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# Hydrogen–Deuterium Equilibration Reaction over Platinum Supported on Polyamide-6

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Catalysis by platinum supported on polyamide-6 was examined for the $H_2$-$D_2$ equilibration reaction at 0 °C in the pressure range of 5—20 Torr (1 Torr=133.3 Pa). Three kinds of polyamides with different molecular weights were prepared as support; the concentration of platinum varied from 0.5 to 2.7 wt%. With preadsorption of hydrogen at 0 °C, the rate of the reaction was found to increase up to 10 times as high as the original level. The rate $k_m$ (HD molecule $s^{-1}$Pt atom$^{-1}$) showed a maximum, depending on surface area of the polyamides used, in the range 0.8—1.0 wt% of Pt content and its dependence on total pressure is represented by $k_m=K_1P/(1+K_2\sqrt{P})^2$ irrespective of Pt content. No significant isotope effect was observed at 0 °C. It was found that a linear relationship exists between the enhancement of $k_m$ and the amount of hydrogen preadsorbed, indicating an important role of the preadsorbed hydrogen in activation of the catalysts. In contrast to $k_m$, the turn-over frequency $k_t$ (HD molecule $s^{-1}$ site$^{-1}$) was nearly independent of Pt concentration. The exchange reaction is explained in terms of the Bonhoeffer-Farkas mechanism. XPS spectra provided the evidence for the presence of Pt(II) complexes on the surface. The structure of active sites is discussed.

Catalysis by metals dispersed on organic polymers has been the subject of particular interest, because the catalytically active sites are different in electronic and geometric factors from metals on inorganic supports. The pioneering work on this subject has been done by Izumi,[1] who employed silk fibroins as supports for palladium and studied the hydrogenation of various organic compounds. Harrison and Rase[2] studied the hydrogenation of benzene on platinum supported on polyamides. They reported the capacity of the catalysts to produce cyclohexene, which is scarcely formed at all on silica-supported platinum. They used polymers with different periodic structures, and pointed out the importance of the geometric arrangement of Pt metal atoms correlating to the position of the amide group in the polymer chains. Dini *et al.*[3] examined the number of chlorine atoms remaining in the catalysts and showed the presence of bivalent platinum ions which are available as sites for the formation of cyclohexene.

The structures and distributions of active sites on polyamides are of interest. So we will examine systematically the effect of platinum metal dispersion upon catalytic activity, since the number of the active sites is likely to depend on that of NHCO and/or $NH_2$ groups exposed to the surface to which Pt is considered to be bonded. Further information is obtained from the change in catalytic activity which occurs when the polyamides which differ as much in molecular weight as possible are used.

In our preliminary study[4] on the hydrogenation of acetylene and butadiene over the Pt–polyamide catalysts, it was found that the major products of the reactions were the saturated hydrocarbons instead of the corresponding monoolefins, indicating that the reactions are quite different in selectivity from those on metal powder and silica-supported catalysts reported earlier.[5] Preadsorbed hydrogen promoted the reactions and there were optimum conditions to give the stable and high catalytic activity, which is apparently associated with the pretreatment by hydrogen. These results led to the consideration that an interaction of hydrogen with Pt on the polymer is characteristic, but no extensive study has been done so far. Thus, the present study was undertaken to examine the equilibration reaction between $H_2$ and $D_2$ on Pt–polyamide catalysts and to determine the effect of Pt dispersion on catalytic activity. In order to get information on the states of Pt supported on polyamides, X-ray photoelectron Spectroscopy (XPS) was employed in this study.

## Experimental

*Catalyst Preparations.* Polyamide-6 (PA) was obtained by the polymerization of ε-caprolactam (Wako Pure Chemical Co.) initiated with 1.0 wt% of 6-aminohexanoic acid at 250 °C in a stream of nitrogen. Unreacted monomer, oligomers, and cyclic oligomers were eliminated from the products with hot water. The polyamide-6 was dissolved into formic acid of extra pure grade, and then the PA powder was obtained by transferring the solution to ion-exchanged water and drying *in vacuo* at room temperature. Three kinds of polyamide-6 with different molecular weights of $6.8\times10^3$, $3\times10^3$, and $1.7\times10^3$ (as denoted by L, M, and S hereafter) were prepared and found to have surface areas of 5.7, 5.5, and 4.6 $m^2/g$, respectively.

The polymers were immersed in an aqueous solution of $H_2PtCl_6$ of about $8\times10^{-3}$ Pt g/l in concentration, heated at 90 °C for 2 h and then washed thoroughly with ion-exchanged water. The catalysts were dried *in vacuo* at room temperature. The concentration of Pt dispersed on PA was determined according to the procedure described in the reference.[6] The catalysts with Pt concentration of 0.5 to 2.7 wt% were prepared. Elemental analysis showed that the amount of chlorine atoms remaining on the treated 2.7 wt% Pt–PA-M catalyst was estimated, in terms of the Cl/Pt ratio, at 1.7.

*Characterization of Catalyst.* In order to examine the valence states of Pt bonded to PA, a Hewlett-Packard 5950A ESCA spectrometer with a monochromatic Al *Kα* X-ray was used and a flood gun was operated at 0.3 mA with 0—0.7 eV to avoid the charging of the samples. The binding energy of C 1 s of $CH_2$ group in PA, 284.8 eV, was taken as standard. X-Ray diffraction and electron microscopic studies were done to ascertain the presence of Pt crystallites and also their distributions on the surface.

*Equilibration Reaction.* The equilibration reaction between $H_2$ and $D_2$ was studied using a closed circulating apparatus which was similar to that used before.[7] Hydrogen, hydrogen deuteride, and deuterium were analyzed by a gas chromatograph connected to the system.[7] Prior to the kinetic run, a fresh catalyst was evacuated at 150 °C for 1 h and then cooled to the reaction temperature, 0—35 °C. Hydrogen (99.98% pure), and deuterium (containing less than 0.5% HD) were obtained from Takachiho Chemical Co. and used without further purification.

## Results

Figure 1 shows the time course of the equilibration reaction at 0 °C using the catalyst evacuated at 150 °C. The rate of equilibration is expressed as

$$\ln (X_0-X_e)/(X_t-X_e) = k_e t \tag{1}$$

where $X_0$, $X_t$, and $X_e$ are, respectively, the fraction of HD at $t=0$, $t$, and equilibrium. In the initial stage of the first run (curve a), the experimental values were considerably off the linearity but, after three or more successive runs, they turned out to fit a linear expression. The reaction rate $k_e$ is derived from the slope and then $k_m$ is defined as

$$k_m = nk_e/N_{Pt} \quad \text{(molecule s}^{-1}\text{ Pt atom}^{-1}) \tag{2}$$

where $n$ is the number of molecules in the gas phase and $N_{Pt}$ the number of Pt atoms. Figure 2 shows the dependence of the reaction rate upon the time of exposure of the catalyst to hydrogen of 20 Torr at 0 °C after evacuation at 150 °C. The catalytic activity increased with the contact time and no further increase was observed after 24 h. The highest activity, about 10 times as high as the original one of the first run without $H_2$-preadsorption, was diminished by evacuation at 150 °C for 3 h to the original level, but the treatment with hydrogen at 0 °C promoted again the activity to the highest level. This cycle of activation and deactivation was quite reversible and reproducible. Evacuation at 0 °C for less than 30 min caused no significant change in the highest activity, which was taken as the measure for comparison of catalytic activity, unless otherwise stated.

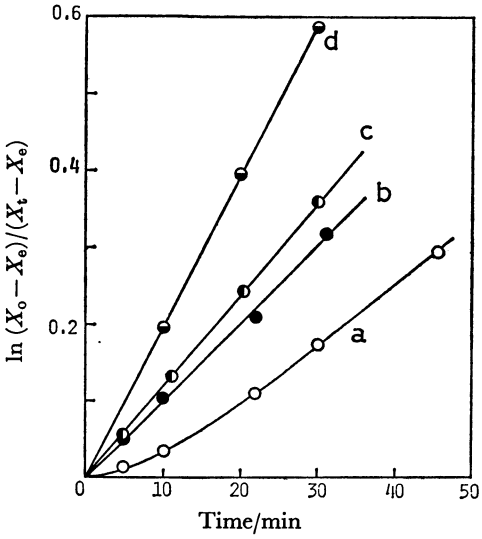


Fig. 1. $H_2$-$D_2$ exchange reaction on 0.5 wt% Pt-PA-M. ○: First run, ●: second, ◐: third, ◒: fourth. Between each run, the catalyst was evacuated at 0 °C for 10 min. The reaction conditions are as follows unless otherwise stated. Total pressure = 20 Torr, $H_2/D_2=1$, reaction temperature = 0 °C.

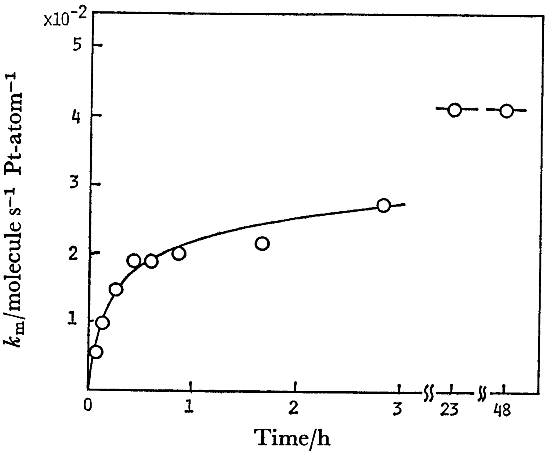


Fig. 2. Increase in $k_m$ as a function of time exposed to hydrogen.
Catalyst: 0.5 wt% Pt-PA-M, $P_H = 20$ Torr, temperature = 0 °C.

The dependence of $k_m$ on Pt concentration for three catalysts, Pt-PA-L, -M, and -S, is shown in Fig. 3. Each catalyst has a maximum $k_m$ value around 0.8—1.0 wt% of Pt. The activity beyond the maximum declined sharply. Figure 4 shows Arrhenius plots for the $H_2$–$D_2$ equilibration on 0.5, 0.8, 1.0, and 2.0 wt% Pt-PA-M catalysts. The evaluated activation energies were almost constant as 7.2±0.2 kcal/mol (1 kcal=4.184 kJ) irrespective of Pt content. The total pressure dependence of the exchange rate for these four catalysts using an equimolar mixture of $H_2$ and $D_2$ as reactant is shown in Fig. 5. The reciprocals of the square root of both total pressure $P$ and $k_m$ provided a linear relationship for each catalyst, indicating that $k_m$ can be represented as $K_1P/(1+K_2\sqrt{P})^2$

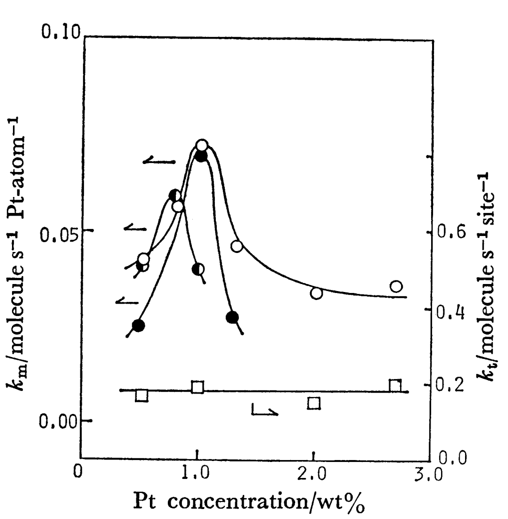


Fig. 3. Change in $k_m$ and invariance of $k_t$ with Pt concentration.
$k_m$, ○: Pt-PA-M, ◐: -S, ●: -L. $k_t$, □: Pt-PA-M.

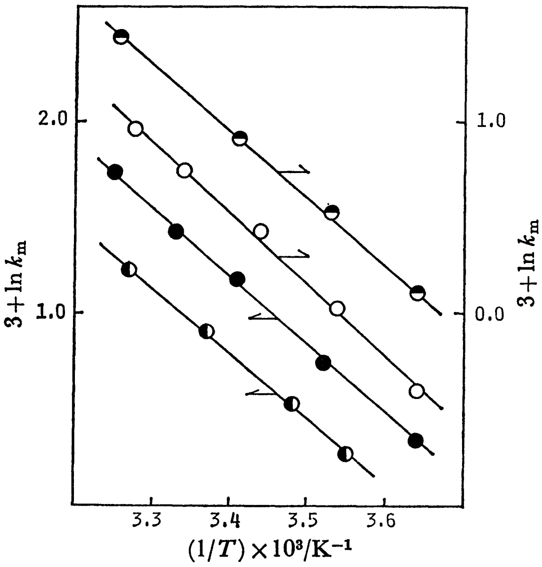


Fig. 4. Arrhenius plots for $H_2$-$D_2$ exchange reaction. ◐: 0.5 wt% Pt-PA-M, ◓; 0.8, ●; 1.0, ○; 2.0.

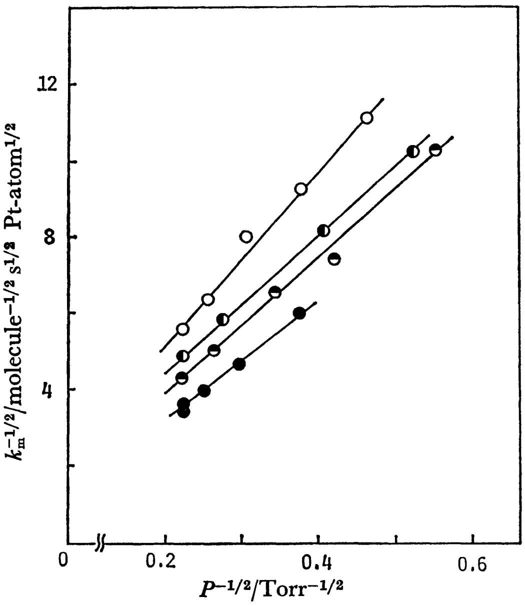


Fig. 5. Total pressure dependence of $k_m$ at 0 °C. ◐: 0.5 wt% Pt-PA-M, ◓; 0.8, ●; 1.0, ○; 2.0.

where $K_1$ and $K_2$ are constants.

In order to see the detailed kinetic behavior of the reaction and also to ascertain whether the isotope effect is present or not, the partial pressure dependence was investigated at 0 °C. For 1.0 wt% Pt–PA-M catalyst, the reaction order with respect to hydrogen pressure, $P_H$, was about 0.5 in a range from 2 to 4.7 Torr at a fixed deuterium pressure, $P_D$, of 7 Torr, and the deuterium order was the same as that of hydrogen in a range of $P_D$ from 0.4 to 4.5 Torr at a fixed $P_H$ of 5 Torr. This close similarity in the partial pressure dependence between $H_2$ and $D_2$ predicts that there exists little isotope effect at the reaction temperature.

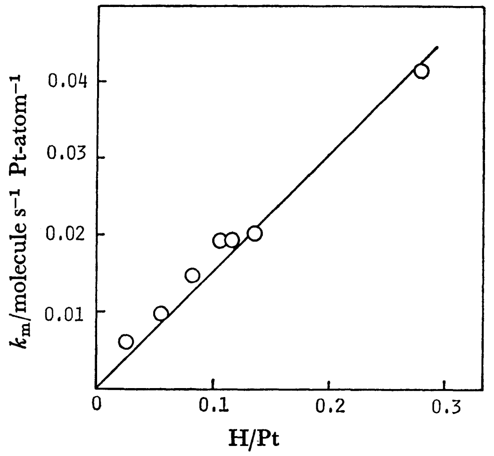


Fig. 6. Relationship between $k_m$ and H/Pt ratio. Catalyst: 0.5 wt% Pt-PA-M.

The adsorption of hydrogen at 0 °C in an activation process occurred in a slow manner analogous to the increase of activity observed in Fig. 2; thus we can obtain a correlation between the amount of the preadsorbed hydrogen and the corresponding catalytic activity. The results are shown in Fig. 6. The linear relationship between $k_m$ and the H/Pt ratio reflects the direct contribution of hydrogen to the activation of catalysts. The saturation of the preadsorbed hydrogen took place after 24 h, and evacuation of the surface at 0 °C for 10 min caused negligible desorption of the hydrogen, since no further adsorption of hydrogen was observed after the introduction of hydrogen following the evacuation. For Pt–PA-M catalysts with Pt loading ranging from 0.5 to 2.7 wt%, the saturated amount of the adsorbed hydrogen per gram Pt increased with the content, passed through a maximum at 1.0 wt%, and decreased. This change is in a close parallel to that observed in the catalytic activity. The number of active sites can be calculated from that of the hydrogen atoms preadsorbed. The turn-over frequency, $k_t$, in terms of molecules s$^{-1}$ site$^{-1}$, is given in Fig. 3.

The effects of the preadsorbed hydrogen on the exchange reaction of catalyst hydrogen with gaseous deuterium were examined at 0 °C. Hydrogen of $3.6\times10^{-6}$ mol was preadsorbed at 0 °C, evacuated for 10 min, and then deuterium of 2.4 Torr was introduced. The rate of HD formation is much the same in the cases of both the presence and the absence of the preadsorbed hydrogen, but smaller by a factor of about 40 compared to the ordinary rate in the steady reactions. In order to confirm whether or not the slow exchange is attributable to the reaction between the structural hydrogen in PA and gaseous deuterium, 1.0 wt% Pt–PA-M catalyst was exposed to a deuterium atmosphere at 150 °C. The number of the exchanged hydrogen atoms was found to amount to approximately 300 times that of Pt atoms, indicating that hydrogens in bulk organic groups participated in the exchange. After the exchange, the catalyst was examined by means of infrared spectroscopy, and, in addition to ordinary bands due to PA, new strong bands at 2400 and 2460 cm$^{-1}$ and also weak bands at 2090 and 2190 cm$^{-1}$ were observed. The former group corresponds to the bands of the characteristic region ascribable to the N–D stretching vibration. The latter two bands are reasonably assigned to the C–D stretching vibration.

For 2.7 wt% Pt–PA-M catalyst without evacuation at high temperature after preparation, the Pt 4f region of X-ray photoelectron spectra showed three peaks, the central one of which is apparently derived from a superposition of two peaks (Fig. 7 and Table 1). From the comparison with binding energies of Pt complexes reported earlier,[8] these peaks can be associated with the 4f level of Pt(IV) and Pt(II). It was found that three peaks gradually changed to two stable peaks, $4f_{7/2}$ and $4f_{5/2}$, during the course of the photoemission measurement and that X-ray irradiation caused the reduction of Pt(IV) to Pt(II), which is analogous to the phenomena observed in XPS studies on Pt complexes.[8,9] For 2.7 wt% Pt–PA-M catalyst, which was evacuated at 150 °C, only two 4f peaks appeared at the binding energies of 72.5 and 75.7 eV, which are higher by 1.3—1.2 eV than those of Pt metal, indicating the presence of Pt(II) on PA. Further exposure of the surface to a hydrogen atmosphere at 0 °C for 24 h gave rise to no significant change in the spectra. The chlorine 2p level was monitored but no strong peak was observed. This is probably attributed either to the low intensity of the level or to the loss of chlorine with X-ray exposure, which occurred in the case of Cl-containing Pt complexes.[8] For N 1s and O 1s levels, neither a significant shift of the peaks nor broadening was observed between PA and Pt–PA.

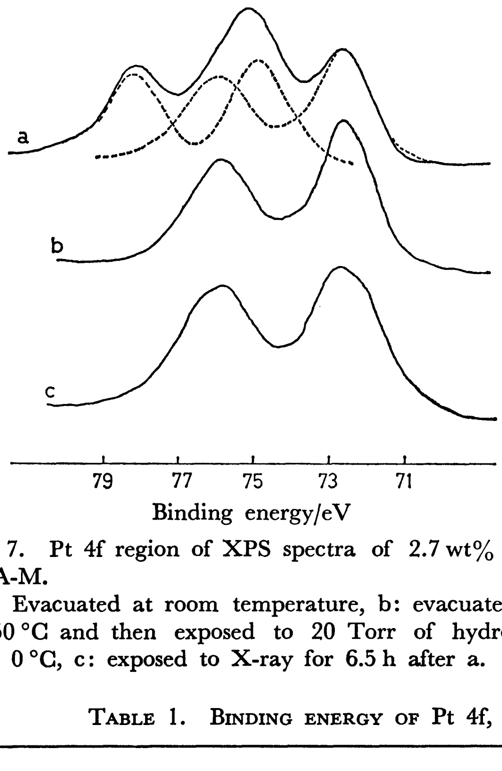


Fig. 7. Pt 4f region of XPS spectra of 2.7 wt% Pt–PA-M.
a: Evacuated at room temperature, b: evacuated at 150 °C and then exposed to 20 Torr of hydrogen at 0 °C, c: exposed to X-ray for 6.5 h after a.

No appreciable change was observed in the infrared spectra of the organic groups characteristic in PA when the platinum complex was deposited on it. The X-ray diffraction measurement provided only a diffused peak due to PA crystallites and showed unambiguous evidence for the absence of large Pt metal particles. Electron microscopy was applied to the catalysts under a magnification of more than 90000, but failed to detect the presence of large Pt particles.

## Discussion

The platinum–PA catalysts are characterized by a gradual increase in the activity for $H_2$–$D_2$ equilibration as the catalysts are exposed to a hydrogen atmosphere. One might argue that such an activity enhancement is ascribable to metal particles produced by the reduction of the Pt complexes. This is unlikely, because the activity was lost upon heat-treatment at 150 °C but again restored to the same level as before when they were exposed to a hydrogen atmosphere at 0 °C. XPS results gave no sign of a Pt 4f peak due to the metallic state, but showed the presence of bivalent platinum cation. The results obtained by electron microscopy and X-ray diffraction also support this view. The reversible change in catalytic activity mentioned above clearly shows that the preadsorbed hydrogen played an important role in the formation of catalytically active sites.

It is of interest to see that the position of peak activity shown in Fig. 3 can be correlated with the surface area of PA used as support; for both PA-L and PA-M catalysts having the surface areas of 5.7 and 5.5 $m^2/g$, each peak appears at a Pt content of 1 wt%, whereas for PA-S the downward shift of the position occurs by a factor of 0.2, almost the same ratio as the decrease in the surface area. This correlation indicates that the functional organic groups of PA exposed on the surface, but not those in bulk, are of importance in catalysis, and also predicts that the number of active

Table 1. Binding energy of Pt 4f, N 1s, and O 1s levels of 2.7 wt% Pt-PA-M catalyst

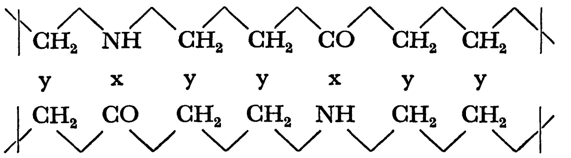
| Samples | Binding energy/eV[b) | | | |
|---|---|---|---|---|
| | Pt $4f_{7/2}$ | Pt $4f_{5/2}$ | N 1s | O 1s |
| 1) PA-6 | — | — | 399.6 | 531.1 |
| 2) 2.7 wt% Pt-PA-M evacuated at room temperature[a) | 72.7 75.4 | 78.1 | 399.6 | 531.1 |
| | 72.7<br>75.0 | 76.0 Pt(II)<br>78.2 Pt(IV) | | |
| 3) 2.7 wt% Pt-PA-M evacuated at 150 °C | 72.5 | 75.7 | 399.5 | 531.2 |
| 4) After 3), exposed to $H_2$ at 0 °C | 72.7 | 76.0 | 399.5 | 531.2 |
| 5) Pt metal | 71.2 | 74.5 | — | — |

a) Prolonged exposure to X-ray gives the values of 72.8 and 76.0 eV for the Pt 4f region. b) C 1s=284.8 eV as standard. The error in binding energy is within 0.2 eV.

sites is proportional to that of such groups.

The (010) face of a polyamide-6 crystal consists of a unit cell with a dimension of 17.2 Å × 4.78 Å and involves two NHCO groups. For 1.0 wt% Pt–PA-M catalyst, a calculation gave the ratio of Pt atoms to surface NHCO groups to be 2.3. Since even the highest value of the H/Pt ratio reaches only 0.4, not all the Pt atoms on PA can work as active sites for both the equilibration and the adsorption of hydrogen. This low ratio of H/Pt is consistent with the results obtained by Dini *et al.*;[3] their 0.6 and 3.8 wt% Pt supported on nylon-6 catalysts gave 0.08 and 0.11, respectively, at 25 °C. It should be noted that no metal crystallites as large as 100 Å, which would be anticipated in such low degrees of exposure, were detected.

The kinetic results showed that the turn-over frequency $k_t$ for the exchange reaction is apparently independent of Pt content and that kinetic behavior such as activation energy and reaction order are almost the same over the whole range of the loading. Thus, it is suggested that there is a single kind of catalytically active site on the surface. For this view, the presence of a maximum in $k_m$ appears somewhat puzzling, but is explained by the model on the basis of the following assumptions. The fundamental unit of polyamide-6 (α-type) is given below, where x and y represent the positions corresponding to the spacing between neighboring polymer chains.



It is likely that an NHCO group (position x) is involved in the coordination with the Pt complex, whereas a $CH_2$ group (position y) has a weak interaction with the complex upon its access. It is assumed that such characteristics in the structure of PA-6 lead to the formation of cluster complexes consisting of two and three Pt metal atoms, denoted as $(Pt)_2$ and $(Pt)_3$ respectively, and that only $(Pt)_3$ is catalytically active. The ratio of existing $(Pt)_3$ to $(Pt)_2$ depends on the numbers of the positions having suitable spacing in the vicinity of NHCO group; thus it follows that the catalytic activity becomes the highest when one unit is occupied by one $(Pt)_3$ and one $(Pt)_2$. Further deposition of Pt beyond this distribution results in the decrease of the catalytic activity per gram Pt. Table 2 shows the results of calculations obtained on the basis of the distribution of $(Pt)_3$ and $(Pt)_2$ on the polyamide-6 with a periodicity of three units which contain six NHCO and fifteen $CH_2 \cdots CH_2$ groups in them. The rather good agreement between the calculated and experimental values shows that the structures of the active sites are well represented by the cluster model.

*Reaction Mechanism.* The adsorption of hydrogen in the formation of the catalytically active sites is undoubtedly slow and irreversible at 0 °C, but induces a drastic rise in activity. The following process seems to take place.

$$(Pt)_3 + H_2 \longrightarrow (Pt^*)_3 \tag{3}$$

where $(Pt^*)_3$ represents the catalytically active sites. The $H_2$–$D_2$ equilibration on this surface is considered in terms of the Bonhoeffer-Farkas mechanism which is shown below.

$$H_2(g) \underset{k_d^H}{\overset{k_a^H}{\rightleftharpoons}} 2H(a) \tag{4}$$

$$HD(g) \underset{k_d^{HD}}{\overset{k_a^{HD}}{\rightleftharpoons}} H(a) + D(a) \tag{5}$$

$$D_2(g) \underset{k_d^D}{\overset{k_a^D}{\rightleftharpoons}} 2D(a) \tag{6}$$

The rate constants of adsorption and desorption are denoted as $k_a^i$ and $k_d^i$, respectively, where i=H, HD, or D. The changes in surface concentration of hydrogen and deuterium atoms as a function of time can be represented by the following equations:

$$\frac{d\theta_H}{dt} = 2k_a^H P_H(1-\theta_H-\theta_D)^2 + k_a^{HD} P_{HD}(1-\theta_H-\theta_D)^2 - 2k_d^H \theta_H^2 - k_d^{HD}\theta_H\theta_D \tag{7}$$

$$\frac{d\theta_D}{dt} = 2k_a^D P_D(1-\theta_H-\theta_D)^2 + k_a^{HD} P_{HD}(1-\theta_H-\theta_D)^2 - 2k_d^D \theta_D^2 - k_d^{HD}\theta_H\theta_D \tag{8}$$

Table 2. The H/Pt ratio and the number of Pt atoms on Pt-PA catalysts

| Catalysts | $(N_n+N_c)$[a] | wt% | Obsd Pt (atom/g) | Obsd H/Pt | Calcd[b] Pt (atom/g) | Calcd[b] H/Pt |
|---|---|---|---|---|---|---|
| Pt-PA-L | $4.9\times10^{19}$ | 1.0 | $3.1\times10^{19}$ | — | $3.5\times10^{19}$ | — |
| Pt-PA-M | $4.7\times10^{19}$ | 1.0 | $3.1\times10^{19}$ | 0.40 | $3.3\times10^{19}$ | 0.40 |
|  |  | 0.5 | $1.5\times10^{19}$ | 0.27 | $1.6\times10^{19}$ | 0.27 |
| Pt-PA-S | $3.9\times10^{19}$ | 0.8 | $2.5\times10^{19}$ | — | $2.8\times10^{19}$ | — |

a) The total number of NHCO and $CH_2$ surface groups per gram of catalyst. b) At the maximum activity, the surface of three units distributes fifteen Pt atoms on twenty one positions (=x+y). Numbers of Pt atoms per gram catalyst were calculated by multiplying $(N_n+N_c)$ by 15/21. The H/Pt ratio is given by 2×(number of $(Pt)_3$)/(number of Pt atoms) under the assumption that a hydrogen molecule occupies a $(Pt)_3$. From the distribution of the cluster described in the text, the H/Pt value is calculated to be 2×3/15=0.4 for 1.0 wt% and 2×1/7.5=0.27 for 0.5 wt%. This model permits the comparison of $k_m$; for 1.0 wt%, $k_m$ is given by $(3/15)k_t$, whereas for 0.5 wt% by $(1/7.5)k_t$. The ratio of $k_m$(1.0 wt%)/$k_m$(0.5 wt%), 1.5, is close to the observed one, 1.7.

where $\theta_H$ and $\theta_D$ are, respectively, the fractions of hydrogen and deuterium occupying the active sites in the complex. The neglect of the isotope effect leads to the simple relations, $k_a^H=k_a^D=k_a^{HD}=k_a$ and $2k_d^H=2k_d^D=k_d^{HD}=k_d$. The factor 2 in the desorption rate constants $k_d^H$ and $k_d^D$ comes from the fact that the probability of making an atom pair HD is twice as large as that of making a pair $H_2$ or $D_2$. Since the amount of hydrogen adsorbed on a catalyst surface was negligibly small compared to that in the gas phase, $P_{HD}$ is represented by 2 $(P_H^\circ-P_H)$ or 2 $(P_D^\circ-P_D)$, where $P_H^\circ$ and $P_D^\circ$ are hydrogen and deuterium pressures at $t=0$, respectively. By introducing the steady-state approximation, $d\theta_H/dt=d\theta_D/dt=0$, and the relations described above, one can obtain the following equations:

$$(1-\theta_H-\theta_D)^2 2KP_H^\circ = \theta_H(\theta_H+\theta_D) \tag{9}$$

and

$$(1-\theta_H-\theta_D)^2 2KP_D^\circ = \theta_D(\theta_D+\theta_H) \tag{10}$$

where $K$ denotes $k_a/k_d$.

*Total Pressure Dependence.* The rate equation which describes the time course of the reaction is given by

$$\left(\frac{N_aV}{RTN_{pt}}\right)\frac{dP_{HD}}{dt} = k_d\theta_H\theta_D - k_aP_{HD}(1-\theta_H-\theta_D)^2 \tag{11}$$

where $N_a$ is Avogadro's number, $V$ the volume of the reaction system, and $R$ the gas constant. Since the equimolar mixtures of $H_2$ and $D_2$ were used as the reactants, the relations, $\theta_H=\theta_D=\theta/2$ and $P_H^\circ=P_D^\circ=P^\circ/2$, always hold in this case. Equation 9 or 10 is then transformed into

$$\theta_H + \theta_D = \theta = \frac{\sqrt{2KP^\circ}}{1+\sqrt{2KP^\circ}} \tag{12}$$

The insertion of Eq. 12 into Eq. 11 provides

$$\left(\frac{N_aV}{RTN_{Pt}}\right)\frac{dP_{HD}}{dt} = \frac{k_dKP^\circ}{(1+\sqrt{2KP^\circ})^2}\left(\frac{1}{2}-\frac{P_{HD}}{P^\circ}\right) \tag{13}$$

By introducing the fraction of HD in the gas phase, $X_{HD}=P_{HD}/P^\circ$ and that in equilibrium, $X_e=P_{HD}^e/P^\circ=1/2$, Eq. 13 can be rewritten as

$$\frac{dX_{HD}}{dt} = k_e(X_e-X_{HD}) \tag{14}$$

where

$$k_e = \frac{k_dKRTN_{Pt}}{N_aV(1+\sqrt{2KP^\circ})^2} \tag{15}$$

The integration of Eq. 14 gives the experimental relation (1), and Eq. 2 on $k_m$ is correlated with $k_e$ in Eq. 15 as

$$k_m = \frac{nk_e}{N_{Pt}} = \frac{k_dKP^\circ}{(1+\sqrt{2KP^\circ})^2} \tag{16}$$

This equation accords well with the observed kinetic behavior shown in Fig. 5.

*Partial Pressure Dependence.* By solving Eq. 9 and 10, one can obtain the following expressions for $\theta_H$ and $\theta_D$:

$$\theta_H = \frac{\sqrt{2KP_H^\circ}}{\sqrt{(P_H^\circ+P_D^\circ)}\,[1+\sqrt{2K(P_H^\circ+P_D^\circ)}]} \tag{17}$$

$$\theta_D = \frac{\sqrt{2KP_D^\circ}}{\sqrt{(P_H^\circ+P_D^\circ)}\,[1+\sqrt{2K(P_H^\circ+P_D^\circ)}]} \tag{18}$$

The measurements on the partial pressure dependence of the rate were carried out only at the initial stage of reaction and then $P_{HD}$ in Eq. 11 was safely omitted from the expression.

$$\left(\frac{N_aV}{RTN_{pt}}\right)\frac{dP_{HD}}{dt} = k_m' = k_d\theta_H\theta_D$$
$$= \frac{2k_dKP_H^\circ P_D^\circ}{(P_H^\circ+P_D^\circ)[1+\sqrt{2K(P_H^\circ+P_D^\circ)}]^2} \tag{19}$$

where $k_m'=k_m/2$ when $P_H^\circ=P_D^\circ$. This equation can be transformed into

$$\sqrt{\frac{P_H^\circ P_D^\circ}{k_m'(P_H^\circ+P_D^\circ)}} = \sqrt{\frac{1}{2k_dK}} + \sqrt{\frac{1}{k_d}}(P_H^\circ+P_D^\circ)^{1/2} \tag{20}$$

Figure 8 shows the plot of experimental values of $\sqrt{P_H^\circ P_D^\circ/k_m'(P_H^\circ+P_D^\circ)}$ against $(P_H^\circ+P_D^\circ)^{1/2}$. Besides, the values of $k_d$ and $K$ were evaluated at 2.2 molecule $s^{-1}$ Pt atom$^{-1}$ and $3.6\times10^{-3}$ Torr$^{-1}$, respectively, from the observed rate shown in Fig. 5. These values were inserted into Eq. 20 and the line thus obtained is also shown in Fig. 8. In spite of the lower accuracy in the values of initial rate, the correspondence between the results of the separate studies seems fairly good and suggests that the proposed mechanism is an acceptable one. The equation derived on the basis of the Rideal-Eley mechanism did not fit with the experimental pressure dependence.

It is of interest to compare the present kinetic results with those on metal platinum. The value of $k_m$ is smaller by a factor of about $10^3$ at 0 °C than the absolute equilibration rate (molecule $s^{-1}$ Pt atom$^{-1}$) on Pt wire cleaned by outgassing around 1100 °C,[10] and the activation energy of about 7 kcal/mol in the present study makes a contrast to the negligibly small value for Pt wire at temperatures higher than −73 °C.[10] The detailed analysis of energy level of the adsorbed hydrogen is permitted by use of the thermal desorption technique and will be presented in a subsequent paper.

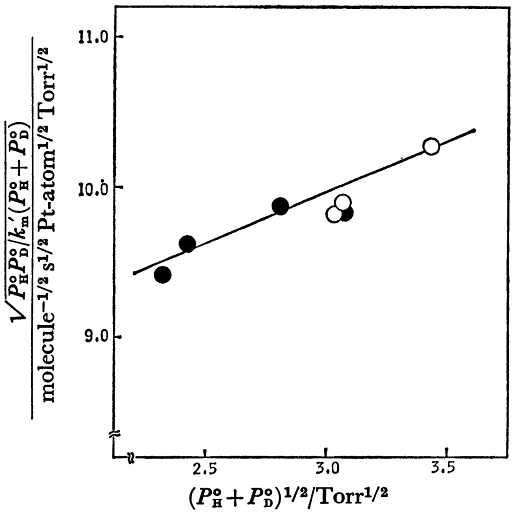


Fig. 8. Plots of $\sqrt{P_H^\circ P_D^\circ/k_m'(P_H^\circ+P_D^\circ)}$ *vs.* $(P_H^\circ+P_D^\circ)^{1/2}$.
○: $P_D=7$ Torr, $2\leq P_H\leq4.7$ Torr, ●: $P_H=5$ Torr, $0.4\leq P_D\leq4.5$ Torr. ——: Calculated line from $k_d$ and $K$ obtained from the total pressure dependence of the rate.

*Structures of Active Sites and Role of Preadsorbed Hydrogen.* There are several possibilities about the structures of the active sites of Pt–polyamide catalysts. The monoatomic dispersion of platinum metal with a suitable arrangement of appropriate amide group spacing was first proposed in order to explain the formation of cyclohexene in the benzene hydrogenation,[2] but confirmative support has not been so far obtained by other workers. Bernard *et al.*[11] observed the formation of Pt metal crystallites on nylon-66 upon heating, but showed that such an aggregation is due to the specific structure of nylon-66. Such formation is not the case in polyamide-6. On the other hand, the importance of platinum complexes containing chlorine atoms has been pointed out; Dini *et al.* reported the ratio of Cl/Pt to be 2 for 0.6 wt% Pt–nylon-6 catalyst.[3] From the diamagnetic properties of Pt on nylon, Rasadkina *et al.* concluded that platinum is nonmetallic in character.[12] These results indicating the presence of Pt(II) are consistent with our XPS results.

The present kinetic results for the equilibration are well explained by the Bonhoeffer-Farkas mechanism. Since the mechanism involves the dissociative adsorption of both hydrogen and deuterium and needs at least four sites available in the neighborhood, it seems unlikely that a complex of single Pt atom can work as the active site. The requirement of such multiple sites and of the presence of a bivalent cation provides further support to the existence of the cluster such as $(Pt)_3$ which was proposed on the basis of the model discussed earlier. Although no experimental evidence has yet been obtained, it seems plausible that the clusters are analogous to complexes with bridging metal–halogen bonds. The process of activation of the catalysts probably involves the dissociation of hydrogen molecules into atoms. The splitting of the hydrogen molecule is likely to take place, since UV spectra on Rh–polyamide catalysts showed the formation of a hydride complex when the catalysts in an aqueous alcoholic solution were exposed to a hydrogen atmosphere.[13] However, the exchangeable hydrogen takes a different configuration and location on the surface from those of the preadsorbed hydrogen used for activation, because the exchange of the former hydrogen is very rapid. The difinite structure of the clusters and the conformation of the hydrogen on them have to await further study. The loss of the activity upon heating at 150 °C can be explained by a reverse process to reproduce the original complex by the desorption of hydrogen.

*Exchange of Hydrogen in PA with Deuterium.* The exchange rate of the structural hydrogen in PA support with gaseous deuterium at 0 °C was lower than that of $H_2$–$D_2$ equilibration by a factor of about 40 under ordinary conditions, and showed no enhancement even for the activated catalysts. The infrared spectra of Pt–PA-M systems in which hydrogen was replaced by deuterium to different extents showed that the exchange of hydrogen atoms in NH and $NH_2$ groups was preferentially invoked as a first step, followed by the exchange of hydrogen in the $CH_2$ group. These results together with those of the measurement of electric conductivity of polyamides by Eley and Spivey[14] suggest that the slow exchange described here takes place with proton diffusing on the surface and also in the bulk of the polyamide.

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