February, 1974] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(2), 355—357 (1974) 355

Fundamental Studies on Palladium Catalysts. IX. Characteristics of Hydrogen Sorption and Hydrogenation Activity of Supported Palladium Catalysts[1)]

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(Received February 27, 1973)

The sorption of hydrogen and the hydrogenation of ethylene on palladium/silica-alumina catalysts with palladium contents of 0.58—4.5 wt% were investigated. It was found that V_x (the amount of molecularly-adsorbed hydrogen) and V_z (that of dissociatively-adsorbed hydrogen) increase, while V_y (that of dissolved hydrogen) decreases, with the increase in the specific surface area of palladium, and that the saturated value of V_z is proportional to the amount of chemisorbed carbon monoxide. It was also shown that the increase in the palladium content results in a growth of the palladium crystallites, their number staying approximately constant. The rate of ethylene hydrogenation was found to be first-order with respect to hydrogen and zero-order with respect to ethylene over the temperature range of −20—20 °C. The activity was proportional to the surface area of palladium, and the activation energy was almost constant for these catalysts.

It has previously been demonstrated[2)] that the equilibrium amount of hydrogen in the first ascending part of the sorption isotherm is expressed by the sum of the amounts of two hydrogen species, that is, molecularly-adsorbed hydrogen and dissolved hydrogen in the case of palladium-black with a surface area of less than 15 m^2/g. However, another species of dissociated hydrogen strongly adsorbed on palladium has been revealed as a result of an investigation[1,3)] using supported catalysts with a large surface area of palladium (>100 m^2/g).

In this investigation, we have studied the effects of the specific surface area of palladium on the equilibrium amount of each hydrogen species and on the hydrogenation of ethylene.

Experimental

Materials and Catalyst Preparation. The palladium/silica-alumina catalyst was prepared by immersing silica-alumina (Neobead D from the Mizusawa Industrial Chemicals, Ltd.) in a hydrochloric acid solution of $PdCl_2$ for a few weeks at room temperature until the solution became almost colorless. The catalyst, after having been washed with ion-exchanged water, was dried by evacuating it in the reaction cell and then reduced with hydrogen at 200 °C for 2 hr. Before each run, the catalyst was evacuated for 10 hr at 200 °C to arrive at a residual pressure of less than 1×10^{-4} Torr. The palladium-black/silica-alumina mixed catalyst was prepared by the Willstätter method[4)] in the presence of silica-alumina, followed by the same pretreatment as in the case of the supported catalyst. The palladium content was determined by the EDTA titration method. The hydrogen was purified by passage through a palladium thimble. The ethylene contained less than 0.3% methane and a trace amount of ethane as impurities. The purity of the carbon monoxide used for the determination of the palladium surface area was more than 99.8%.

Apparatus and Procedure. Our measurements of the sorption isotherms and the desorption rate were carried out in a conventional static-sorption apparatus incorporating a rotary MacLeod gauge, as has been described in Ref. (3). The catalytic activity was estimated by measuring the rate of ethylene hydrogenation in a batch recirculation system. The amounts of ethylene and ethane were monitored by the measurement of the pressure change in the total gas and checked by a chromatographic analysis of the gas mixture at appropriate intervals.

Results

Relation between the Specific Surface Area of Palladium S *and the Amount of Each Type of Hydrogen.* As has already been indicated in a previous paper,[1)] the amount of dissociatively-adsorbed hydrogen, V_z, is expressed as follows:

$$V_z=b_3\sqrt{K_3P}/(1+\sqrt{K_3P}) \tag{1}$$

where b_3, K_3 and P represent the site number per atom of palladium (H/Pd), the equilibrium constant, and the equilibrium hydrogen pressure respectively. The assumption that the dissociated hydrogen atoms combine with exposed palladium atoms in the ratio of 1 to 1 makes it possible to calculate the specific surface area of palladium S (m^2/g-Pd) from the b_3 values. Thus, S is determined by assuming that the number of palladium atoms per square meter is 1.2×10^{19}; this is the mean value for the crystallographic planes (100), (110), and (111).

$$S=472b_3 \tag{2}$$

On the other hand, Scholten and his co-workers have proposed a method of determining the surface area of supported palladium from the chemisorbed amount of carbon monoxide.[5)] Therefore, we have also examined the adsorption of carbon monoxide on a series

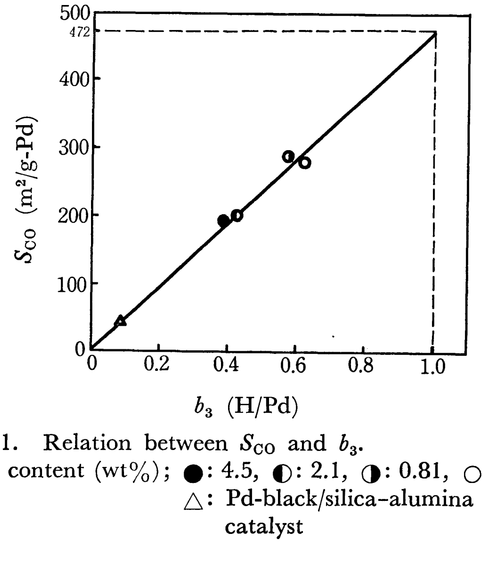

Fig. 1. Relation between S_{CO} and b_3.
Pd content (wt%); ●: 4.5, ◐: 2.1, ◑: 0.81, ○: 0.58
△: Pd-black/silica-alumina mixed catalyst

TABLE 1. RESULTS FOR DISSOCIATIVELY-ADSORBED HYDROGEN

Pd content (wt%)	b_3 (H/Pd)	Temperature (°C)	$\sqrt{K_3}$ (Torr)$^{-1/2}$	Heat of Adsorption (kcal/mol)	k_3' (H/Pd·min)$^{-1}$	Activation energy for desorption (kcal/mol)
0.81	0.571	0	35.0	7.5	3.82×10^{-4}	8.7
		20	23.0		9.50×10^{-4}	
		35	16.3		2.22×10^{-3}	
2.1	0.424	0	34.7	7.5	3.75×10^{-4}	8.7
		20	22.7		1.03×10^{-3}	
		35	15.9		2.25×10^{-3}	

of catalysts at 20 °C and calculated the S values according to their procedure. The relation between b_3 and S obtained by means of carbon monoxide chemisorption (S_{CO}) is presented in Fig. 1; it suggests the validity of Eq. (2). In Fig. 1, we also show the results obtained with a palladium-black/silica-alumina mixed catalyst, assuming that the amount of residual hydrogen after 1 hr's evacuation at 20 °C is equal to b_3. In addition, we calculated the heat of dissociative adsorption from the temperature dependency of K_3; we thus obtained approximately 7.5 kcal/mol (see Table 1).

Then we have investigated the desorption process of hydrogen taken up at 20 °C, 100 Torr according to the procedure described in Ref. 1. We first determined V_z; then we estimated the amount of molecularly-adsorbed hydrogen, V_x, and that of hydrogen dissolved in the lattice, V_y, assuming that the molecularly-adsorbed hydrogen had just been desorbed by the 30-second's evacuation to the residual pressure of $1\times10^{-1}-8\times10^{-2}$, and that the dissolved hydrogen is not desorbed under the above conditions. The relation between V_x and b_3 (or S) as well as V_y and b_3 (or S) is illustrated in Fig. 2. It is demonstrated in Fig. 2 that V_x increases proportionally, while V_y decreases, with the increase in S.

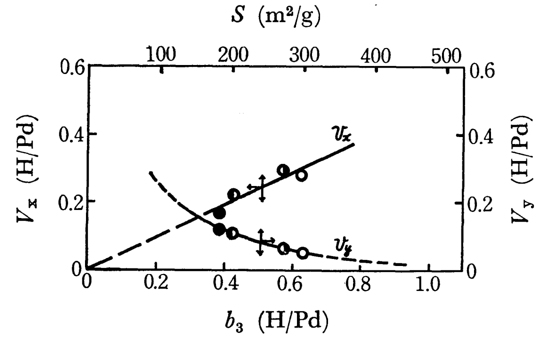

Fig. 2. Relation between (V_x, V_y) and (b_3, S) at 20 °C, 100 Torr.
Pd content (wt%); ●: 4.5, ◐: 2.1, ◑: 0.81, ○: 0.58

In addition, it was found that values of k_3' (the desorption rate constant of dissociatively-adsorbed hydrogen) for the catalysts with the palladium contents of 0.81 wt% and 2.1 wt% were almost identical and that the activation energies calculated from the temperature dependency of k_3' were about 8.7 kcal/mol in both cases (see Table 1).

Hydrogenation of Ethylene. The hydrogenation of ethylene was studied over the temperature range from −20 °C to 20 °C. The circulation velocity of the reactant gas does not influence the kinetics under the standard conditions: the initial pressures of hydrogen and ethylene are around 25 Torr, and no diluent is used. Since the activity was found to decrease slightly with the progress of the reaction, a fresh catalyst was used for each run. The reaction rate, R, was proved to be as follows:

$$R=kP_hP_e^0 \qquad (3)$$

where k is the rate constant and where P_h and P_e denote the partial pressures of hydrogen and ethylene respectively. The rate constants[6)] per gram of palladium in the catalyst were calculated; they are plotted against b_3 and against S_{co} in Fig. 3. The linear relationship indicates that the hydrogenation activity is proportional to the specific surface area of palladium. The activation energies were about 2.5 kcal/mol for all the catalysts used.

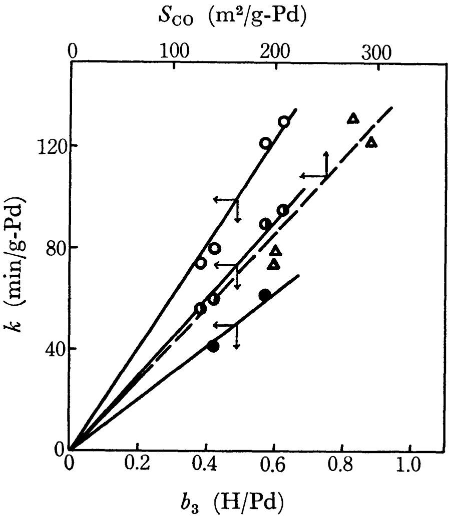

Fig. 3. Relation between k and (b_3, S_{CO}).
Temperature (°C); ○, △: 20, ◑: 0, ●: −20

Discussion

As for dissociatively-adsorbed hydrogen, the validity of the assumption that the hydrogen atoms combine strongly with the palladium atoms exposed in 1-to-1 ratio is supported by Fig. 1. Since b_3 can be easily determined by means of Eq. (1), Eq. (2) may be thought to be very convenient for the estimation of the palladium surface area. In Scholten's method, the modes of the binding of carbon monoxide on palladium, namely, linear type and bridged type, must be considered in contrast to the method described above, in which only one hydrogen species is concerned. Furthermore, Dorling and Moss have reported[7] that the ratio of linear bonding to bridge bonding varies according to the metal crystallite size in the case of platinum/silica catalysts, so the surface area calculated from b_3 may be thought to be more precise than that determined by means of carbon monoxide chemisorption. This can be seen from Fig. 3, which illustrates better the linearity in the plot of k *vs.* b_3 than in that of k *vs.* S_{co}.

The dependency of V_x on S is similar to the results in Ref. 2. At present, we may suppose that the two surface species are adsorbed on different sites of the palladium, but the situation has not yet been ascertained in detail.

V_y decreases with an increase in S, probably because the number of sites in the lattice decreases with a decrease in the crystallite size of the palladium. In the case of $b_3=1.0$, it can be expected that each palladium atom is exposed to gaseous hydrogen and V_y becomes zero. Thus, b_3 means not only the total site number of the Langmuir isotherm, but also the proportion of palladium atoms exposed.

It may be concluded from the above results that the main role of the support is to disperse palladium, and that the spillover phenomenon reported by Boudart[8] in supported platinum catalysts does not take place in this system.

The increase in the palladium content resulted in a reduction of S, thus suggesting the growth of palladium crystallites. We have examined the relation between the total surface area of palladium per unit of weight of the support, S_t, and its weight, W, by plotting S_t *vs.* $W^{2/3}$ in Fig. 4. The linear relationship shows that the number of crystallites per gram of support is unchanged, irrespective of the palladium content. If the palladium crystallites are regarded as spheres, the number of crystallites per gram of support is calculated to be approximately 3.7×10^{17}; the diameter of the crystallites is considered to change over the range from 10 Å to 30 Å.

It may be concluded from the results obtained by ethylene hydrogenation that all sites are of the same quality in these catalysts, and that their difference in number per unit weight of palladium is reflected in the difference in catalytic activity. However, further research employing the catalysts with palladium crystallites larger than 30 Å is needed to characterize the catalytic behavior. The results of the present study give no information about the active species of hydrogen, because both V_x and V_z are proportional to S. Nevertheless, the b_3 value appears to be a useful parameter for the activity as long as the reaction in question is "facile". Which of the two surface species of hydrogen contributes to ethylene hydrogenation is an interesting subject for further study.

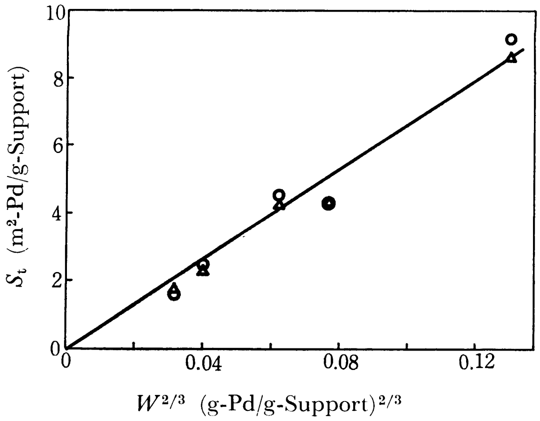

Fig. 4. S_t *vs.* $W^{2/3}$.
S_t: Determined by CO and H_2 adsorption
○: CO, △: H_2

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