].

3. Results and interpretations

Hydrogen adsorbed on evaporated thin Fe films at 0°C induces the ellipsometric response shown in fig. 1(a) along with changes in the electrical resistance, the work function and the heat of adsorption plotted against the adsorbed amount. Hydrogen is adsorbed irreversibly on the Fe surface under hydrogen pressures less than 10^{-3} Torr (0.1 Pa). The observed effects are found to be similar to those observed for the H/Pd system as seen in fig. 1(b) which was obtained previously [20]. The observed positive $\delta\Delta$ indicates the presence of an adsorbed layer on the Fe surface. It is known that there are few kinds of adsorbed hydrogen on the surface [4,21] as indicated by the coverage dependence of Q, $\Delta\rho$ and $\Delta\phi$. Specific interpretations may be unnecessary for understanding changes



(a) H/Fe at 273 K

(b) H/Pd at 273 K

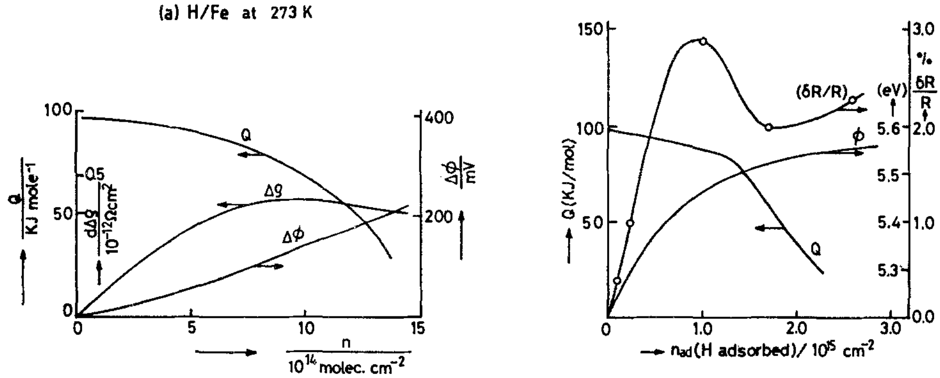
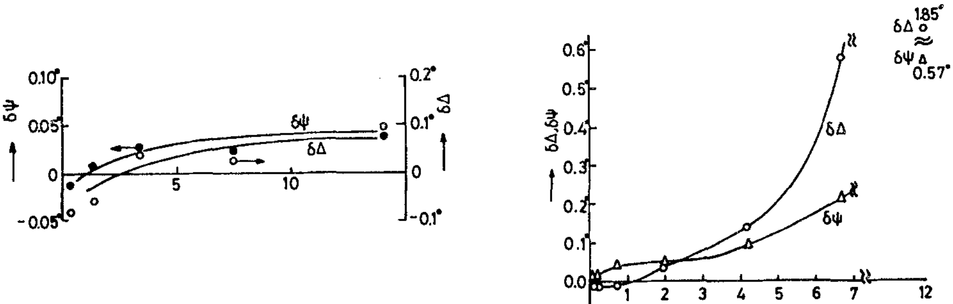


Fig. 1. Ellipsometric responses to adsorption of hydrogen at 273 K on (a) Fe and (b) Pd films along with changes in the film resistivity ρ (or resistance $\delta R/R$), work function ϕ, and heat of adsorption Q. $\Delta\rho$ values are normalized by multiplying the film thickness d [20]. He-Ne laser of $\lambda = 1152$ nm is used for ellipsometry.



(a) H/Fe at 77 K

(b) H/Pd at 77 K

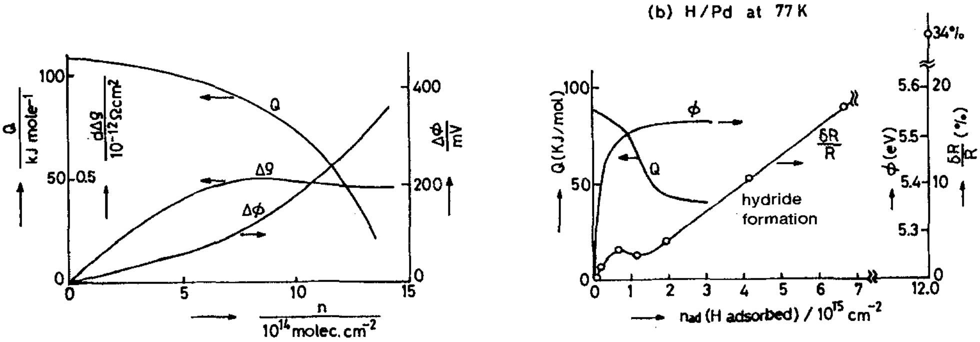


Fig. 2. Ellipsometric responses to adsorption of hydrogen at 77 K on (a) Fe and (b) Pd films along with changes in the film resistivity, work function and heat of adsorption. Note that the very large effects in (b) are caused by the formation of β hydride.

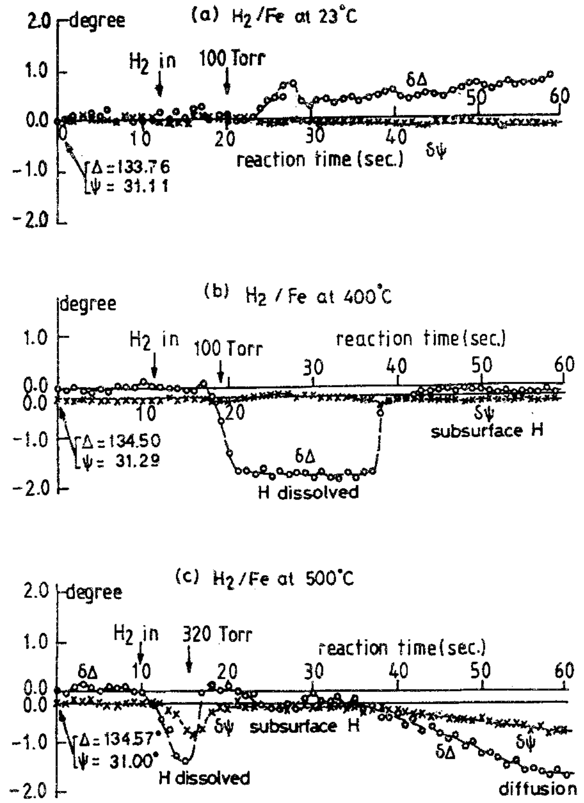
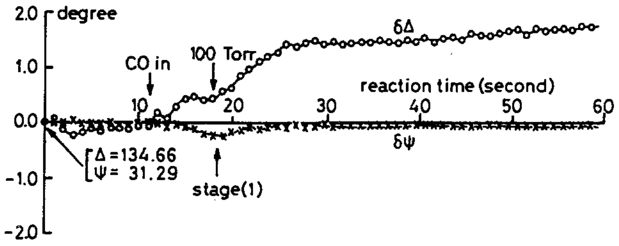


Fig. 3. Ellipsometric responses to reaction of hydrogen on surfaces of Fe plate samples. A microcomputer starts the observation at $t = 0$. H_2 gas has begun to dose at 10 to 12 sec and the pressure becomes steady after 16 to 20 sec.

in Q and $\Delta\phi$ but $\Delta\rho$, which results from the scattering of conduction electrons by adsorbed hydrogen [8]. The ellipsometric response at 77 K shown in fig. 2 confirms the similar effects in the two systems. On Pd films, however, β hydride is formed at high coverages producing the large and positive changes in $\delta\Delta$ and $\delta\psi$ [20].

Hydrogen adsorbed on the surface of the polycrystalline Fe plates at 23 ° C and higher H_2 pressures produces the ellipsometric response shown in fig. 3, which is compared with those at 400 ° C and 500 ° C. Here hydrogen gas is dosed to the Fe surface at about 10 sec after starting the observation by a microcomputer and then the adsorbed hydrogen is equilibrated with gas phase hydrogen of 200 Torr. The responses to hydrogen at 400 ° C and 500 ° C are quite different from that at 23 ° C. There is no doubt an adsorbed layer of hydrogen [4,21–24] on Fe at 23 ° C, which consists of atomic H^+ and H^-, as well as molecular H_2^+ and H_2. However, at the high temperatures there may be no adsorbed hydrogen on the Fe surface, otherwise hydrogen atoms are possibly dissolved into the Fe lattice because of the

(a) CO/Fe at 400 °C



(b) H_2/C/Fe at 400 °C

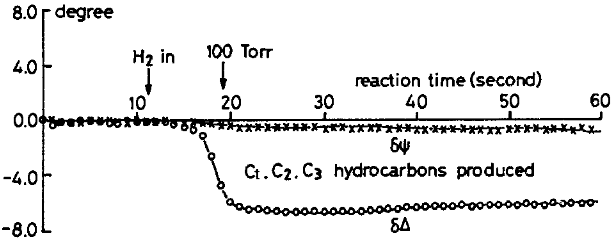


Fig. 4. Ellipsometric reaction time courses on Fe surfaces. (a) Reaction of CO gas with a clean Fe surface to produce carbon species. (b) Hydrogenation reaction of the carbon species with H_2 gas at 400 ° C.

large and negative $\delta\Delta$. Though the absorbed hydrogen in Fe seems to form a dissolved layer at 400 ° C, it is unstable so that it disappears suddenly as seen at the reaction time of 38 sec resulting in the formations of a subsurface layer of hydrogen after 40 sec with the small and negative $\delta\Delta$ as observed. The layer model analysis concludes $\varepsilon = -9.5$–$33i$ for the H dissolved layer and its thickness $D = 2.8$ nm at the stage of 40 sec. The obtained dielectric function is understood by increase in the conduction electrons by 29% due to protonic hydrogen. The thickness of the subsurface hydrogen layer is one to two atomic layers from $\delta\Delta = -0.25°$. At 500 ° C, on the other hand, the dissolved hydrogen may produce a reconstructed surface layer because of the large $\delta\psi$ but it is also unstable and disappears soon. Then the H atoms form a subsurface hydrogen layer of two atomic layers ($\delta\Delta = -0.38°$ at $t = 35$ sec) and start to diffuse into the interior producing the large $\delta\Delta$ and $\delta\psi$ at the later stage.

On the basis of the above result, we analyze the ellipsometric response to the hydrogenation of carbon on Fe catalysts. We produced carbon species on the Fe surface by the Boudouard reaction at 400 ° C, of which ellipsometric response is shown in fig. 4(a). Carbon atoms deposited from CO molecules react with Fe atoms forming a carbidic carbon layer of 0.4 nm at stage (1) which induces the considerable effect on $\delta\psi$ as well as on $\delta\Delta$, and then an amorphous carbon layer [12,14] is formed on it inducing the large increase of $\delta\Delta$. It should be mentioned that the increase in $\delta\Delta$ continues until 15 min and the surface is fully covered by the carbon species. The hydrogenation reaction was then carried out at 400 ° C as

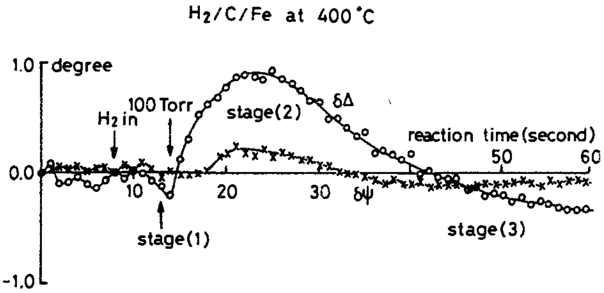


Fig. 5. Ellipsometric response to reaction of surface carbon species [14] covering partially the Fe surface with hydrogen gas at 400 ° C.

shown in fig. 4(b), where a very rapid and large decrease in $\delta\Delta$ is seen due to an elimination of the carbon layer with producing CH_4 molecules which was observed by a quadrupole mass spectrometer. The initial and rapid reaction finishes soon but a slow reaction follows long. In this experiment we obtained no clear evidence how surface hydrogen behaves during the hydrogenation reaction. However, in the initial period of 14 to 16 sec $\delta\Delta = -0.4°$ and $\delta\psi = 0.0°$ are seen possibly due to the formations of subsurface hydrogen. Fig. 5 shows the ellipsometric response to the hydrogenation reaction on an Fe sample whose surface is partially covered with graphitic carbon which emerges from the interior of Fe sample and produces a band of Raman scattering [12] at 1358 cm^{-1}. It is evidenced that a subsurface hydrogen is initially formed at stage (1) and CH compounds are possibly accumulated on the surface in stage (2) and then the desorption of them takes place in stage (3).

4. Discussion

The ellipsometry experiment shown in the preceding section indicates that surface hydrogen on Fe at high temperatures exists under the surface rather than on the surface. We intend hereafter to deliberate such a state of hydrogen. The subsurface sites are defined as the sites between first and second atomic layers on surfaces. The existence of subsurface hydrogen is now established on several kinds of single crystal surfaces [1–3,25–29] such as Pt(111), Pd(111), (100) and (110), Ni(111), Cu(111), (110) and (100), and Ru(0001). One may expect the existence of it on Fe surfaces under certain conditions. Several specific properties have been unveiled concerning subsurface hydrogen. It is often accompanied by a surface lattice reconstruction to reduce strain at the surface [2,3,27]. Adsorbed hydrogen atoms on Ru(0001), Pd(111) and other surfaces are observed in the thermal desorption experiment to desorb no only to the gas phase but also to the subsurface sites [28]. We come to realize that a solid surface possesses two sides of surfaces, i.e., the front and back(sub) surfaces. Furthermore, it is gradually recognized that surface and subsurface hydrogens are stabilized by interacting mainly with conduction electrons rather than with d electrons [25,29]. Hydrogen in iron has been intensively studied from the viewpoint of hydrogen embrittlement [30,31]. Adsorbed hydrogen is found to reduce the surface energy(tension) and release stresses near the surface [32]. The adsorbed hydrogen atoms tend to concentrate around strained regions in iron lattice, and the density of adsorbed hydrogen determines the diffusion rate of hydrogen in iron lattice [33]. When the actual iron surface under the FT synthesis reaction is considered, one becomes aware of the fact that the surface is strained by coexisting several kinds of subproducts in the reaction such as carbides, graphitic carbons, oxides, carbene complexes, OH groups as well as hydrogen species. The surface is so dirty and stressed that the ordinary subsurface sites may not be defined and found. In addition, Fe surface tends to be rough at high temperatures as suggested by the statistical theory of surface lattice dynamics [38]. The roughening temperature t_R is defined by $kT_R/E_{in} = 0.6$, where E_{in} is the nearest neighbor bond energy of an Fe atom on an Fe surface. Since E_{in} is not known, the theory enables us to point out the possibility that Fe surface under the FT reaction becomes rough due to the thermodynamic property. Based on the above discussions, we confine ourselves to define subsurface hydrogen layers on iron surfaces as a thin defective surface layer, where the lattice is stressed and a large concentration of hydrogen is realized. Such a situation of surface hydrogen is schematically illustrated in fig. 6.

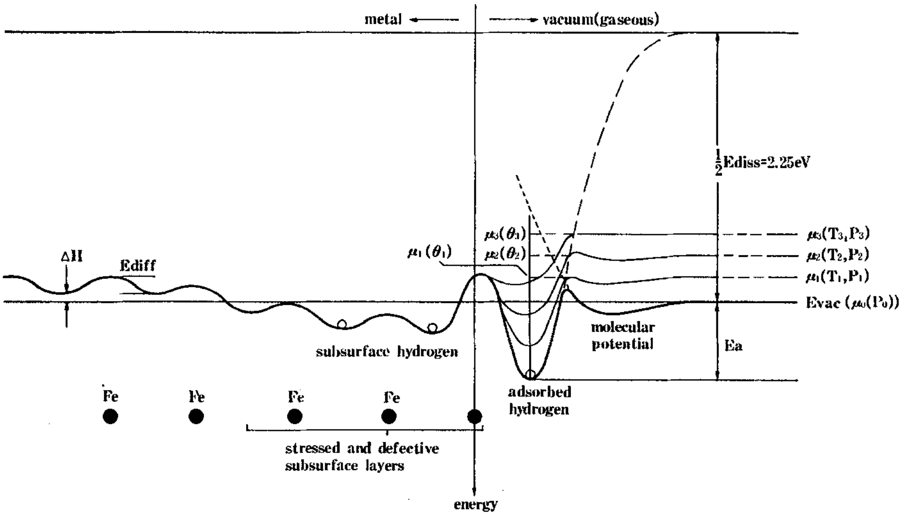


Fig. 6. Schematic illustration of the proposed potential curves for a hydrogen atom trapped at a surface or subsurface site on a roughened and strained Fe surface. Note that the electronic potential energy and the statistical chemical potential μ of hydrogen are simultaneously shown. The origin of the chemical potential of gas phase is fixed at $E_{vac} = 0$ with assuming $\mu_g = kT \ln[(p/kT)h^3/(2\pi mkT)^{3/2}J_g(T)] = 0$, which is equivalent to a low H_2 gas pressure of $p_0 = kT(2\pi mkT)^{3/2}J_g(T)/h^3$.

Recently a theory called embedded atom method (EAM) is developed by Daw et al. [34,35]. The stability of an adsorbed atom is determined by the embedded energy of the atom immersed in the electron sea of metal and by repulsive pair potentials of ion cores. It is shown that the potential energy of a subsurface hydrogen is almost the same as that of adsorbed hydrogen on Pd(111) and becomes lower when the hydrogen coverage becomes higher [36], and further adsorbed hydrogen weakens the metallic bond and reduces stresses near the surface [37]. The EAM theory supports the idea shown in fig. 6.

The effect of ambient hydrogen pressure on the state of adsorbed hydrogen on Fe surface is reviewed. The instability of adsorbed hydrogen at high temperatures in equilibrium with gas phase hydrogen will be rationalized. Underlying assumptions are that adsorbed hydrogen at 400 ° C under one atmospheric pressure is atomic, weakly adsorbed and mobile; it interacts repulsively with each other; the adsorbed layer is equilibrated with the gas phase. The available surface area may be limited due to the other species occupying the surface. According to the standard statistical calculation of two dimensional free gas with the volume exclusion effect [39] among adsorbed hydrogen and an approximation of the nearest neighbor interaction [39,40], one obtains the chemical potential of an adsorbed H atom as

$$\mu = -\left(E_\mathrm{a} = \frac{\alpha}{a_0}\theta\right)\left(\frac{\theta}{1-\theta}\right)\left[\ln\left(\frac{\theta}{1-\theta}\right) + K_1\right] \tag{2}$$

with

$$K_1 = \ln\left[\frac{h^2}{2\pi mkT}\,\frac{1}{a_0 J_\mathrm{ad}(T)}\right] \tag{3}$$

where a_0, the specific area(volume) of an adsorbed hydrogen and $a = A/N_\mathrm{a}$ with surface area A and the number N_a of adsorbed H atoms; $J_\mathrm{ad}(T)$, the internal partition function of adsorbed hydrogen, $\theta = a_0/a$, the coverage; E_a, the adsorption energy and α, an interaction parameter between two hydrogen atoms. The coverage θ is determined by the condition $\mu_\mathrm{gas} = 2\mu_\mathrm{ad}$ yielding

$$p^{1/2} = K_2\left(\frac{\theta}{1-\theta}\right)\exp\left(\frac{\theta}{1-\theta}\right)\exp\left[-\left(\frac{E_\mathrm{a}}{kT} + \frac{\alpha\theta}{a_0 kT}\right)\right] \tag{4}$$

where p is the pressure of gaseous hydrogen and K_2 is a constant similar to K_1. It is emphasized in eq. (4) that θ is strongly restricted to be small by the factor $\exp(\theta/(1-\theta))$ compared with the case of the localized adsorption [39,40]. In addition, remembering the fact that the iron surface under the FT reaction is covered by several surface species, the factor $(1-\theta)$ in eqs. (2) and (4) can be approximately replaced with $(1-\theta_0-\theta)$, where θ_0 is the coverage occupied by other surface species which makes the coverage of hydrogen further small. The above discussion enables us to conclude for the mobile hydrogen atoms at high temperatures and high pressures that their state is unstable and their number is very limited. This situation is explained in fig. 6, where it is understood that the adsorbed state is almost vacant and the subsurface sites become occupied.

5. Conclusion

The adsorbed states of hydrogen on Fe surfaces were analyzed by the ellipsometric method at temperatures from 77 K to 500 ° C. The ellipsometric responses at high temperatures are compared with those at low temperatures, which leads to the conclusion that hydrogen is adsorbed very little on Fe surfaces at 400 ° C and 500 ° C, though hydrogen molecules collide frequently at the surface. This fact can be understood on the basis of (a) mobile adsorbates in equilibrium with gas phase, and (b) subsurface hydrogen is created in a strained and defective surface layer. The above ideas are supported by the fundamental statistical dynamics and the recent EAM theory. From the above conclusion it is strongly suggested that the surface carbon species on Fe catalysts in the FT synthesis reaction are attacked by hydrogen from the metal side to produce hydrocarbon species.

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