Catalyst Surface Coverages of Adsorbed Species in the Nickel-Catalyzed Ethylene Hydrogenation

ISAO MATSUZAKI AND AKIO TADA*

From the Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, Japan

Three different views have been expressed about the degree to which the surface of nickel is covered by adsorbed species during the hydrogenation of ethylene: (1) coverage varies with reaction temperature and reactant pressures, (2) invariably full coverage, and (3) invariably negligible coverage. We have examined the validity of these views by the analysis of data obtained in 1934 and of recent data obtained by us. The 1934 data of Farkas, Farkas, and Rideal for pairs of successive runs of parahydrogen conversion and ethylene hydrogenation using parahydrogen were analyzed on the premise that conversion proceeds via the Bonhoeffer-Farkas mechanism and that hydrogenation proceeds via the associative mechanism. In the recent experiments, pairs of successive runs of equilibration and ethylene hydrogenation using protium and deuterium mixtures were made at 30°, 80°, and 150°C and the data obtained were analyzed in a similar fashion. Our analysis indicates that surface coverage by adsorbed ethylene plus monoadsorbed ethane varies substantially with reaction temperature and reactant pressures.

INTRODUCTION

Even now, independent determination of the identities of adsorbed intermediates and their coverages is sufficiently difficult that kineticists have been compelled to make *ad hoc* assumptions as to structures, coverages, etc., of adsorbed species in the course of kinetic analysis. An example of this sort is the investigation of the nickel-catalyzed ethylene hydrogenation.

Rideal (1), zur Strassen (2), Schwab (3), Farkas, Farkas, and Rideal (4), and Toyama (5) interpreted their kinetic data on the assumption that the catalyst surface is occupied by ethylene and hydrogen of coverages varying with reaction temperature and reactant pressures; Twigg and Rideal (6) and Twigg (7) interpreted their results on the assumption that the catalyst surface is always fully covered by ethylene; while Horiuti (8) applied his statistical mechanical theory of chemical reactions with the

assumption that the catalyst surface is always practically bare. The Horiuti assumption has recently been given semi-quantitative experimental support by Miyahara, Teratani, and Tsumura (9), but the experimental conditions studied by these authors seem too limited to allow generalization.

In view of the important role of coverage by adsorbed species in kinetics, the present authors have reanalyzed former data and added data of a new experiment in an attempt to resolve the obvious incompatibility of the three assumptions mentioned above. We conclude that coverages by ethylene and monoadsorbed ethane vary with reaction temperature and reactant pressures during hydrogenation of ethylene on nickel catalysts.

METHOD OF DATA ANALYSIS

Farkas *et al.* (4) exposed 25 mm of an ortho- and parahydrogen mixture of 45% para content to a nickel catalyst at 20°C and followed the decrease in para. They then allowed 23 mm of a similar ortho- and

* Present address: Chemical Process Engineering Department, Faculty of Technology, Hokkaido University, Sapporo, Japan.

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parahydrogen mixture and 19 mm of ethylene to react on the same catalyst at the same temperature and they followed both the decrease in the total pressure and that in content of para. They ascertained that the partial pressure of ethane had no influence on rate, i.e., ethane acted as an inert diluent. We have analyzed these data for the coverages by adsorbed species during nickel-catalyzed ethylene hydrogenation at 20°C. The procedure for the analysis is described below.

Let us first consider the conversion occurring when an ortho- and parahydrogen mixture of total pressure P_{P_2} mm and parahydrogen fraction $x^{p\text{-}P_2}$ is brought into contact with a nickel catalyst at 20°C, where P_2 denotes protium, i.e., the light hydrogen molecule. From the evidence cited by Trapnell (10), the Bonhoeffer-Farkas mechanism (11)

$$P_2 \rightleftharpoons 2P(a)$$
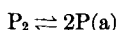
might well be considered the main mechanism responsible for the conversion. Here, (a) denotes the adsorbed state, and the catalyst surface is regarded as uniform for the sake of semiquantitative purpose intended, so that the following equations hold for the conversion in question:

$$(V_{ads})_0 = k_+ P_{P_2}(1 - (\theta_P)_0)^2 \qquad (1)$$

$$(V_{des})_0 = k_-(\theta_P)_0^2 \qquad (2)$$

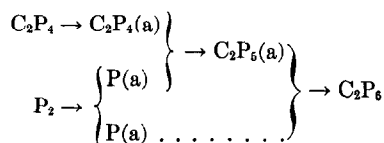$$(V_{ads})_0 = (V_{des})_0 \qquad (3)$$

and

$$P_{P_2}dx^{p\text{-}P_2}/dt = -(V_{ads})_0 x^{p\text{-}P_2} + (V_{des})_0 x_{eq}^{p\text{-}P_2} \qquad (4)$$

where $(V_{ads})_0$ and k_+ are, respectively, the rate of adsorption of hydrogen and its rate constant; $(V_{des})_0$ and k_- are, respectively, the rate of desorption of P(a) and its rate constant; $(\theta_P)_0$ is the coverage of P(a), and $x_{eq}^{p\text{-}P_2}$ is the equilibrium parahydrogen fraction at the temperature concerned. The subscript $_0$ in $(V_{ads})_0$, $(V_{des})_0$, and $(\theta_P)_0$ denotes the absence of ethylene. From Eqs. (3) and (4)

$$(V_{ads})_0 = P_{P_2}(dx^{p\text{-}P_2}/dt)/(x_{eq}^{p\text{-}P_2} - x^{p\text{-}P_2}) \qquad (5)$$

Let us next consider the simultaneous

occurrence of conversion and hydrogenation when an ortho- and parahydrogen mixture, of total pressure P_{P_2} mm and parahydrogen fraction $x^{p\text{-}P_2}$, reacts with ethylene at 20°C on the same catalyst as used in the conversion above. Since the associative mechanism put forward by Horiuti and Polanyi (12)

$$P_2 \rightarrow \begin{cases} C_2P_4 \rightarrow C_2P_4(a) \\ \begin{cases} P(a) \\ P(a) \dots \dots \end{cases} \end{cases} \rightarrow C_2P_6(a) \Bigg\} \rightarrow C_2P_6$$

has been shown to be capable of accounting for various aspects relevant to the nickel-catalyzed ethylene hydrogenation (8), the present authors will adopt this mechanism as the one mainly responsible for ethylene hydrogenation. According to this mechanism we obtain the following equations for the reactions of ethylene, ortho-, and parahydrogen.

$$(V_{ads})_E = k_+ P_{P_2} \times [1 - (\theta_P)_E - \theta_{El} - \theta_{Et}]^2 \qquad (6)$$

$$(V_{des})_E = k_-(\theta_P)_E^2 \qquad (7)$$

$$(V_{des})_E = (V_{ads})_E - V_P \qquad (8)$$

and

$$d(P_{P_2}x^{p\text{-}P_2})/dt = P_{P_2} dx^{p\text{-}P_2}/dt - V_P x^{p\text{-}P_2}$$
$$= -(V_{ads})_E x^{p\text{-}P_2} + (V_{des})_E x_{eq}^{p\text{-}P_2} \qquad (9)$$

where θ_{El} and θ_{Et} are the coverages of $C_2P_4(a)$ and $C_2P_5(a)$, respectively; $(V_{ads})_E$, $(V_{des})_E$, and $(\theta_P)_E$ are quantities similar to $(V_{ads})_0$, $(V_{des})_0$, and $(\theta_P)_0$ with the subscript $_E$ implying the presence of ethylene; and $V_P(\equiv -dP_{P_2}/dt)$ is the rate of hydrogenation. From Eqs. (8) and (9)

$$(V_{ads})_E = V_P + P_{P_2}(dx^{p\text{-}P_2}/dt)/(x_{eq}^{p\text{-}P_2} - x^{p\text{-}P_2}) \qquad (10)$$

Dividing both sides of Eq. (2) by Eq. (7) and replacing $(V_{ads})_0$ and $(V_{des})_0$ by Eqs. (3) and (8), respectively;

$$(\theta_P)_E = (\theta_P)_0\{[(V_{ads})_E - V_P]/(V_{ads})_0\}^{1/2} \qquad (11)$$

Dividing both sides of Eq. (1) by Eq. (6) and replacing $(\theta_P)_E$ by Eq. (11)

$$\theta_{El} + \theta_{Et} = 1$$
$$- (\theta_P)_0 \{ [(V_{ads})_E - V_P]/(V_{ads})_0 \}^{1/2}$$
$$- [1 - (\theta_P)_0][(V_{ads})_E/(V_{ads})_0]^{1/2} \quad (12)$$

Equation (12) permits determination of the range of values which $\theta_{El} + \theta_{Et}$ can take, because $(V_{ads})_0$ and $(V_{ads})_E$ are determinable from experimentally measurable quantities by Eqs. (5) and (10) and the values which $(\theta_P)_0$ can take are restricted by the condition $0 < (\theta_P)_0 < 1$.

In the treatment above, we have assumed the enthalpies of adsorption and the rate constants to be independent of coverage. Undoubtedly, this is incorrect and values of $\theta_{El} + \theta_{Et}$ derived from this treatment are subject to error. However, our conclusions will not depend upon small changes in $\theta_{El} + \theta_{Et}$ and we believe the approximation we use to be one suitable to the present purpose.

EXPERIMENTAL

Experiments were carried out at three reaction temperatures: 30°, 80°, and 150°C. The same clean nickel catalyst was used first to catalyze the equilibration, $P_2 + D_2 = 2PD$, and then the hydrogenation, $P_2 + D_2 + C_2H_4 \rightarrow C_2H_6$, where D denotes deuterium and H is the generic notation for P and D.

The C_2P_4, P_2, and D_2 used were supplied by Takachiho Chemical Co., Ltd., Tokyo, 99.8%, 99.99%, and 99.7% purity being guaranteed, respectively. The catalyst was 99.9% pure nickel wire, 0.1 mm in diameter, supplied by Tanaka Noble Metal Co., Ltd., Tokyo. The mixture of C_2H_4-d and C_2H_6-d, both of $\sim 50\%$ D content, was prepared by allowing 15 mm of C_2P_4 and 45 mm of D_2 to react at 150°C on a nickel catalyst to about 45% completion.

The volume of the apparatus was 300 cc. It consisted essentially of a 100-cc reaction vessel equipped with a preheating tubing, two U-type traps immersed in methanol–Dry Ice mixture, a mercury manometer, and a gas circulation pump of 30 cc volume. A nickel wire sealed into the reaction vessel served as an arm of a Wheatstone bridge, the wire could be heated electrically and its temperature could be measured continuously

from the electric resistance. The length of the wire was 300 cm for reaction at 30°C and 30 cm for those at 80° and 150°C. The two traps, one on either side of the reaction vessel, protected the wire from contact with poisonous matters such as tap grease and mercury vapor. The circulation pump was composed of a cylinder and a piston. The piston had an iron bar sealed in and was driven magnetically by means of several solenoids surrounding the cylinder. The circulation capacity of the pump was determined to be 30 cc/sec by measuring the time required to condense all ethylene by liquid nitrogen from a circulating mixture of hydrogen and ethylene.

The nickel wire was activated by oxidation in 200 mm of oxygen at 600°C followed by reduction in 30 mm of hydrogen at 300°C. It was reactivated in a similar manner when necessary. The reaction vessel was first immersed empty in a thermostated oil bath. The reaction mixture was then expanded from the remainder of the system into the reaction vessel under circulation to initiate the reaction. It was established by measuring the electric resistance of the nickel wire that thermal equilibrium was attained almost instantly after expansion. The progress of hydrogenation was followed by measuring the pressure by means of the mercury manometer observed with a travelling microscope, and that of the conversion, by measuring the P_2–PD–D_2 composition of the gas-phase hydrogen by means of a mass spectrometer. The samples subjected to the mass spectrometric analysis were obtained by withdrawing 3 cc of the reacting mixture at known times and transferring the sample to a 50-cc vessel. Ethylene and ethane were removed by condensation by liquid nitrogen.

The data are analyzed in a manner similar to that in the case of the ortho- and parahydrogen mixtures. The approximation that there would be no isotope effect between P and D will be adopted. All the Eqs. (1)–(12), with the following alterations, are applicable to this case using P_2 and D_2 mixtures.

(1) $(V_{ads})_0$ and $(V_{ads})_E$ are the rates of adsorption of H_2, $(V_{des})_0$ and $(V_{des})_E$ are the rates of desorption of H(a), and θ_{El}

and θ_{Et} are the coverages of $C_2H_4(a)$ and $C_2H_5(a)$, respectively.

(2) The notations $(\theta_P)_0$, $(\theta_P)_E$, P_{P_2}, and V_P, which relate to P, are replaced, respectively, by the notations $(\theta_H)_0$, $(\theta_H)_E$, P_{H_2}, and V_H each defining a similar quantity with respect to H, and the notations x^{p-P_2} and $x_{eq}^{p-P_2}$, which relate to parahydrogen, replaced, respectively, by the notations x^{PD} and x_{eq}^{PD} each defining a similar quantity with respect to PD.

(3) Equations (9) and (10) are substituted for the following two equations:

$$d(P_{H_2}x^{PD})/dt = P_{H_2}\,dx^{PD}/dt - V_H x^{PD}$$
$$= -(V_{ads})_E x^{PD}$$
$$+ [(V_{ads})_E - V_H] \times 2y^D(1 - y^D)$$
$$d(P_{H_2}x^{D_2})/dt = P_{H_2}\,dx^{D_2}/dt - V_H x^{D_2}$$
$$= -(V_{ads})_E x^{D_2}$$
$$+ [(V_{ads})_E - V_H](y^D)^2$$

where y^D is the deuterium atom fraction of H(a) and x^{D_2} is the D_2 fraction of H_2. On solving the two equations above simultaneously one can obtain the value of $(V_{ads})_E$ together with that of y^D.

RESULTS AND DISCUSSION

The result of the data analysis is shown in Table 1. The values of $\theta_{E1} + \theta_{Et}$ in the

table show that when the hydrogenation starts with ethylene and hydrogen of 19 and 23 mm, respectively, the catalyst surface is largely covered by $C_2P_4(a)$ and $C_2P_5(a)$ until the ethylene pressure has decreased to about 1 mm, at which point the surface changes abruptly to a sparse coverage. Hence it follows that surface coverage by $C_2P_4(a)$ and $C_2P_5(a)$ varies with the reactant pressures. That the pairs of the data used in our analysis refer to the same clean catalyst, is evident from the description given below about the experiment at 30°C. It should be added here that a similar pair of experimental data was obtained at -78°C by Twigg (7) and that the analysis of these data led to a similar conclusion with respect to variation of $\theta_{E1} + \theta_{Et}$ with reactant pressures.

The experiment at 30°C consisted not merely of a pair of successive runs of equilibration and hydrogenation, but of a more complicated sequence of reactions aimed at assessing the susceptibility of the nickel catalyst to poisoning.

First an equilibration run, $P_2(5\text{ mm}) + D_2(5\text{ mm}) \rightarrow 2PD$, was conducted, where the pressure in the parentheses denotes the initial pressure, $(dx^{PD}/dt)_{t=0} = 0.030/\text{min}$ being obtained. The same catalyst was then

TABLE 1

THE ANALYTICAL RESULTS FROM THE DATA OF FARKAS, FARKAS, AND RIDEAL[a]

Reaction treated:	$p\text{-}P_2 \rightleftharpoons o\text{-}P_2$			$p\text{-}P_2 + o\text{-}P_2 + C_2P_4 \rightarrow C_2P_6$			
React. temp. (°C):		20°			20°		
React. time (min):	0	2.5	5	0	15	30	40
P_{P_2} (mm Hg):	25	25	25	23	15.2	7.8	5.0
Ethylene press. (mm Hg):	—	—	—	19	11.2	3.8	1.0
Ethane press. (mm Hg):	—	—	—	0	7.8	15.2	18.0
$x^{p\text{-}P_2 b}$	0.45	0.365	0.309	0.45	0.435	0.405	0.305
$dx^{p\text{-}P_2}/dt$ (min⁻¹)	—	-0.027	-0.0145	-0.001	-0.0015	-0.0022	-0.016
V_P (mm Hg/min)	—	—	—	0.5	0.5	0.4	0.165
$(V_{ads})_0$ (mm Hg/min)	—	5.86	6.14	5.75[c]	4.47[c]	2.98[c]	2.27[c]
$(V_{des})_0$ (mm Hg/min)	—	—	—	0.615	0.623	0.511	1.621
$\theta_{E1} + \theta_{Et}$							
$\quad(\theta_P)_0 = 0$	—	—	—	0.672	0.626	0.586	0.154
$\quad(\theta_P)_0 = 0.5$	—	—	—	0.765	0.730	0.697	0.177
$\quad(\theta_P)_0 = 1.0$	—	—	—	0.858	0.834	0.807	0.199

[a] Reference (4).

[b] $x_{eq}^{p\text{-}P_2} = 0.25$ at 20°C.

[c] Fajans (13) measured the rates of the ortho- and parahydrogen conversion on a nickel catalyst at 12°C over the range of $P_{P_2} = 0.004$–4.5 mm Hg. Equation (5) applied to these data indicates that $(V_{ads})_0 \propto (P_{P_2})^{0.6}$. On the basis of this the listed values were calculated using $(V_{ads})_0$ (at $P_{P_2} = 25$ mm) $= 6.0$ (average) as obtained from the listed values of $(V_{ads})_0$ for the conversion run.

used for a hydrogenation run, $P_2(5 \text{ mm}) + D_2(5 \text{ mm}) + C_2P_4(10 \text{ mm}) \rightarrow C_2H_6$, followed by a repeat equilibration run, in which $(dx^{PD}/dt)_{t=0} = 0.0025/\text{min}$. The large loss in activity between the two equilibration runs indicates that some adsorbed matter from hydrogenation runs is not rapidly removed from the nickel surface in a flow of pure hydrogen. After having reactivated the catalyst, we made a series of runs as follows: an equilibration run, $P_2(3.5 \text{ mm}) + D_2(3.5 \text{ mm}) \rightarrow 2PD$, was conducted and $(dx^{PD}/dt)_{t=0} = 0.022/\text{min}$ obtained; then a hydrogenation run, $P_2(5.28 \text{ mm}) + D_2(5.28 \text{ mm}) + C_2P_4(10.52 \text{ mm}) \rightarrow C_2H_6$ was followed for 57 min until P_{H_2} decreased to 7.22 mm. The C₂H₄ and C₂H₆ were then condensed out by immersing a U section of the circulation path in liquid nitrogen and equilibration was followed for a while. Hydrogenation was again studied by removing the liquid nitrogen. Values thus obtained were

just before condensation:

$$V_H = 0.046 \text{ mm Hg/min}$$

just after condensation:

$$dx^{PD}/dt = 0.0226/\text{min}$$
$$x^{PD} = 0.05$$
$$x^{PD}_{eq} \doteq 0.5$$

just after the recovery:

$$V_H = 0.046 \text{ mm Hg/min}$$

These values, coupled with the above-mentioned finding that poisonous matter is not easily removed by hydrogen, indicate that the poisonous matter is not formed instantly by contact of the catalyst with an ethylene and hydrogen mixture and that the successive operation of condensation and reevaporation of ethylene and ethane causes no change in the catalytic activity. Consequently, the values of $(V_{ads})_E$ and $(V_{ads})_0$, calculated from the data obtained just before and after the condensation, respectively, may be regarded as referring to the same clean catalyst and the same P_{H_2} value (4% decrease in pressure resulting from the condensation operation may well be neglected). Hence, the values can be used for the evaluation of $\theta_{El} + \theta_{Et}$, to which Table 2 refers. It is evident from the values of $\theta_{El} + \theta_{Et}$ that over 50% of the catalyst surface is certainly covered by C₂H₄(a) and C₂H₅(a) at 30°C and $P_{H_2} = P_{C_2H_4} \approx 7$ mm. The value of y^D needs comment. As shown in the table, the value of y^D exceeds 0.5 because of neglect of isotope effect between P and D in the analytical procedure. The increase in deuterium fraction of H₂ (see the table) shows that an

TABLE 2
ANALYSIS OF THE DATA AT 30°, 80°, AND 150°C

Reaction treated:	P₂ + D₂ + C₂P₄ → C₂H₆		P₂ + D₂ = 2PD	P₂ + D₂ = 2PD	P₂ + PD + D₂ + C₂P₄ → C₂H₆	P₂ + D₂ = 2PD	P₂ + D₂ + C₂H₄ → C₂H₆
React. temp. (°C):	30°		30°	80°	80°	150°	150°
React. time (min):	0	57	0	0	0	0	0
P_{P_2} (mm Hg):	5.28	—	—	5.22	—	5.12	5.04
D₂ press. (mm Hg):	5.28	—	—	5.22	—	5.03	5.01
P_{H_2} (mm Hg):	—	7.22	—	10.44	10.44	10.15	10.05
Ethylene press. (mm Hg):	10.52	7.17	—	—	10.56	—	10.6[b]
Ethane press. (mm Hg):	—	3.17	—	—	0	—	6.3
x^{PD}	0[a]	0.05[a]	0.05[a]	0	0.105	0	0
x^{D_2}	0.5[a]	0.516[a]	0.516[a]	0.5	0.440	0.496	0.502
dx^{PD}/dt (min⁻¹)	—	0.0015	0.0226	0.0582	0.0073	0.090	0.070
dx^{D_2}/dt (min⁻¹)	—	0.00064	−0.0113	−0.0291	−0.0037	−0.045	−0.031
V_H (mm Hg/min)	—	0.046	—	—	0.0520	—	0.144
$(V_{ads})_0$ (mm Hg/min)	—	—	0.363	0.304	—	1.82	—
$(V_{ads})_E$ (mm Hg/min)	—	0.0865	—	—	0.245	—	1.562
y^D	—	0.788	—	—	0.499	—	0.531
$\theta_{El} + \theta_{Et}$							
$\quad (\theta_H)_0 = 0$	—	0.512	—	—	0.102	—	0.075
$\quad (\theta_H)_0 = 0.5$	—	0.589	—	—	0.153	—	0.096
$\quad (\theta_H)_0 = 1.0$	—	0.666	—	—	0.203	—	0.118

[a] $x^{PD}_{eq} = 0.5$ for the H₂ listed.

[b] A mixture of C₂H₄-d and C₂H₆-d used.

isotope effect is actually present. We should, therefore, take into account the isotope effect between P and D in attempting to draw a more quantitative conclusion from such an experimental application of deuterium as this.

At 80° and at 150°C equilibration runs with $P_{H_2} \approx 10$ mm were made. They were followed by hydrogenation runs with $P_{H_2} = P_{C_2H_4} \approx 10$ mm and the data obtained were analyzed as shown in Table 2. In contrast with the case at 30°C the value of $\theta_{E1} + \theta_{Et}$ is very small, indicating sparse coverages of the catalyst surface. From the value of $\theta_{E1} + \theta_{Et}$ listed in Table 2, which may each be considered as referring to the same reaction condition, $P_{H_2} = P_{C_2H_4} = 10$ mm, it is obvious that the coverages of $C_2H_4(a)$ and $C_2H_5(a)$ are highly dependent upon reaction temperature.

The combined results of Tables 1 and 2 unequivocally lead to the conclusion that the catalyst surface is neither fully covered by ethylene, nor nearly bare, but is occupied by ethylene and monoadsorbed ethane to a degree which varies with temperature and reactant pressures. This accords with the assumption of Rideal (1), zur Strassen (2), Schwab (3), Farkas, Farkas, and Rideal (4), and Toyama (5) that the coverages by adsorbed species vary with reaction condition, and disagrees with the assumptions of Twigg and Rideal (6), Twigg (7), and Horiuti (8).

It should be noted in connection with the well-known phenomenon of an optimum temperature in the nickel-catalyzed ethylene hydrogenation that the optimum temperature for hydrogen pressure = ethylene pressure = 10 mm is about 130°C (14), and that, as seen from Table 2, at this temperature the catalyst surface changes to one which is practically bare with respect to $C_2H_4(a)$ and $C_2H_5(a)$. The following theories for the occurrence of an optimum temperature have been proposed: zur Strassen (2), Schwab (3), Farkas et al. (4) and so on attributed it to the vaporization of adsorbed ethylene; Twigg and Rideal (6) to the vaporization of the van der Waals' adsorbed hydrogen from the saturated adsorption layer of ethylene; and Horiuti (8), on the

assumption of bare catalyst surface, to the switchover of the rate-determining step from the step $H_2 \rightarrow 2H(a)$ with positive activation energy to the step $C_2H_5(a) + H(a) \rightarrow C_2H_6$ with negative one. Since the value of $\theta_{E1} + \theta_{Et}$ has been shown to change appreciably with temperature and reactant pressures, the second and third views should be reexamined with consideration of changes in coverages by all species $C_2H_4(a)$, $C_2H_5(a)$, and $H(a)$ and the first should be reexamined with consideration of the nature of the adsorbed species.

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