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RESEARCH ON THE PURE IRON AND AMMONIA SYNTHETIC CATALYST BY MEANS OF HYDROGEN ADSORPTION.

By Takao KWAN.

In the previous paper¹⁾ the present author has concluded that the surface of nickel or cobalt catalyst was homogeneous or its every portion was equally available for the hydrogen adsorption on the basis of the fact that the covered fraction calculated statistical mechanically from the observed differential heat was found coincident with that given by the surface area determined by B.E.T. method and the observed adsorbed quantity.

In the case of ammonia synthetic iron catalyst containing promoters such as K_2O or Al_2O_3 , the nature of the surface may be more or less complicated compared with that of pure metallic catalyst. BRUNAUER and EMMETT²⁾ concluded from the observation of adsorption of carbon monoxide or carbon dioxide on ammonia synthetic catalyst promoted by K_2O and Al_2O_3 that the latter promoters covered 50~75 percent of the catalyst's surface.

It is the purpose of the present paper to investigate the surface nature of the ammonia synthetic catalyst in comparison with that of pure iron by extending the method developed in the previous work.

Materials and Experimental Procedure

Pure iron; Two grams magnetite powder from "Tokio Kagaku Yakuhi Co." (Tokio Chemicals Co.) was reduced at 500°C in the stream of atmospheric pressure hydrogen for one week and then transferred in a Terex reaction vessel and the latter fused to the vacuum apparatus for measurement of adsorption.

The catalyst was further reduced at the same temperature statically in the atmosphere of several cm Hg hydrogen, condensing out the water produced into a liquid air trap attached to the reaction vessel.

In the mean time the reaction vessel was occasionally evacuated and

1) KWAN; This Journal. p. 81

2) BRUNAUER and EMMETT; J. Am. Chem. Soc., 64 (1940) 1732.

charged with fresh hydrogen. It took thus 6 months until the pressure decrease of hydrogen in the course of 24 hours became imperceptible by means of McLEOD gauge.

Ammonia synthetic catalyst; Two grams I.G. catalyst with a few percent of K_2O and Al_2O_3 as promoters was similarly reduced statically as in the case of pure iron without preliminary reduction in hydrogen stream there. It took several months for the catalyst to be reduced to the same extent as in the above case. The quantity of hydrogen consumed was found almost equivalent to the oxygen content of the magnetite.

Hydrogen; Hydrogen formed from zinc and sulphuric acid was passed through liquid air trap, platinized asbestos heated at $300^\circ C$ and then through liquid air trap again for purification.

The apparatus and the procedure for measurement of adsorption are almost the same as reported in the foregoing two papers.

Experimental Results

Surface area of the catalyst;

Surface area of the pure iron as well as of the ammonia synthetic catalyst was determined by B.E.T. method at several stages along with the progress of reduction. The results are shown in Fig. 1.

Fig. 1 shows that the surface area of the ammonia synthetic catalyst was increased about ten times in the course of the reduction i.e. from $0,4 \times 10^4 \text{ cm}^2$ area of the unreduced material to $4,2 \times 10^4 \text{ cm}^2$ of the completely reduced material whereas in the case of iron the area remained almost constant at $4,8 \times 10^4 \text{ cm}^2$.

Adsorption isotherms and differential heat of adsorption;

Each catalyst was evacuated before the measurement of hydrogen adsorption at $500^\circ C$ for one hour and then maintained at a desired temperature of adsorption measurement.

Measured quantity of hydrogen was then admitted into the reaction

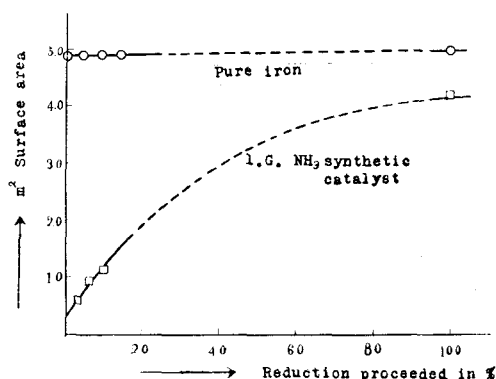


Fig. 1 Changes in surface area along with the progress of reduction.

vessel containing the catalyst. The rate of adsorption was found more or less small in any case of these catalyst compared with that of nickel and it took several hours until the pressure attained a constant value. The equilibrium pressure was now determined approaching the latter both from desorption and adsorption side similarly as in the previous cases*).

After the adsorption equilibrium was thus attained and appropriate pressure determined additional portions of hydrogen were now successively admitted into the reaction vessel and the corresponding equilibrium pressures were determined in respective cases similarly as above.

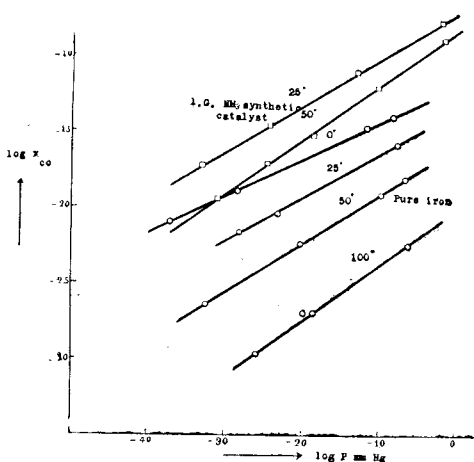


Fig. 2 Adsorption isotherms of hydrogen on pure iron or ammonia synthetic catalyst.

Calculating now the adsorbed quantity from the equilibrium pressure and the known quantity of admitted gas, adsorption isotherms were thus determined at temperatures 0°, 25°, 50° and 100°C for pure iron and at 25° and 50°C for ammonia synthetic catalyst, the equilibrium pressures being lower than 1 mm Hg both in the cases. The results are shown by the plot of logarithm of the adsorbed quantity x in cc N.T.P. against logarithm of the equilibrium pressure P mm Hg in Fig. 2.

It was found as shown in Fig. 2 that the adsorbed quantity per unit area of the ammonia synthetic catalyst was about five times as large as that of pure iron.

Differential heat of adsorption $\Delta\varepsilon$ at different degree of adsorption was calculated according to the usual equation,

$$\Delta\varepsilon = RT^2 \left(\frac{\partial \log P}{\partial T} \right)_x$$

The covered fraction of the surface was on the other hand calculated from the adsorbed quantity of hydrogen and the observed B.E.T. area, assuming that there exist $1 \times 10^5/\text{cm}^2$ surface Fe atoms in both cases,

*) Cf, p. 86

irrespective of the surface nature, each one being capable of adsorbing one hydrogen atom.

Fig. 3 shows the plot of $\Delta\varepsilon$ against the above calculated coverage. As seen from the Figure the differential heat of adsorption decreases monotonously with increasing adsorption from 17,5 Kcal/mole at $\theta = 0,01$ to about 5 Kcal/mole at $\theta = 0,1$ in the case of the ammonia synthetic catalyst and following almost the same line of decrease from 17,5 Kcal at $\theta = 0,005$ to 13 Kcal at $\theta = 0,03$ in the case of pure iron. Such an appreciable decrease of the heat in the case of nickel or cobalt catalyst at so small low coverage was not observed.

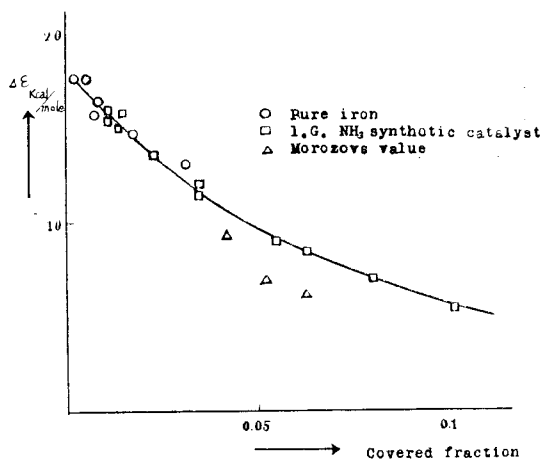


Fig. 3 Differential heat of adsorption of hydrogen on pure iron or ammonia synthetic catalyst.

Heat of adsorption of hydrogen on pure iron reported by Morozov³⁾ who determined it from the adsorption isotherm observed at higher pressure than that of the present case is about 7 Kcal/mole which appears to be natural result of extrapolation from the present observation to that condition of the measurement.

Statistical Mechanical Consideration

The covered fraction of the surface at a very low pressure was now calculated statistical mechanically similarly as in the case of nickel and cobalt catalyst putting the observed value $\Delta\varepsilon = 17,5$ Kcal/mole assuming a single crystal plane exposed for the adsorption, the result being 70 or 14 times respectively for the case of pure iron or ammonia synthetic catalyst, as large as that derived from the B.E.T. area and the adsorbed quantity.

This result markedly contrasted with the corresponding factor unity in the case of nickel or cobalt catalyst reported previously on which basis the homogeneity of the catalyst's surface in the latter cases has

3) MOROZOV; Trans. Far. Soc., 31 (1935) 659,

been concluded. Assuming now alternatively two kinds of crystal plane are exposed in the present case which together are measured as B.E.T. area the present results were analysed as follows:

The heat of adsorption $\Delta\varepsilon$ which remains almost constant over an appreciable range of temperature as observed is expressed as described elsewhere*) in terms of the chemical potential μ^{H_2} of hydrogen gas and that of adsorbed hydrogen atom $H(a)$ as that,

$$\Delta\varepsilon = \mu^{H_2} - T \left(\frac{\partial \mu^{H_2}}{\partial T} \right)_p - 2 \left\{ \mu^{H(a)} - T \left(\frac{\partial \mu^{H(a)}}{\partial T} \right)_N \right\}, \quad (1)$$

and those, $\Delta\varepsilon_1$ and $\Delta\varepsilon_2$ for individual crystal planes 1 and 2 in terms of individual chemical potential $\mu_1^{H(a)}$ and $\mu_2^{H(a)}$ of $H(a)$ as that,

$$\Delta\varepsilon_1 = \mu^{H_2} - T \left(\frac{\partial \mu^{H_2}}{\partial T} \right)_p - 2 \left\{ \mu_1^{H(a)} - T \left(\frac{\partial \mu_1^{H(a)}}{\partial T} \right)_{\theta_1} \right\} \quad (2.1)$$

$$\Delta\varepsilon_2 = \mu^{H_2} - T \left(\frac{\partial \mu^{H_2}}{\partial T} \right)_p - 2 \left\{ \mu_2^{H(a)} - T \left(\frac{\partial \mu_2^{H(a)}}{\partial T} \right)_{\theta_2} \right\} \quad (2.2)$$

where N is the total number of the adsorbed hydrogen atoms.

We have however at the adsorption equilibrium that,

$$\mu^{H(a)} = \mu_1^{H(a)} = \mu_2^{H(a)} \quad (3)$$

and for the total number N of the adsorbed hydrogen atoms that,

$$N = N_1\theta_1 + N_2\theta_2 \quad (4)$$

and since $\mu_1^{H(a)}$ or $\mu_2^{H(a)}$ are function of the temperature and coverage of respective crystal plane θ_1 and θ_2 that,

$$d\mu_1^{H(a)} = \left(\frac{\partial \mu_1^{H(a)}}{\partial T} \right)_{\theta_1} dT + \left(\frac{\partial \mu_1^{H(a)}}{\partial \theta_1} \right)_T d\theta_1 \quad (5.1)$$

$$d\mu_2^{H(a)} = \left(\frac{\partial \mu_2^{H(a)}}{\partial T} \right)_{\theta_2} dT + \left(\frac{\partial \mu_2^{H(a)}}{\partial \theta_2} \right)_T d\theta_2 \quad (5.2)$$

where N_1 and N_2 the respective total number of the crystal plane 1 and 2 each capable of adsorbing a hydrogen atom.

we have immediately from Eq. (3) that,

$$\left(\frac{\partial \mu^{H(a)}}{\partial T} \right)_N = \left(\frac{\partial \mu_1^{H(a)}}{\partial T} \right)_N = \left(\frac{\partial \mu_2^{H(a)}}{\partial T} \right)_N \quad (6)$$

*) Cf. p. 91 of this Volume. Eliminating \bar{X}^{H_2} and $\bar{X}^{H(a)}$ from Eqs. (7), (8. H_2) and (8. $H(a)$) there we arrive at (1) immediately.

from Eqs. (5.1) and (5.2) that,

$$\left(\frac{\partial \mu_1^{H(a)}}{\partial T}\right)_N = \left(\frac{\partial \mu_1^{H(a)}}{\partial T}\right)_{\theta_1} + \left(\frac{\partial \mu_1^{H(a)}}{\partial \theta_1}\right)_T \left(\frac{\partial \theta_1}{\partial T}\right)_N \quad (7.1)$$

$$\left(\frac{\partial \mu_2^{H(a)}}{\partial T}\right)_N = \left(\frac{\partial \mu_2^{H(a)}}{\partial T}\right)_{\theta_2} + \left(\frac{\partial \mu_2^{H(a)}}{\partial \theta_2}\right)_T \left(\frac{\partial \theta_2}{\partial T}\right)_N \quad (7.2)$$

and from Eq. (4) that,

$$N_1 \left(\frac{\partial \theta_1}{\partial T}\right)_N + N_2 \left(\frac{\partial \theta_2}{\partial T}\right)_N = 0 \quad (8)$$

Eliminating now, $\left(\frac{\partial \mu_1^{H(a)}}{\partial T}\right)_N$, $\left(\frac{\partial \mu_2^{H(a)}}{\partial T}\right)_N$, $\left(\frac{\partial \theta_1}{\partial T}\right)_N$ and $\left(\frac{\partial \theta_2}{\partial T}\right)_N$ from Eqs. (6), (7.1), (7.2) and (8) it is obtained that,

$$\left(\frac{\partial \mu^{H(a)}}{\partial T}\right)_N = \frac{N_1 \left(\frac{\partial \mu_1^{H(a)}}{\partial T}\right)_{\theta_1} \left(\frac{\partial \mu_2^{H(a)}}{\partial \theta_2}\right)_T + N_2 \left(\frac{\partial \mu_2^{H(a)}}{\partial T}\right)_{\theta_2} \left(\frac{\partial \mu_1^{H(a)}}{\partial \theta_1}\right)_T}{N_1 \left(\frac{\partial \mu_2^{H(a)}}{\partial \theta_2}\right)_T + N_2 \left(\frac{\partial \mu_1^{H(a)}}{\partial \theta_1}\right)_T} \quad (9)$$

or remembering Eq. (3) that,

$$\begin{aligned} \mu^{H(a)} - T \left(\frac{\partial \mu^{H(a)}}{\partial T}\right)_N &= \\ N_1 \left\{ \mu_1^{H(a)} - T \left(\frac{\partial \mu_1^{H(a)}}{\partial T}\right)_{\theta_1} \right\} \left(\frac{\partial \mu_2^{H(a)}}{\partial \theta_2}\right)_T &+ N_2 \left\{ \mu_2^{H(a)} - T \left(\frac{\partial \mu_2^{H(a)}}{\partial T}\right)_{\theta_2} \right\} \left(\frac{\partial \mu_1^{H(a)}}{\partial \theta_1}\right)_T \\ &= \frac{N_1 \left(\frac{\partial \mu_2^{H(a)}}{\partial \theta_2}\right)_T + N_2 \left(\frac{\partial \mu_1^{H(a)}}{\partial \theta_1}\right)_T}{N_1 \left(\frac{\partial \mu_2^{H(a)}}{\partial \theta_2}\right)_T + N_2 \left(\frac{\partial \mu_1^{H(a)}}{\partial \theta_1}\right)_T} \end{aligned} \quad (10)$$

and further, subtracting the both sides from $\mu^{H_2} - T \left(\frac{\partial \mu^{H_2}}{\partial T}\right)_P$ and remembering Eqs. (1), (2.1) and (2.2) that,

$$\Delta \varepsilon = \frac{N_1 \left(\frac{\partial \mu_2^{H(a)}}{\partial \theta_2}\right)_T \Delta \varepsilon_1 + N_2 \left(\frac{\partial \mu_1^{H(a)}}{\partial \theta_1}\right)_T \Delta \varepsilon_2}{N_1 \left(\frac{\partial \mu_2^{H(a)}}{\partial \theta_2}\right)_T + N_2 \left(\frac{\partial \mu_1^{H(a)}}{\partial \theta_1}\right)_T} \quad (11)$$

or in word $\Delta \varepsilon$ directly observable overall heat of adsorption is the weighted mean of $\Delta \varepsilon_1$ and $\Delta \varepsilon_2$ respectively with weights y and $1-y$, where

$$y = \frac{N_1 \left(\frac{\partial \mu_2^{H(a)}}{\partial \theta_2}\right)_T}{N_1 \left(\frac{\partial \mu_2^{H(a)}}{\partial \theta_2}\right)_T + N_2 \left(\frac{\partial \mu_1^{H(a)}}{\partial \theta_1}\right)_T} \quad (12)$$

$$\text{i. e.} \quad \Delta\varepsilon = y\Delta\varepsilon_1 + (1-y)\Delta\varepsilon_2 \quad (13)$$

The differential coefficients $\left(\frac{\partial \mu_1^{H(a)}}{\partial \theta_1}\right)_T$ and $\left(\frac{\partial \mu_2^{H(a)}}{\partial \theta_2}\right)_T$ in the above equation may be expressed as follows.

μ 's is given according to HORIUTI⁴⁾ as that,

$$\mu^{H(a)} = -RT \log q^{H(a)} + RT \log \frac{\theta}{1-\theta} \quad (14)$$

where $-RT \log q^{H(a)}$ is the reversible work required to bring up a hydrogen atom from its standard state to a particular site for adsorption. Since the latter may be taken a constant in the case when $\theta \ll 1$ due to the absence of mutual interaction between adsorbed atoms, it follows from Eq. (13) that,

$$\left(\frac{\partial \mu^{H(a)}}{\partial \theta}\right)_T = \frac{RT}{\theta}, \quad \text{when } \theta \ll 1 \quad (15)$$

θ_1 and θ_2 are now expressed as in the previous paper⁵⁾ respectively as that,

$$\theta_1 = \sqrt{\frac{P}{Q_0}} e^{\frac{\Delta\varepsilon_1}{2KT}}, \quad \theta_2 = \sqrt{\frac{P}{Q_0}} e^{\frac{\Delta\varepsilon_2}{2KT}} \quad (16.1) \quad (16.2)$$

where $Q_0 = kT \frac{(2\pi mkT)^{3/2}}{h^3} \frac{4\pi^2 I kT}{h^2} \left(1 - e^{-\frac{h\nu}{kT}}\right)^{-1} e^{\frac{7}{2}}$

It follows from Eq. (12), (15) and (16) that,

$$y = \frac{N_1 \theta_1}{N_1 \theta_1 + N_2 \theta_2} = \frac{N_1 e^{\frac{\Delta\varepsilon_1}{2KT}}}{N_1 e^{\frac{\Delta\varepsilon_1}{2KT}} + N_2 e^{\frac{\Delta\varepsilon_2}{2KT}}} \quad (17)$$

We are now ready for drawing conclusions from the observed constancy of $\Delta\varepsilon$: rewriting Eq. (13) in the form,

$$\Delta\varepsilon = (\Delta\varepsilon_1 - \Delta\varepsilon_2) y + \Delta\varepsilon_2 \quad (18)$$

We see immediately that it follows from the observed constancy of $\Delta\varepsilon$ that either y is constant or $(\Delta\varepsilon_1 - \Delta\varepsilon_2) y$ is negligibly small granting that $\Delta\varepsilon_1$ and $\Delta\varepsilon_2$ are respectively constant.

4) HORIUTI; J. Res. Inst. Catalysis, Vol. 1 No. 1 (1948) 8.

5) KWAN; This Volume p. 93

For y being a constant it is necessary according to Eq. (17) that,

$$\Delta\varepsilon_1 = \Delta\varepsilon_2 \quad (19)$$

For $(\Delta\varepsilon_1 - \Delta\varepsilon_2)/y$ being negligibly small, it is now required either the validity of Eq. (19) or otherwise y itself being negligibly small, the latter in turn necessitates according to Eq. (17) that,

$$N_2 e^{\frac{\Delta\varepsilon_2}{2RT}} \gg N_1 e^{\frac{\Delta\varepsilon_1}{2RT}} \quad (20)$$

or in words according to Eq. (16.2) the adsorption takes practically exclusively on the crystal plane 2.

Summing up, it is concluded either that Eq. (19) or (20) must be valid: in the former case (i) assumes the form according to Eq. (18) that,

$$\Delta\varepsilon = \varepsilon_1 = \Delta\varepsilon_2 \quad (21. i)$$

and in the latter case (ii) that,

$$\Delta\varepsilon = \Delta\varepsilon_2 \quad (21. ii)$$

On the other hand θ_{obs} and θ_{calc} experimentally determined above may be expressed on the basis of the present picture as follows. θ_{calc} was now simply given by the expression,

$$\theta_{\text{calc}} = \sqrt{\frac{P}{Q_0}} e^{\frac{\Delta\varepsilon}{2RT}} \quad (22)$$

whereas θ_{obs} must be expressed, on the basis of the above assumption that B.E.T. area measures the sum of the crystal plane 1 and 2, as that,

$$\theta_{\text{obs}} = \frac{N_1\theta_1 + N_2\theta_2}{N_1 + N_2} \quad (23)$$

or according to Eqs. (16.1) and (16.2) as that,

$$\theta_{\text{obs}} = \sqrt{\frac{P}{Q_0}} \frac{N_1 e^{\frac{\Delta\varepsilon_1}{2RT}} + N_2 e^{\frac{\Delta\varepsilon_2}{2RT}}}{N_1 + N_2} \quad (24)$$

The ratio $\theta_{\text{obs}}/\theta_{\text{calc}}$ is now given for case (i) according to Eqs. (21. i) (22) and (24) as that,

$$(i) \quad \frac{\theta_{\text{obs}}}{\theta_{\text{calc}}} = 1 \quad (25. i)$$

and for case (ii) according to Eqs. (20), (21. ii), (22) and (24) as that,

$$(ii) \quad \frac{\theta_{\text{obs}}}{\theta_{\text{calc}}} = \frac{N_2}{N_1 + N_2} \quad (25. ii)$$

The following Table shows now θ_{obs} and θ_{calc} derived from the observation described above.

TABLE 1 The covered fraction of hydrogen on pure iron or ammonia synthetic catalyst $T = 50^\circ\text{C}$

Equi. Press. mm Hg	Catalyst θ	I.G. Catalyst			Pure Iron		
		θ_{obs}	θ_{calc}	$\theta_{\text{obs}}/\theta_{\text{calc}}$	θ_{obs}	θ_{calc}	$\theta_{\text{obs}}/\theta_{\text{calc}}$
0,001		0,015	0,26	0,06	0,0028	0,26	0,011

The results shown in the Table are obviously not fitted in by the conclusion Eq. (25. i) for case (i) but by that for case (ii) and hence that value of $\theta_{\text{obs}}/\theta_{\text{calc}}$ there may be taken for giving directly the fraction of the area of the crystal plane 2 to the total area, so far as our picture of the catalyst's surface goes. It may then be concluded comparing $\theta_{\text{obs}}/\theta_{\text{calc}}$ for ammonia synthetic catalyst to that for the pure iron that the promoter in the former catalyst increases the fraction of the available area for adsorbing hydrogen about five times.

Present method of analysis may applied to the case of $\angle\epsilon$ varying with temperature, $\angle\epsilon$, $\angle\epsilon_1$ as $N_2/N_1 + N_2$ being numerically determined therefrom. Without entering the case further, we might slightly modify our picture taking the conclusion arrived at by BRUNAUER and EMMETT¹³ into account.

These authors conclude namely from their experimental results that an appreciable fraction of the catalyst's surface is occupied by K_2O . If the latter fraction were disable for adsorbing hydrogen atom by the coverage but accessible to the B.E.T. area measurement, Eq. (23) derived directly from the above picture should be replaced in the case of ammonia synthetic catalyst but not of pure iron by the relation that,

$$\theta_{\text{obs}} = K \frac{N_1\theta_1 + N_2\theta_2}{N_1 + N_2} \quad (26)$$

where K is the remaining proper fraction of the surface not covered by K_2O .

We have henceforth instead of Eq. (25. i) and (25. ii) that,

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$$(i) \quad \theta_{obs} / \theta_{calc} = K \quad (27. i)$$

$$(ii) \quad \theta_{obs} / \theta_{calc} = K \quad N_2 / N_1 + N_2 \quad (27. ii)$$

In the case of pure iron which is of course unaffected by the promoter, however, case (i) should be excluded by comparison of Eq. (25. i) with the results given in the Table.

Assuming now that the similar situation prevails with the uncovered part of the synthetic catalyst's surface, it may be concluded according to Eq. (27. i) that $\theta_{obs} / \theta_{calc}$ given in the Table for the synthetic catalyst gives the lower limit of $N_2 / N_1 + N_2$ and hence the factor 5 of multiplication of $N_2 / N_1 + N_2$ due to the promoter gives its lower limit as well.

In conclusion, the present author wish to express my sincere thanks to the Director of the Institute J. HORIUTI for his valuable discussions and helps for the present research and also to Nippon Academy for financial grant.

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