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Gas Chromatographic Determination of Reversible Adsorption of Hydrogen

VIII. Reversible Adsorption of Hydrogen over Cobalt Oxide

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The rapid and reversible part of the stationary adsorption of hydrogen at low temperatures has been measured by means of a gas chromatographic technique utilizing deuterium as a tracer, in addition to the conventional static measurement of adsorption. The deuterium isotope effect was taken into account in estimating the amount of reversible adsorption assuming a Langmuir isotherm.

The amount of reversible adsorption over the cobalt oxide sample at liquid nitrogen temperature and atmospheric pressure was 2-4 $\times$ 10^{14} molecules/cm^2 increasing with the preevacuation temperature of the sample from 160 to 470°C. A molecular adsorption is suggested for this temperature. The observed isotope effect in the adsorption constant, K_D/K_H, was 1.4 to 1.9, increasing with the evacuation temperature of the sample. A small amount of irreversible adsorption was found at -195°C in addition to the reversible adsorption. When the oxide was preevacuated at 470°C, the irreversible adsorption was considerable above -75°C and seemed to be a reaction with the oxide surface rather than adsorption.

INTRODUCTION

The gas chromatographic determination of the reversible adsorption of hydrogen has been undertaken over metals (*1*, *2*). The rapid and reversible part of the stationary adsorption of hydrogen as determined by this technique seems to be closely related to catalysis such as hydrogenation and H_2–D_2 exchange. Cobalt oxide is known to be extremely active in these reactions (*3*, *4*), while the activity depends on the evacuation temperature of the sample before the run.

The gas chromatographic measurements were made over the Co_3O_4 pretreated in various ways, in addition to the measurements of total uptake of H_2.

RELATION BETWEEN THE DEUTERIUM RETENTION AND THE ISOTOPE EFFECT

It has been shown that the corrected deuterium retention volume, $(V_{RD} - V_0)$, in the hydrogen carrier is equal to the amount of reversible adsorption, provided that the rate of adsorption and desorption is rapid enough to establish the isotopic equilibrium between the carrier gas and the adsorbed phase, and that the deuterium isotope effect is negligible so that the adsorption isotherm of the deuterium fraction in hydrogen carrier is linear. When these two conditions are fulfilled, the elution peak of the deuterium pulse should be symmetrical in its shape. In the case of an appreciable isotope effect involved, however, the isotherm of deuterium fraction in hydrogen (*1*) should be nonlinear as illustrated in Fig. 1. Accordingly if the deuterium isotope effect is appreciable, the deuterium retention volume depends on the partial pressure of deuterium over the oxide and consequently on the size of deuterium pulse so that the estimation of the reversible adsorption is not so simple as in the absence of the isotope effect.

The implication of the deuterium retention involving the isotope effect is analyzed

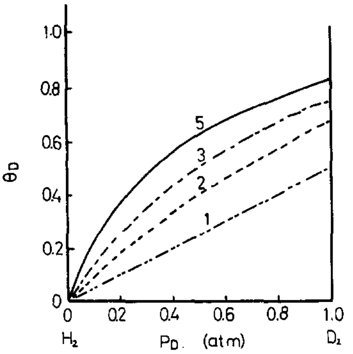


FIG. 1. Schematic isotherm of deuterium fraction θ_D in adsorbed hydrogen. Numbers attached to the lines indicate the assumed values of K_D with K_H being unity.

on the basis of a Langmuir model of molecular adsorption. The amount of adsorption of hydrogen, V_{H_2}, (or deuterium, V_{D_2}) under atmospheric pressure is given as follows:

$$V_{H_2} = \frac{K_H}{1 + K_H} V_m \text{ at } P_H = 1 \quad \text{(H)}$$

and (1)

$$V_{D_2} = \frac{K_D}{1 + K_D} V_m \text{ at } P_D = 1 \quad \text{(D)}$$

where K_H and K_D are the adsorption equilibrium constants of H_2 and D_2, respectively, and V_m is the volume adsorbed which gives a complete monolayer. V_{H_2} or V_{D_2} may be obtained by the static adsorption measurement under 1 atm.

When both H_2 and D_2 are competitively adsorbed on the same surface, the fractions, θ_H and θ_D, covered by H_2 and D_2, respectively, are given as follows:

$$\theta_H = \frac{K_H P_H}{1 + K_H P_H + K_D P_D} \quad \text{(H)}$$

$$\theta_D = \frac{K_D P_D}{1 + K_H P_H + K_D P_D} \quad \text{(D)}, \quad (2)$$

where P_H and P_D are the partial pressures of H_2 and D_2, respectively, and

$$P_H + P_D = 1 \quad (3)$$

under 1 atm. Equation (2) is illustrated in Fig. 1.

The deuterium retention in hydrogen carrier gas under 1 atm is expressed by

$$V_{RD} = (v + v\mu) l T_0 / T, \quad (4)$$

where v is the volume of free space per unit length of the column, l is the length of the column, T_0 and T are the standard and the ambient temperature in °K, respectively, and μ is the distribution coefficient given by

$$\mu = \frac{n_S \theta_D}{P_D v / RT}, \quad (5)$$

where n_S is the number of site per unit length of the column. Substituting (5) into (4),

$$V_{RD} - V_0 = l n_S R T_0 \frac{\theta_D}{P_D} = V_m \frac{\theta_D}{P_D}$$

$$(V_m = n_S l R T_0), \quad (6)$$

where $V_0 \left(= lv \frac{T_0}{T} \right)$ is the net volume of carrier gas involved in the column. θ_D / P_D depends on P_D according to Eq. (2-D). Hence the retention volume depends on P_D in the sample pulse. Equation (2-D) is differentiated to give the equation,

$$\frac{d\theta_D}{dP_D} = \frac{K_D(1 + K_H)}{(1 + K_H + (K_D - K_H)P_D)^2}, \quad (7)$$

when $P_D \approx 0$,

$$\left(\frac{d\theta_D}{dP_D} \right)_{P_D = 0} = \frac{K_D}{1 + K_H}. \quad (7')$$

Substituting (7′) into (6),

$$V_{RD} - V_0 = \frac{K_D}{1 + K_H} V_m. \quad \text{(D)} \quad (8)$$

When the sample pulse of H_2 is introduced into D_2 carrier gas, the retention volume of H_2 is similarly derived as follows:

$$V_{RH} - V_0 = \frac{K_H}{1 + K_D} V_m. \quad \text{(H)} \quad (8)$$

By comparing the retention volumes given by Eqs. (8-H) and (8-D) with the amount of adsorption given by Eqs. (1-H) and (1-D), the following sequence may be obtained if $K_D \geqslant K_H$

$$V_{RD} - V_0 \geqslant V_{D_2} \geqslant V_{H_2} \geqslant V_{RH} - V_0. \quad (9)$$

If the surface is homogeneous as assumed, K_H, K_D and V_m can be obtained from the retention volume and the total uptake by using Eqs. (1-H), (1-D), (8-H) and (8-D). The ratio of K_D to K_H is obtained from Eqs. (1) and (8) as follows:

$$\frac{V_{RD} - V_0}{V_{H_2}} = \frac{K_D}{K_H}, \qquad (10)$$

$$\frac{V_{D_2}}{V_{RH} - V_0} = \frac{K_D}{K_H}. \qquad (11)$$

When nonadsorbing gas such as helium is used as the carrier gas, the retention volume of hydrogen or deuterium introduced as small size pulse is given by neglecting the adsorption constant of the carrier gas as follows:

$$V_{RH}{}^{He} - V_0 = K_H V_m \quad (H)$$

and (12)

$$V_{RD}{}^{He} - V_0 = K_D V_m. \quad (D)$$

EXPERIMENTAL

1. *Cobalt oxide*

The hydroxide obtained by precipitation from the nitrate using ammonia was decomposed in the atmosphere at 500°C. The oxide was crushed to granules of 10–20 mesh. The BET area of the oxide was 7.9–8.9 m^2/g depending on the pretreatment.

2. *Procedure*

The oxide (31.6 g net) was packed into a glass U tube of 10 mm diam, and was pretreated as described later. The apparatus and procedure for the gas chromatographic measurement was essentially the same as described in the previous paper (*1*). Briefly, the D_2 sample (or H_2) was introduced into the carrier gas (H_2, D_2 or He) by means of a doser made of glass tubing, passed to the oxide column and detected by a thermal conductivity cell. No separation of *o*- and *p*-hydrogen was observed even in the case of helium carrier gas. The volume of doser was as low as 0.2 ml and thus the resultant partial pressure of the sample gas was below a few mm Hg over the oxide.

3. *Pretreatment of the Oxide*

The oxide was pretreated in three different ways:

(i) Treatment with water vapor. A flow of gaseous nitrogen contaminated with water vapor by passing over liquid water at 20°C was sent to the oxide column at 75°C for 13 hr and then the column was evacuated for 10 min at 75°C.

(ii) Evacuation at a moderate temperature. The column was evacuated at 160°C for 2 hr.

(iii) Evacuation at a high temperature. The column was evacuated at 470° ± 5°C for 9 hr.

4. *Types of Measurements*

The following measurements were made:

(a) Measurement of the temperature dependence of the deuterium retention in hydrogen carrier from −195 to 20°C, accompanied by the detection of HD in the effluent pulse from the column.

(b) Static adsorption measurement under 1 atm at −195° to 20°C.

(c) Measurements of the quantities defined by Eqs. (1), (8), and (12) at −195°C.

(c_1) Amount of adsorption by the static measurement, V_{H_2} and V_{D_2}.

(c_2) Retention volume of H_2 and D_2 in D_2 or H_2 carrier ($V_{RH} - V_0$) or ($V_{RD} - V_0$).

(c_3) Retention volumes of H_2 and D_2 in helium carrier ($V_{RH}{}^{He} - V_0$) and ($V_{RD}{}^{He} - V_0$).

The column was evacuated between runs, if necessary, first at −195°C and second at room temperature for 15–20 min down to 10^{-3} mm Hg.

RESULTS

1. *Deuterium Retention in the Hydrogen Carrier*

The deuterium retention was measured at increasing temperatures from −195° to 20°C with the CoO column under atmospheric pressure. As the retention volume is expected to depend on the partial pressure of the sample (described in the section on the relation between deuterium retention and the isotope effect), the doser volume was reduced to 0.2 ml so that the sample pressure in the carrier gas could be regarded to be nil. This was further examined by changing the deuterium pressure in the doser. As shown on Fig. 2, the retention volume does not depend on the deuterium pressure under this experimental condition. Accordingly the third

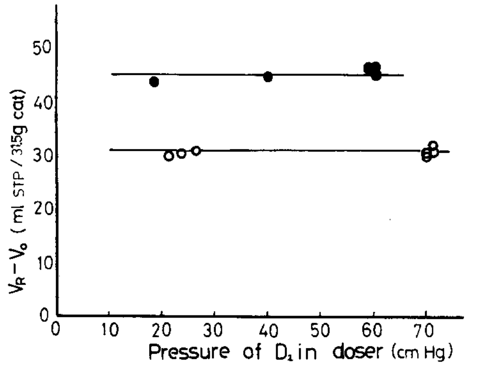


FIG. 2. Effect of D_2 pressure in doser on the D_2 retention volume. ○, pretreatment (i), ●, pretreatment (ii)

term in the denominator of Eq. (7), $(K_D - K_H)P_D$, can be neglected. The peak shape on the chromatogram is symmetrical as shown on Fig. 3. This indicates that the dynamic equilibrium of hydrogen adsorption is established. Such a condition of dynamic equilibrium is realized in all the runs of the hydrogen carrier.

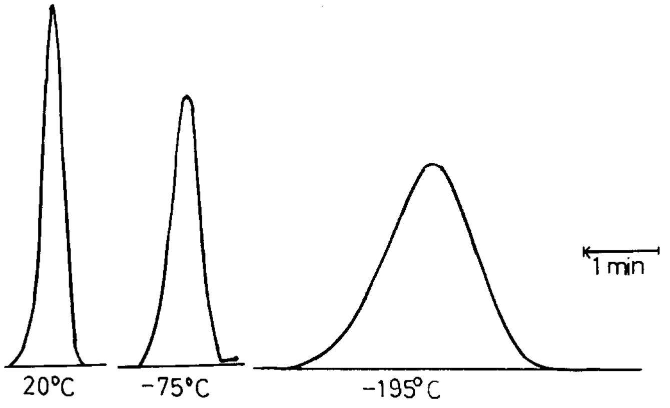


FIG. 3. Peak shape of D_2 pulse in H_2 carrier gas at different temperatures in the case of pretreatment (iii).

The retention volumes of D_2 thus obtained are listed in Table 1. As shown in this table, the reversible adsorption of hydrogen is appreciable in the low temperature range and decreases with increase in temperature down to nil above −75°C, while no H–D exchange is detected at any temperature. These results demonstrate an undissociated reversible adsorption of hydrogen at low temperature.

TABLE 1
DEUTERIUM RETENTION IN H_2 CARRIER GAS (ml STP/100 m^2)

Column temp (°C) Pretreatment	−195	−183	−75	20
(i)	12.0	—	—	—
(ii)	16.4	8.3	0.3	0
(iii)	22.8	—	0.5	0.1

After a series of runs at increasing temperatures up to 20°C, the temperature was again dropped to −195°C. In the case of the pretreatment (ii), the previously measured retention volume was reproduced, but in the case of (iii) there was a reduction in the retention volume from 22.8 to 12.5 ml (STP)/100 m^2. This result suggests that the evacuation at the high temperature involved in the pretreatment (iii) gives the oxide a capacity for the irreversible adsorption of hydrogen at the higher temperature which reduces the retention volume at the low temperature. This will be clearer in the following results.

2. Adsorption of Hydrogen by Static Measurement

The amount of adsorption was measured in the static system at increasing temperatures of −195° to 20°C with 31.6 g of the oxide under atmospheric pressure. As shown in Fig. 4, it is found in the case of the pretreatment (iii) that a slow adsorption, in addition to the low temperature type fast adsorption, is detectable at −75°C and appreciable at 20°C. After a series of measurements at increasing temperatures up to 20°C, the oxide column was evacuated at

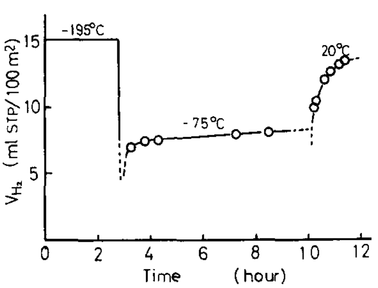


FIG. 4. Total uptake of H_2 at different temperatures in the case of pretreatment (iii).

20°C and cooled to −195°C *in vacuo*. It was found that there was a reduction in the amount of adsorption from 15 ml/100 m² for the fresh oxide to 9.4 ml/100 m². This result suggests that the slow adsorption of hydrogen in the higher temperature range is irreversible, thus reducing the adsorption at the low temperature. The oxide modified by such irreversible hydrogen was readily regenerated by flowing oxygen at 380°C.

3. Effect of the Various Pretreatments on the Reversible or Irreversible Adsorption at −195°C

The quantities defined by Eqs. (1), (8), and (12) were measured at −195°C after the pretreatment described in subsection 3 under Experimental. The results are listed in Table 2. The effect of the hydrogen treatment of the oxide at 20°C is also shown in the fifth column.

Adsorption of hydrogen by the static measurement. The amount of adsorption increased with the high temperature treatment of the oxide. In the case of the pretreatment (iii), there was a reduction in the amount of adsorption from 15 ml/100 m² for the fresh oxide to 12.8 ml/100 m² for the second measurement after evacuation at −195° and second at 20°C, which was shown on Table 2. This decrease in the amount of adsorption indicates an irreversible adsorption at −195°C.

The retention volume in helium carrier. In the case of the pretreatment (iii), there was a considerable amount of irreversible adsorption at −195°C. Although the amount of the column oxide was reduced to 3.5 g to facilitate the measurement, the initial pulses were completely trapped by the column. The amount of the irreversible adsorption thus observed was estimated to be about 3 ml/100 m², which was in agreement with the irreversible adsorption observed in the static measurement. Accordingly the retention volume measurements were made over the oxide with the preadsorbed irreversible hydrogen.

It was found that the retention volume depended on the sample pressure in the doser. The listed values were obtained by

TABLE 2
THE QUANTITIES DEFINED BY EQUATIONS (1), (8), AND (12) AT −195°C

Pretreatment	(i)	(ii)	(iii)	(iii) + H_2[a]
V_{H_2} (ml STP/100m²)	8.4	10.7	12.8[b]	9.4
V_{D_2}	11.2	12.6	15.4[b]	10.5
$V_{RH} - V_0$	5.9 ± 0.7	6.8 ± 0.7	7.0 ± 0.7	6.3 ± 0.7
$V_{RD} - V_0$	12.0	16.4	22.8	12.5
$V_{RH}^{He} - V_0$	17.1	57.0	193.0	30.0
$V_{RD}^{He} - V$	23.3	111.0	318.0	47.0
V_{H_2}(rev.)	8.4	10.6	11.8	9.4
V_{D_2}(rev.)	11.2	12.5	14.4	10.5
K_D/K_H $(V_{RD} - V_0)/V_{H_2}$(rev.)	1.4_3	1.5_5	1.9_4	1.3_3
V_{D_2}(rev.)/$(V_{RH} - V_0)$	1.9 ± 0.2	1.8 ± 0.2	2.0 ± 0.2	1.6_7 ± 0.2
V_m(rev.)(ml STP/100 m²)	—	18.0_3	18.0_7	$16._3$
K_H (atm⁻¹)	—	1.3	1.7	1.3_7
K_D (atm⁻¹)	—	2.1	3.3	1.8_2
Surface area (m²/g)	8.1	8.9	7.9	8.8

[a] The oxide was treated with hydrogen at 20°C after the pretreatment (iii).

[b] Stabilized value of amount of adsorption after the second measurement.

extrapolation to zero pressure even in the case of the pretreatment (ii).

It is seen in the results shown in Table 2 that the effect of evacuation temperature of the oxide column is much more remarkable on the retention volume in He carrier than on the other quantities. Furthermore as shown in Fig. 5, the peak shape in the chromatograms is deformed by the high temperature evacuation to an asymmetric one which has a sharp front. These results suggest that the heat treatment in vacuum increases the adsorption strength for hydrogen and that this effect of the heat treatment is more remarkable on the bare surface as obtained in the atmosphere of He.

It should be mentioned here that Eq. (12) cannot be applied to those data of retention volume in He, because the dynamic equilibrium of hydrogen adsorption is required for Eq. (12) which was not the case in the present measurements as shown by the asymmetry of chromatograms. The observed retention volume must be corrected for the slow desorption before Eq. (12) is applied.

Another point to be mentioned is the big difference in the retention volume between He and H_2 carrier gases. The large value of the retention volume in He is partly due to the above mentioned slow desorption. But even after the correction for the slow adsorption, the retention volume in He should be larger than in H_2, because the key quantity of gas chromatographic retention of deuterium, $(\theta_D/P_D)_{P_D=0}$ should be larger in He than in H_2, if the adsorption isotherm of hydrogen is normal.

The retention volume in hydrogen carrier. The effect of the evacuation at high temperature is also seen in this case in a similar manner, although the effect is less pronounced. It may be concluded that the amount of reversible adsorption increases with the high temperature treatment of the column material.

4. The Deuterium Isotope Effect

The deuterium isotope effect in the adsorption of hydrogen at −195°C is found both in $V_{H_2}(V_{D_2})$ and $(V_{RH} - V_0)(V_{RD} - V_0)$. The isotope effect on the adsorption constant (K_D/K_H) may be obtained from Eq. (10) or Eq. (11), provided that the surface is homogeneous and the adsorption is reversible. Since the adsorption observed in the static system evidently involves the irreversible one, the amount of adsorption should be corrected to obtain K_D/K_H.

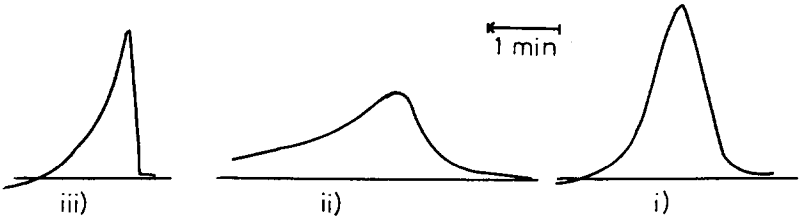


FIG. 5. Effect of pretreatment condition (i), (ii), and (iii) on the peak shape of D_2 pulse in helium carrier at −195°C.

The amount of irreversible adsorption was estimated by extrapolation to zero pressure of the amount of low pressure adsorption in the static system at −195°C. The irreversible adsorption thus obtained is substracted from the total uptake to estimate the reversible adsorption. The amounts of the reversible adsorption, V_{H_2}(rev.) and V_{D_2} (rev.) thus estimated are shown on Table 2, together with the values of the isotope effect, K_D/K_H, calculated by Eqs. (10) and (11).

DISCUSSION

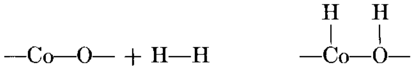
As is generally accepted, the oxide surface is usually covered by a hydroxyl group in the presence of water vapor. The dehydration from such a surface caused by the heating under vacuo results in exposed metal atoms on the oxide surface (*5*, *6*). When the cobalt oxide surface is dehydrated, it is activated for the catalytic isotope exchange in H_2–D_2 (*3*) and in C_2H_4–C_2D_4 (*6*) and also for the catalytic hydrogenation of olefin (*4*).

These catalytic activities of the cobalt oxide are lost on adsorption of water vapor.

In the present study, the effects of the dehydration from the surface of cobalt oxide (as shown by the pretreatment (iii)) were observed as follows: (a) Increase in the reversible adsorption of hydrogen at low temperature; (b) increase in the isotope effect on the low temperature reversible adsorption of hydrogen. (c) Activation for the irreversible slow adsorption of hydrogen which takes place above −75°C. These effects disappeared on adding back water.

It has been found in a separate study (*7*) that the irreversible adsorption of hydrogen mentioned in (c) drastically retards both the hydrogenation of ethylene and the chemisorption of carbon monoxide on the cobalt oxide evacuated at 400°C. It was found in this study that the irreversible adsorption of hydrogen (c) retards the low temperature reversible adsorption in a way similar to the preadsorption of water vapor.

The slow irreversible adsorption of hydrogen may be interpreted as an addition of a hydrogen molecule to the surface cobalt–oxygen bond.



$$\text{—Co—O—} + \text{H—H} \qquad \text{—}\overset{\substack{\text{H}\\|}}{\text{Co}}\text{—}\overset{\substack{\text{H}\\|}}{\text{O}}\text{—}$$

The observed retardation in the ethylene hydrogenation and in the carbon monoxide chemisorption can be ascribed to the occupation of the exposed cobalt by hydrogen. In this way the previously found effects of high temperature evacuation can be understood in terms of the exposed cobalt.

Accordingly, the effects (a) and (b) found in this study also seem to result from the same origin. However, the number of adsorption sites, V_m, for the low temperature reversible adsorption, which is estimated on the basis of the Langmuir model assuming a molecular adsorption and shown in Table 2, is nearly independent of the evacuation temperature and close to 18 ml/100 m^2 ($5 \cdot 10^{14}$ molecules/cm^2). This suggests that the observed increase in the low temperature reversible adsorption is caused by an increase in the adsorption strength or the adsorption constant per site rather than in the number of adsorption sites. An electrostatic effect by the exposed cobalt ion may contribute to the increase in the adsorption strength.

As described before, the low temperature reversible adsorption can be considered a molecular adsorption. Even in the case of molecular adsorption, the isotope effect originates from a vibration between adsorbent and adsorbed molecule (*8*). The increase in the isotope effect observed in this study is reasonable when the adsorption strength increases.

The isotope effect in the adsorption of hydrogen over oxides has been measured by the static method (*9*) at low pressure or by the gas chromatographic method (*10*) using nonadsorbing carrier gas. Those measurements mainly concern the initial adsorption over bare surface, while the measurement in this study concerns the reversible adsorption on a surface equilibrated with hydrogen under one atmosphere. Since the isotope effect decreases with the amount of adsorption over silica gel as found by Melkonian *et al.* (*9*), the isotope effect found in this study is reasonably smaller in its magnitude than those reported on silica (*9*) or alumina (*10*).

According to Ohtsuka and Keii (*11*), the rate of ortho-para hydrogen conversion over cobalt oxide at low temperatures, which takes place by the physical mechanism, drastically decreases with increase in temperature from −195° to −75°C. This decrease in the reaction rate has been supposed to be due to the decrease in the amount of adsorption of hydrogen with temperature increase. The amount of reversible adsorption of hydrogen observed in this study decreases remarkably with temperature increase from −195° to −75°C as shown in Table 1. Since the hydrogen adsorption must be reversible as the intermediate of the ortho-para conversion, the above agreement is quite reasonable.

REFERENCES

1. OZAKI, A., NOZAKI, F., MARUYA, K., AND OGASAWARA, S., *J. Catal.* **7**, 234 (1967).

2. OZAKI, A., SHIGEHARA, Y., AND OGASAWARA, S., *J. Catal.* **8**, 22 (1967); OZAKI, A., KIMURA, T., AND MOTOHASHI, M., *J. Chem. Soc. Jap. Pure Chem. Sect.* **88**, 834 (1967); SHIGEHARA, Y., AND OZAKI, A., *J. Chem. Soc. Jap. Pure Chem. Sect.* **88**, 838, 844 (1967); SHIGEHARA, Y., AND OZAKI, A., *J. Catal.* **10**, 183 (1968), **15**, 224 (1969).

3. DOWDEN, D. A., MACKENZIE, N., AND TRAPNELL, B. M. W., *Proc. Roy. Soc. A* **237**, 245 (1956).
4. HARRISON, D. L., NICHOLLS, D., AND STEINER, H., *J. Catal.* **7**, 359 (1967).
5. MILLS, G. A., AND HINDEN, S. G., *J. Amer. Chem. Soc.* **72**, 5549 (1950); YAO, Y. F. Y., *J. Phys. Chem.* **69**, 3930 (1965).
6. OZAKI, A., AI, H., AND KIMURA, K., *Int. Congr. Catal. 4th, Moscow, 1968,* preprint of paper 40.
7. TANAKA, K., NIHIRA, H., AND OZAKI, A., to be published in *J. Phys. Chem.*
8. ROSS, S., AND OLIVIER, J. P., "On Physical Adsorption," p. 236. John Wiley, New York, 1964.
9. MELKONIAN, G. A., AND REPS, B. Z., *Elektrochem.* **58**, 616 (1954).
10. MOORE, W. R., AND WARD, H. R., *J. Phys. Chem.* **64**, 832 (1960).
11. OTSUKA, K., AND KEII, T., 23rd meeting of the catalysis society, *Shokubai* **10**, 170 (1968).