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# Catalytic Activity of Highly Dispersed Palladium. I. The Mechanism of Cyclohexene Hydrogenation and the Role of $ZrO_2$ Support

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The hydrogenation of cyclohexene vapor on dispersed palladium was studied in the pressure range of 10—40 Torr[†] at temperatures between 283 and 323 K. Palladium was impregnated on $ZrO_2$ and $\alpha$-$Al_2O_3$ over the wide range of 0.03 to 2.1 wt%, and the percentage exposed was varied from 13 to 96% for Pd/$ZrO_2$ and from 2 to 15% for Pd/$\alpha$-$Al_2O_3$. The hydrogenation activity, $V_g$, per unit of weight of the Pd dispersed on $ZrO_2$, exhibited a sharp maximum at 0.05 wt%, but the turn-over frequency, $V_s$, per exposed atom around this maximum remained almost constant, which shows the reaction to be structure-insensitive. The value of $V_s$ for Pd/$ZrO_2$ at 301 K was larger than those for Pd/$\alpha$-$Al_2O_3$ and Pd bulk metal by one order of magnitude. The $ZrO_2$ carrier affected the catalytic behavior of palladium; the reaction orders with respect to the hydrogen and cyclohexene pressures changed to $0.73 \pm 0.04$ and $0.64 \pm 0.04$ respectively from the corresponding values, $0.97 \pm 0.03$ and $0.07 \pm 0.04$ for Pd/$\alpha$-$Al_2O_3$ and Pd metal. The deuterium distributions in the reactant and product molecules in the reaction with $D_2$ suggested that the hydrogenation on Pd/$ZrO_2$ and Pd/$\alpha$-$Al_2O_3$ proceeds *via* the associative mechanism; the slow step is assumed to be the reaction of the surface cyclohexyl radical with the adsorbed hydrogen atom. The poisoning due to preadsorbed CO decreased the catalytic activities of Pd/$ZrO_2$ and Pd/$\alpha$-$Al_2O_3$ almost linearly with the amounts of surface CO and caused a complete deactivation at about a half coverage of the surface Pd atoms, irrespective of the percentage exposed. On the basis of these results, the structure-insensitivity of the cyclohexene hydrogenation on Pd and the carrier effect of $ZrO_2$ are discussed.

In order to get a fundamental understanding of heterogeneous catalysis by metals, the effect of the surface structure on the activity has been extensively studied using metals dispersed on supports[1] as well as their single crystals.[2] It appears that attention has been forcused on the shapes and size distributions of metal crystallites in connection with their activity, while supports have simply been regarded as inert matrices. Recently, however, it has been pointed out that the peculiar catalytic activity might be induced by the interactions between metal particles and support; this has been known as the "support effect."[3] In this regard, the oxides of Group $IV_a$ metals have exerted noteworthy effects as supports or promotors of the catalytic hydrogenation.

Maxted and Ali[4] reported that palladium metal loaded on $ZrO_2$, $ThO_2$, and $TiO_2$ exhibited not only a higher activity for the liquid-phase hydrogenation of cyclohexene than that of the unsupported metal, but also its maximum in activity at a definite concentration of Pd, depending on the respective supports. Recently, Fujimoto *et al.*[5] showed that the addition of $ThO_2$ to the silica-supported Pd catalyst markedly increased the activity for the hydrogenation of CO. These positive effects of the oxides are of particular interest, but they have not yet been analyzed in detail.

Since the influence of the oxides on the catalytic behavior of Pd seems to become smaller as the size of metal crystallites increase, distinct evidence of the support effect can be obtained by the use of catalysts in a state of high dispersion or with a large percentage exposed. In the present study, the first one of this series, $ZrO_2$ was taken as a potentially interesting support on which palladium metal was dispersed over a wide range of surface concentrations and the hydrogenation of cyclohexene was studied. The reaction on $\alpha$-$Al_2O_3$-supported and bulk metal palladium was also examined for comparison. Both supported catalysts were characterized by CO chemisorption and X-ray diffraction methods, and the percentage exposed was determined. Although most of the works on cyclohexene hydrogenation over Pd blacks[6] and Pd/$Al_2O_3$[7] have been carried out in the liquid phase, we studied the reaction in the gas phase because of easier kinetic analysis. The kinetics was supplemented by the results of an examination of the deuterium distributions in the product and reactants in the reaction with $D_2$.

The relationship between the percentage exposed and the turnover frequency enables us to inspect the effect of the surface structure upon the catalytic behavior, but it is not sufficient for us to evaluate the surface density of active sites. Accordingly, the poisoning due to preadsorbed CO was applied to the present catalyst system in order to evaluate the density and, further, to study the nature of the active sites, which may change through the interaction with carries.

## Experimental

*Catalysts.* Palladium supported on zirconia or $\alpha$-alumina was prepared by the impregnation method at room temperature. Both supports were washed with 0.1 mol $dm^{-3}$ nitric acid and then rinsed thoroughly with ion-exchanged water. The surface area, as evaluated by the BET method using nitrogen, were 38.5 $m^2/g$ for $ZrO_2$ and 3.8 $m^2/g$ for $\alpha$-$Al_2O_3$. The impregnation of palladium was carried out by adding, drop by drop, an aqueous solution of palladium nitrate, in a concentration of about 13 g/l, to a batch of the supports which were slowly being stirred. The addition was stopped at the incipient wetness of the support, and then the catalysts were dried in air at 393 K for 12 h. The concentration of Pd was thus widely changed, *i.e.*, from 0.03 to 2.1 wt% for Pd/$ZrO_2$ and from 0.05 to 2.1 wt% for Pd/$\alpha$-$Al_2O_3$. Palladium metal powder was prepared by reducing $PdCl_2$ with an aqueous solution of $NaBH_4$.

In order to determine the conditions which provide a

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[†] 1 Torr = 133.322 Pa.

catalytic activity as stable and high as possible, the influence of the reduction temperature on the catalytic activity of Pd/$ZrO_2$ and Pd/$\alpha$-$Al_2O_3$ was investigated up to 875 K; reduction at 523 K was found to be a suitable treatment. The catalyst activity was also examined at the same temperature as a function of the reduction time for up to 5 h, but no significant difference was observed after 1 h. Thus, a fresh catalyst was subjected to pretreatment by oxidation with 20 Torr of oxygen at 523 K for 1 h, followed by reduction with 20 Torr of hydrogen at 523 K for 1 h and then evacuation for 1 h at the same temperature. This series of treatments was also employed prior to each kinetic run.

*Kinetics of Reaction.* The gas-phase hydrogenation of cyclohexene was carried out by using a closed circulation system with a volume of 450 ml. The cyclohexene was degassed, subjected several times to a trap-to-trap distillation, and then transferred to the reaction system. The pressure decrease during the course of the reaction was followed by means of a glass Bourdon gauge. A gas chromatographic analysis verified that cyclohexane was the only product under the present experimental conditions and that the rate of the pressure decrease corresponded exclusively to the rate of cyclohexane formation. The hydrogenation was studied in the pressure range of 10—40 Torr at temperature between 283 and 323 K. The reaction with deutrium was carried out under exactly the same conditions as those used in the hydrogenation. After the reduction, the cyclohexene and cyclohexane were separated gas chromatographically by the use of a 6 m column of Celite-545, with Dinonyl phthalate added, and then analysed by means of a mass-spectrometer, Hitachi RMU-7M, at an ionization voltage of 15 eV. The mass patterns including isotope peak ($^{13}C$) and the isotope effect on the ionization were corrected.[8] The hydrogen, hydrogen deuteride, and deuterium were analysed by means of gas chromatograph.[9] In order to determine the percentage exposed of palladium atoms, the adsorption of CO was employed at 301 K in a static system with a volume of 150 ml after the catalysts had been treated in the same manner as that employed in the kinetic study. X-Ray diffraction was also applied to the catalysts.

*Material.* Zirconia of an extra pure grade was obtained from the Koso Chemical Co., and $\alpha$-alumina, from the Shimadzu Seisakusho, Ltd. Cyclohexene of an extra pure grade, purchased from Yoneyama Chemical Industries, Ltd., was distilled *in vacuo* and found to be gas chromatographically pure. Hydrogen (99.99% pure) and deuterium (containing less than 0.5% HD) were obtained from Takachiho Kagaku Kogyo and were purified through a molecular-sieve trap cooled to 80 K.

## Results

Figure 1 shows the variation in the catalytic activity, $V_g$, (molecule $min^{-1}$ g $Pd^{-1}$) of Pd/$ZrO_2$ and Pd/$\alpha$-$Al_2O_3$ for the hydrogenation of cyclohexene with different Pd contents. The Pd/$ZrO_2$ catalyst was characterized by a marked rise in the activity with an increase in the Pd content and by a maximum at 0.05 wt%, whereas Pd/$\alpha$-$Al_2O_3$ shows only a slight increase around 0.2 wt%. A comparison between the highest activities showed that the activity per gram of Pd dispersed on $ZrO_2$ was about 170 times greater than that of Pd on $\alpha$-$Al_2O_3$. Kinetic studies were carried out for most of these catalysts; the results thus obtained are summarized in Tables 1 and 2.

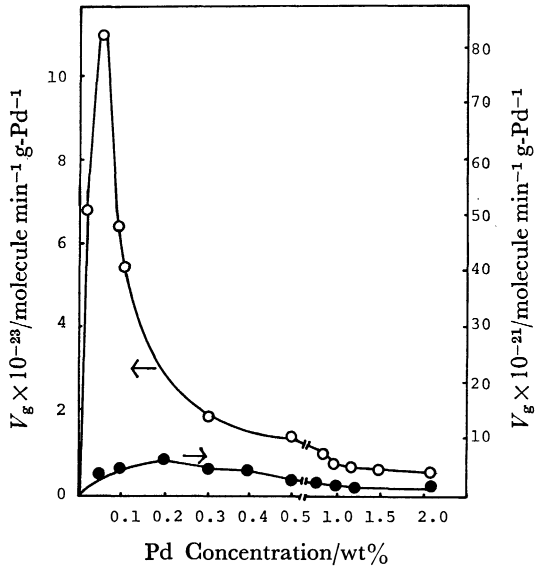

Fig. 1. Change in catalytic activity $V_g$ with Pd content.

Unless otherwise stated, the following conditions were used: $P_h$=40 Torr, $P_e$=40 Torr, reaction temp=301 K.

○: Pd/$ZrO_2$, ●: Pd/$\alpha$-$Al_2O_3$.

It should be noted that, for a series of each kind of catalyst, the reactions gave almost the same activation energy and pressure dependence, irrespective of the Pd concentration, but there were significant differences in these kinetic parameters between the reaction on Pd/$ZrO_2$ and Pd/$\alpha$-$Al_2O_3$; the activation energy for the reaction on Pd/$ZrO_2$ was, on the average, higher by about 13 kJ $mol^{-1}$ than for Pd/$\alpha$-$Al_2O_3$ and Pd bulk metal. The reaction orders with respect to the partial pressures of hydrogen and cyclohexene were, respectively, 0.73±0.04 and 0.64±0.04 for Pd/$ZrO_2$, whereas the corresponding values were 0.97±0.03 and 0.07±0.04 for Pd/$\alpha$-$Al_2O_3$ and Pd bulk metal.

The detailed analysis of the reaction was performed by using deuterium as a tracer, and the deuterium distributions in gaseous cyclohexene, cyclohexane, and hydrogen were investigated. The results are summarized in Table 3. Neither hydrogenation nor exchange reaction of cyclohexene with $D_2$ occurred on either of the supports, $ZrO_2$ and $\alpha$-$Al_2O_3$, under the present experimental conditions. The reaction of cyclohexene with $D_2$ or with $H_2+D_2$ on Pd/$ZrO_2$ and Pd/$\alpha$-$Al_2O_3$ demonstrated that considerable amounts of cyclohexene [$D_1$] and [$D_2$] were formed at a conversion of from 8 to 10%. Equilibration among $H_2$, HD, and $D_2$ in the gas phase proceeded completely in the case of Pd/$\alpha$-$Al_2O_3$; the values of $K$, defined as the $P^2_{HD}/P_hP_D$ radio, were 3.1—4.2(±0.4) in the $C_6H_{10}+D_2$ system and 3.5—3.7(±0.3) in the $C_6H_{10}+H_2+D_2$ system. In the reaction using the Pd/$ZrO_2$ catalyst, however, although appreciable amounts of HD and $H_2$ were produced, the equilibrium among them did not hold; the $K$'s were 0.6—0.8 (±0.2) in the $C_6H_{10}+D_2$ system and 1.2—1.3(±0.1) in the $C_6H_{10}+H_2+D_2$ system. As for the product, cyclohexane, a distribution ranging from [$D_0$] and

TABLE 1. KINETIC PARAMETERS OF CYCLOHEXENE HYDROGENATION AND CO ADSORPTION ON $Pd/ZrO_2$

| Pd wt% | $V_g$[a)] Molecule/min g-Pd | CO[b)] Molecule/g-Pd | D(%)[c)] | $V_s$ $s^{-1}$ | Reaction order[d)] | | Activation energy[e)] $E_a$ kJ $mol^{-1}$ |
|---|---|---|---|---|---|---|---|
| | | | | | $m$ | $n$ | |
| 0.03 | $6.8\times10^{23}$ | $4.48\times10^{21}$ | (79.2) | 2.5 | 0.75 | 0.60 | 48.1[g)] |
| 0.05 | 11.0 | 5.47 | (96.6) | 3.3 | 0.71 | 0.66 | 51.5 |
| 0.08 | 6.4 | 3.77 | (66.6) | 2.8 | 0.71 | 0.60 | 46.1 |
| 0.1 | 5.3 | 3.68 | (65.0) | 2.4 | 0.68 | 0.68 | 49.4 |
| 0.3 | 1.7 | 1.33 | (23.5) | 2.1 | 0.75 | 0.62 | 47.7 |
| 0.5 | 1.4 | 0.84 | (14.8) | 2.8 | 0.76 | 0.60 | 51.1 |
| 0.7 | 1.1 | 0.78 | (13.8) | 2.4 | 0.78 | 0.60 | 49.8 |
| 1.0 | 0.7 | 0.76 | (13.4) | 1.5 | 0.70 | 0.60 | 47.7 |
| 1.2 | 0.7 | — | — | — | 0.75 | 0.60 | 50.2 |
| 1.5 | 0.6 | — | — | — | 0.73 | 0.65 | 46.1 |
| 2.1 | 0.4 | 0.57 | (10.1)[f)] | 1.2 | 0.70 | 0.60 | 46.1 |

a) $P_h=40$ Torr, $P_e=40$ Torr; reaction temperature $=301$ K. b) Saturated adsorption at 301 K. c) Percentage exposed (%), evaluated on the assumption that a CO molecule adsorbs on a Pd atom. d) $V=kP_h^mP_e^n$. e) Temperature range $=283$—323 K. f) X-Ray diffraction gave a value of 9.7%. g) ±1.5 kJ/mol.

TABLE 2. KINETIC PARAMETERS OF CYCLOHEXENE HYDROGENATION AND CO ADSORPTION ON $Pd/\alpha$-$Al_2O_3$ AND Pd METAL

| Pd wt% | $V_g$[a)] Molecule/min g-Pd | CO[b)] Molecule/g-Pd | D(%)[c)] | $V_s$ $s^{-1}$ | Reaction order[d)] | | Activation energy[e)] $E_a$ kJ $mol^{-1}$ |
|---|---|---|---|---|---|---|---|
| | | | | | $m$ | $n$ | |
| 0.05 | $3.9\times10^{21}$ | — | — | — | 0.95 | 0.0 | 35.2[g)] |
| 0.1 | 4.4 | $5.7\times10^{20}$ | (10.1) | 0.13 | 0.97 | 0.0 | 31.0 |
| 0.2 | 6.4 | 8.4 | (15.0) | 0.12 | 1.00 | 0.0 | 33.5 |
| 0.3 | 4.0 | — | — | — | 1.00 | 0.0 | 35.2 |
| 0.4 | 3.8 | — | — | — | 1.00 | 0.0 | 38.5 |
| 0.5 | 2.1 | — | — | — | 1.00 | 0.0 | 38.1 |
| 0.7 | 1.9 | 1.7 | (2.8) | 0.19 | 1.06 | 0.1 | 33.9 |
| 1.0 | 0.7 | — | — | — | 1.00 | 0.0 | 36.9 |
| 1.3 | 0.7 | — | — | — | 1.00 | 0.0 | 33.5 |
| 2.1 | 0.8 | 1.3 | (2.2)[f)] | 0.10 | 1.00 | 0.1 | 38.5 |
| Pd Black | $7.8\times10^{19}$ | $1.4\times10^{19}$ | — | 0.09 | 1.00 | 0.0 | 32.7 |

a), b), c), d), e): See Table 1. f) X-Ray diffraction gave a value of 2.5%. g) ±1.5 kJ/mol.

$[D_5]$ was observed in the reactions using the respective catalysts, but there was a tendency for $Pd/ZrO_2$ to provide a higher concentration of cyclohexane $[D_0]$.

Figure 2 shows the isotherms of CO adsorbed at 301 K on 0.05 wt% $Pd/ZrO_2$ and $ZrO_2$. Carbon monoxide was introduced up to 60 Torr, and then, after the evacuation at the same temperature for 20 min, the adsorption was repeated under the same conditions. As may be seen from Fig. 2, the amount of CO adsorbed on $Pd/ZrO_2$ in the second run was much the same as that on the $ZrO_2$ surface, on which only the reversible adsorption took place. Thus, the difference between the first and second runs gave the amount of irreversible adsorption on the surface of metallic palladium. By assuming that an exposed Pd atom can accommodate one carbon monoxide molecule,[10)] the number of Pd atoms exposed was evaluated. Tables 1 and 2 involve the percentage exposed and also the hydrogenation activity per exposed atom, *i.e.*, the turn-over frequency $V_s$, represented in terms of molecule $s^{-1}$ exposed Pd atom$^{-1}$. It should be noted that the change in $V_s$ was rather small throughout the whole range of Pd loading. The $V_s$ at 0.05 wt% was only twice as large as that at 1.0 wt%. However, the $V_s$ on $Pd/ZrO_2$ was 20 to 30 times higher than those on $Pd/\alpha$-$Al_2O_3$ and Pd bulk metal.

The poisoning effect of CO was examined at 301 K. A known amount of CO was preadsorbed on a bare Pd surface after the pretreatment, after which the catalyst was evacuated for 20 min and the reaction gas was introduced. Figure 3 shows the change in the activity with the increase in the fraction of CO coverage, which was defined as the ratio of the amount of CO adsorbed to that at saturation. In all cases of 0.05, 0.3, and 1.0 wt% $Pd/ZrO_2$ catalysts as well as of 0.2 wt% $Pd/\alpha$-$Al_2O_3$ studied, an almost linear decrease in the activity occurred with the increase in the fraction of the surface occupied by CO, and zero activity was attained at around $\theta=0.45$ when the lines were extrapolated.

Table 3. Deuterium distributions in the reactions of cyclohexene with $D_2$ or $H_2+D_2$ on $Pd/ZrO_2$ and $Pd/\alpha\text{-}Al_2O_3$

| Catalysts | | 0.05 wt% $Pd/ZrO_2$ | | | | 0.2 wt% $Pd/\alpha\text{-}Al_2O_3$ | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $D_2+C_6H_{10}$[a)] | | $D_2+H_2+C_6H_{10}$[b)] | | $D_2+C_6H_{10}$[a)] | | $D_2+H_2+C_6H_{17}$[b)] | |
| Conversion (%) | | 8 | 15 | 8 | 15 | 10 | 17 | 10 | 17 |
| Cyclohexane | $D_0$(%) | 28 | 22 | 32 | 41 | 9 | 17 | 19 | 10 |
| | $D_1$ | 37 | 34 | 40 | 44 | 19 | 26 | 22 | 24 |
| | $D_2$ | 23 | 28 | 21 | 13 | 34 | 31 | 35 | 43 |
| | $D_3$ | 8 | 8 | 6 | 2 | 16 | 16 | 21 | 19 |
| | $D_4$ | 3 | 3 | 1 | 0 | 10 | 10 | 1 | 3 |
| | $D_5$ | 2 | 2 | 0 | 0 | 6 | 0 | 0 | 0 |
| | $D_6$ | 0 | 1 | 0 | 0 | 3 | 0 | 0 | 0 |
| | $D_7$ | 0 | 0 | 0 | 0 | 2 | 0 | 0 | 0 |
| | $D_8$—$D_{12}$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Cyclohexene | $D_0$ | 79 | 69 | 94 | 81 | 79 | 82 | 98 | 80 |
| | $D_1$ | 10 | 16 | 3 | 6 | 10 | 8 | 1 | 6 |
| | $D_2$ | 4 | 11 | 3 | 6 | 5 | 6 | 1 | 6 |
| | $D_3$ | 3 | 2 | 0 | 5 | 4 | 2 | 0 | 5 |
| | $D_4$ | 2 | 1 | 0 | 2 | 2 | 1 | 0 | 3 |
| | $D_5$ | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | $D_6$—$D_{10}$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $H_2$(%) | | 8 | 5 | 27 | 30 | 2 | 2 | 13 | 20 |
| HD | | 19 | 17 | 35 | 36 | 25 | 22 | 45 | 48 |
| $D_2$ | | 73 | 78 | 38 | 34 | 73 | 76 | 42 | 32 |

Reaction temp=301 K, a) $P_D=P_e=40$ Torr, b) $P_H=P_D=20$ Torr, $P_e=40$ Torr.

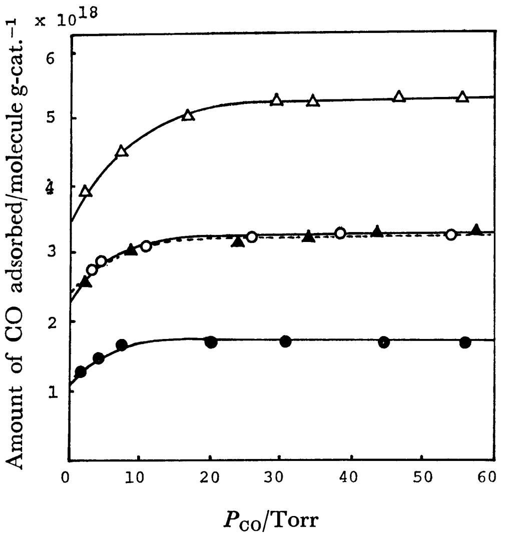

Fig. 2. Adsorption of CO on 0.05 wt% $Pd/ZrO_2$ and $ZrO_2$.
△: Total adsorption of CO, ▲: reversible adsorption of CO, ○: adsorption on $ZrO_2$, ●: irreversible adsorption of CO.

## Discussion

It is a feature of the cyclohexene hydrogenation on $Pd/ZrO_2$ that the high activity appears in a narrow range of Pd concentrations, as is shown in Fig. 1. Such a drastic change in the activity contrasts with the results on $Pd/\alpha\text{-}Al_2O_3$. This maximum activity was also observed in the liquid-phase hydrogenation.[4)] The measurement of the CO-adsorption on $Pd/ZrO_2$, however, revealed that the fraction of Pd exposed per unit weight of the metal varied with the amount of Pd loading in a manner parallel to the change in the activity. Accordingly, the turn-over frequency, $V_s$, was rather constant around the maximum of activity ($V_g$) and then gradually decreased to about a half of the value with an increase in the Pd content. A similar relation between $V_g$ and $V_s$ was also observed in the case of $Pd/\alpha\text{-}Al_2O_3$, but the value of $V_s$ for $Pd/\alpha\text{-}Al_2O_3$ was smaller by one order of magnitude than that for $Pd/ZrO_2$, irrespective of the Pd content. The small variation in $V_s$ as well as the similarity in the kinetic parameters over the wide range of percentage exposed suggests that the hydrogenation of cyclohexene is "structure-insensitive" in character and that the sharp maximum in $V_g$ is attributable to the highest density of active sites. The slight fall in $V_s$ with the decrease in the percentage exposed may be due to the decrease in the virtual site density; the steric hindrance between adsorbed cyclohexene molecules may become more distinct on the smooth surfaces of larger particles, or the stoichiometry between the adsorbed CO and the Pd atom may vary with the percentage exposed. From the amount of CO chemisorbed on 0.05 wt% $Pd/ZrO_2$, the average diameter of Pd particles was calculated to be about 17 Å, provided that the particles are spherical. This estimation indicates that, as a primary effect, the $ZrO_2$ surface has a high capability of dispersing Pd metal as very fine particles or crystallites which possess a high density of active sites.

Since the surface density of the active site varies in proportion to the percentage exposed of Pd atoms,

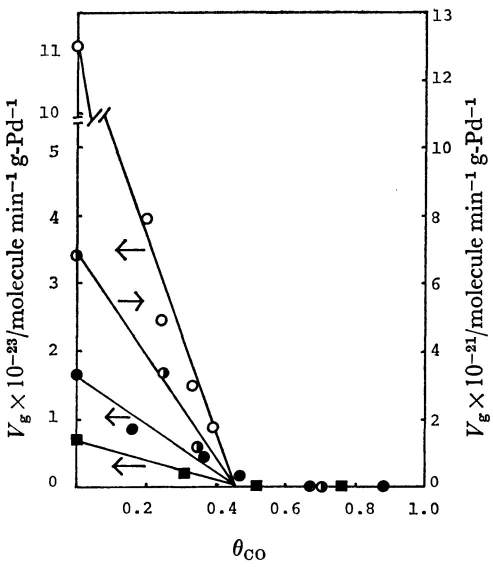

Fig. 3. Poisoning effect of adsorbed CO on cyclohexene hydrogenation.
○: 0.05 wt% $Pd/ZrO_2$, ●: 0.3 wt% $Pd/ZrO_2$, ■: 1.0 wt% $Pd/ZrO_2$, ◑: 0.2 wt% $Pd/\alpha$-$Al_2O_3$.

the poisoning due to preadsorbed CO permits us to evaluate the density. As may be seen from Fig. 3, a nearly linear relationship exist between the decline in the activity and $\theta_{CO}$, and the zero activity was brought about at $\theta_{CO}=0.45$ for all the $Pd/ZrO_2$ and $Pd/\alpha$-$Al_2O_3$ catalysts examined. This coincidence of CO coverage where the activity vanishes suggests that the topography of the active sites is similar for Pd particles dispersed on both $ZrO_2$ and $\alpha$-$Al_2O_3$.

There are clear differences in the pressure dependence and activation energy between the reactions on the $Pd/ZrO_2$ and $Pd/\alpha$-$Al_2O_3$ catalysts, but the general features of wide distributions in the reactant and product were rather analogous in both cases and suggest that the hydrogenations proceed via the associative mechanism described by the following pathway;

$$H_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 2H(a) \tag{1}$$

$$C_6H_{10}(g) \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} C_6H_{10}(a) \tag{2}$$

$$C_6H_{10}(a) + H(a) \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} C_6H_{11}(a) \tag{3}$$

$$C_6H_{11}(a) + H(a) \underset{k_4}{\rightarrow} C_6H_{12}(g) \tag{4}$$

were $k_i$ and $k_{-i}$ denote, respectively, the rate constants of the forward and reverse reactions at the ith step. The changes in the fractions of the surface covered with hydrogen atoms, $\theta_H$, cyclohexene, $\theta_e$, and cyclohexyl radicals, $\theta_y$, as functions of the time are described as:

$$\frac{d\theta_h}{dt} = 2k_1P_h\theta_v^2 - 2k_{-1}\theta_h^2 - k_3\theta_h\theta_e + k_{-3}\theta_y\theta_v - k_4\theta_h\theta_y \tag{5}$$

$$\frac{d\theta_e}{dt} = k_2P_e\theta_v - k_{-2}\theta_e - k_3\theta_e\theta_h + k_{-3}\theta_y\theta_v \tag{6}$$

$$\frac{d\theta_y}{dt} = k_3\theta_e\theta_h - k_{-3}\theta_v\theta_y - k_4\theta_y\theta_h, \tag{7}$$

where $\theta_v$ denotes the fraction of the vacant surface and is equivalent to $(1-\theta_h-\theta_e-\theta_y)$. The wide deuterium distributions in cyclohexane permit us to assume that Step 3 is in pseudo-equilibrium; thus, the following relationship;

$$K_3\theta_e\theta_h = \theta_y\theta_v \tag{8}$$

is obtained, where $K_3=k_3/k_{-3}$. The employment of the steady-state approximation on the adsorbed hydrogen atoms and cyclohexene molecules, *i.e.*, $d\theta_h/dt=d\theta_e/dt=0$, and the insertion of Eq. 8 into Eqs. 5 and 6 lead to;

$$2k_1P_h\theta_v^2 - 2k_{-1}\theta_h^2 - k_4\theta_y\theta_h = 0 \tag{9}$$

$$k_2P_e\theta_v - k_{-2}\theta_e = 0. \tag{10}$$

Solving the set of Eqs. 8, 9, and 10, we can obtain these expressions for $\theta_y$ and $\theta_h$ in a steady state;

$$\theta_y = K_2K_3P_e\theta_h \tag{11}$$

and;

$$\theta_h = \frac{\sqrt{2k_1P_h}}{[(1+K_2P_e)\sqrt{2k_{-1}+k_4K_2K_3P_e}+(1+K_2K_3P_e)\sqrt{2k_1P_h}]}, \tag{12}$$

where $K_i=k_i/k_{-i}$. Accordingly, the rate of cyclohexene hydrogenation, $V_g$, is given by;

$$V_g = k_4\theta_y\theta_h$$
$$= \frac{2k_1k_4K_2K_3P_hP_e}{[(1+K_2P_e)\sqrt{2k_{-1}+k_4K_2K_3P_e}+(1+K_2K_3P_e)\sqrt{2k_1P_h}]^2}. \tag{13}$$

In order to examine the validity of the derived equation for the observed pressure dependences, Eq. 13 is transformed into;

$$\sqrt{\frac{P_h}{V_g}} = \sqrt{\frac{1}{(2k_1k_4K_2K_3)P_e}}[\sqrt{2k_1P_h}(1+K_2K_3P_e) + (1+K_2P_e)\sqrt{2k_{-1}+k_4K_2K_3P_e}], \tag{14}$$

which provides a linear relationship between $(P_h/V_g)^{1/2}$ and $P_h^{1/2}$ under the condition of a constant $P_e$. A similar transformation of Eq. 13 with respect to the cyclohexene pressure gives;

$$\sqrt{\frac{P_e}{V_g}} = \sqrt{\frac{1}{(k_4K_1K_2K_3)P_h}}\left[(1+K_2K_3P_e)\sqrt{K_1P_h} + (1+K_2P_e)\sqrt{1+\frac{k_4K_2K_3}{2k_{-1}}P_e}\right], \tag{15}$$

which can not be used for the examination of the pressure dependence. Considering that the desorption of hydrogen is still much faster than the hydrogenation, *i.e.*, $2k_{-1}\theta_h^2 > k_4K_2K_3P_e\theta_h^2$, one can expand the second term in brackets in Eq. 15 as:

$$(1+K_2P_e)\sqrt{1+\frac{k_4K_2K_3P_e}{2k_{-1}}}$$
$$=\left[1+\left(K_2+\frac{k_4K_2K_3}{4k_{-1}}\right)P_e+\frac{k_4K_2^2K_3}{4k_{-1}}P_e^2+\cdots\right]. \tag{16}$$

Accordingly, Eq. 15 is rewritten in an approximate form:

$$\sqrt{\frac{P_e}{V_g}} = \sqrt{\frac{1}{(k_4K_1K_2K_3)P_h}} \times\left[1+\sqrt{K_1P_h}+\left(1+K_3\sqrt{K_1P_h}+\frac{k_4K_3}{4k_{-1}}\right)K_2P_e\right]. \quad (17)$$

It follows, therefore, that a linear relationship of $(P_e/V_g)^{1/2}$ *vs.* $P_e$ exists under the condition of a constant $P_h$. As for the hydrogenation on Pd/$\alpha$-$Al_2O_3$, in which gaseous hydrogen molecules are in equilibrium with the adsorbed hydrogen atoms, the rate equation was simplified to:

$$V_g = \frac{k_4K_1K_2K_3P_hP_e}{\{1+\sqrt{K_1P_h}+K_2P_e+K_2K_3P_e\sqrt{K_1P_h}\}^2}. \quad (18)$$

It is apparent that this equation provides relationships similar to those described above for the hydrogen- and cyclohexene-pressure dependences. Figure 4 shows good linear plots of the observed values for the above-mentioned relationships, which verifies the validity of Eqs. 13 and 18, and hence the mechanism proposed. The assumption that one of the reactions other than Step 4 is a slow process leads to an unsatisfactory conclusion in explaining the observed pressure dependence and isotope distribution. When Gonzo and Boudart[11] studied the hydrogenation of cyclohexene on $\gamma$-alumina-supported Pd in the gas and liquid phases, they observed no appreciable difference in the mechanism of reaction between these systems. They showed that the rate-determining step is the addition of a hydrogen atom to the cyclohexyl species, which accords with the present conclusion. The value of the turn-over frequency, 3.3 $s^{-1}$ at 301 K ($P_h$=$P_e$=40 Torr) on 0.05 wt% Pd/$ZrO_2$ was close to the value, 3.4 $s^{-1}$, obtained by correcting their data[11] to the present reaction conditions.

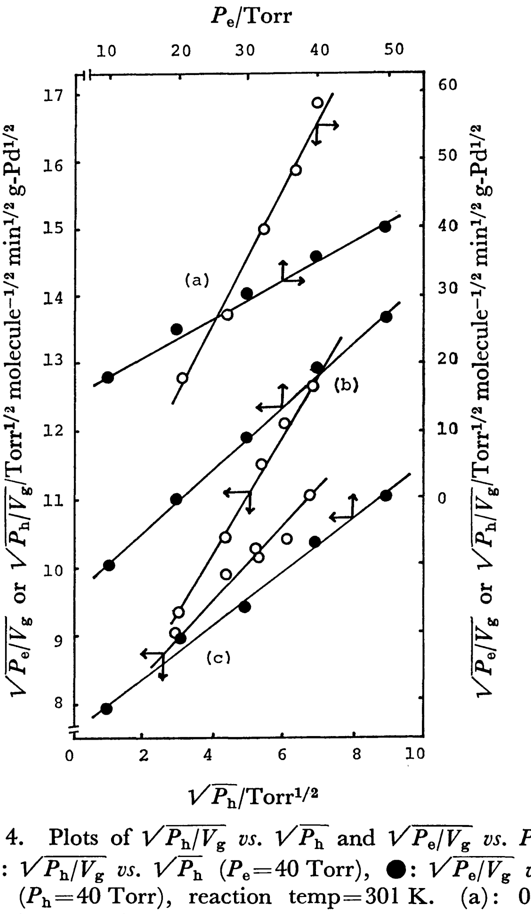

Fig. 4. Plots of $\sqrt{P_h/V_g}$ *vs.* $\sqrt{P_h}$ and $\sqrt{P_e/V_g}$ *vs.* $P_e$. ○: $\sqrt{P_h/V_g}$ *vs.* $\sqrt{P_h}$ ($P_e$=40 Torr), ●: $\sqrt{P_e/V_g}$ *vs.* $P_e$ ($P_h$=40 Torr), reaction temp=301 K. (a): 0.2 wt% Pd/$\alpha$-$Al_2O_3$, (b): 1.0 wt% Pd/$ZrO_2$, (c): 0.08 wt% Pd/$ZrO_2$.

These characteristic features of the hydrogenation by Pd/$ZrO_2$, *viz.*, the high $V_g$ value and the different kinetics as compared to those on Pd/$\alpha$-$Al_2O_3$ and Pd bulk metals, are certainly associated with carrier effects caused by $ZrO_2$. If one assumes the dispersed state of metal to be a spherical particle, the percentages exposed of 96% (0.05 wt% Pd/$ZrO_2$) and 13% (2.1 wt% Pd/$ZrO_2$) correspond to particle sizes of about 17 and 140 Å in diameter respectively. As is shown in Table 2, there is evident lack of variation in the kinetic behavior through the whole range of the percentage exposed, while the CO-poisoning results clearly show that almost all the surface atoms exposed are responsible for the catalytic hydrogenation. Thus, these facts lead to two plausible models: a long-range influence caused by the $ZrO_2$ substrate strongly affects the character of the dispersed metal particles, irrespective of their size, and, alternatively, Pd metal aggregates with a specific morphology are formed on the $ZrO_2$ surface, thus increasing the fraction of active interface between the metal and the carrier. In a special case, a small fraction of $ZrO_2$ might be embedded in the crystallites of Pd metal. The latter situation appears to produce noteworthy interaction.

As has been described, the general feature of the Pd/$ZrO_2$ catalyst was a homogeneous distribution of the active sites over almost the entire surface. However, it was found that the reaction orders with respect to the hydrogen and cyclohexene pressures shifted to 1.0 and 0.1 respectively when the 0.05 wt% Pd/$ZrO_2$ catalyst was poisoned by adsorbed CO so severely that more than 93% of the catalytic activity was lost. For the reaction on the 0.3 wt% Pd/$ZrO_2$ catalyst poisoned to the same extent, however, the hydrogen order remained unchanged, though the cyclohexene order was attenuated to 0.35. Although a detailed study will be needed to confirm whether such reaction-order shifts occur gradually with an increase in the amount of adsorbed CO or only in the extreme case of an almost complete deactivation, the almost linear relationships observed in Fig. 3 indicate that the latter is more plausible. The variations in the kinetic behavior are presumably caused by the electronic effect of preadsorbed CO upon the state of palladium-surface atoms rather than by the geometrical blocking of active sites by the CO, so as to put more restriction on the adsorption of hydrogen compared to that of cyclohexene. The finding that the change in the kinetic parameters of the hydrogenation on the catalysts with higher percentages exposed is more prominent gives support to this consideration. It should be noted that the shifts in the kinetic parameters occurred in an opposite direction from those caused by the $ZrO_2$ substrate. The adsorption of CO on the Pd (111) surface was found to increase the work function by 1.02 eV,[12] indicating an electron transfer from the Pd surface to CO. By taking the present results together with this face into consideration, we can predict that $ZrO_2$ works as an electron donor.

In order to confirm this view, it is necessary to examine the effect of added $ZrO_2$ to Pd upon the catalytic properties, and therefore the analysis of these sytems by X-ray photoelectron spectroscopy seems to be essential. These studies are now in progress by using Pd+$ZrO_2$ dispersed on inactive substrates such as $\alpha$-$Al_2O_3$.

## References

1) A. D. O. Cinneide and J. K. A. Clarke, *Catal. Rev.*, **7**, 213 (1973).

2) G. A. Somorjai, *Catal. Rev.*, **7**, 1 (1973); *Adv. Catal.*, **26**, 1 (1977).

3) G. M. Schwab, *Adv. Catal.*, **27**, 1 (1978).

4) E. B. Maxted and S. I. Ali, *J. Chem. Soc.*, **1961**, 4137.

5) K. Fujimoto, H. Hashimoto, and T. Kunugi, *J. Jpn. Petrol. Inst.*, **21**, 135 (1978).

6) V. I. Spitsyn, A. A. Balandin, and L. I. Barsova, *Russ. J. Phys. Chem.*, **42**, 184 (1968).

7) A. S. Hussey and G. P. Nowack, *J. Org. Chem.*, **34**, 439 (1969).

8) J. Turkevich, L. Frieman, E. Solomon, and F. M. Wrightson, *J. Am. Chem. Soc.*, **70**, 2638 (1948); J. Turkevich, *Discuss. Faraday Soc.*, **10**, 46 (1951).

9) S. Ohno and I. Yasumori, *Bull. Chem. Soc. Jpn.*, **41**, 2227 (1969).

10) M. Boundart, *Adv. Catal.*, **20**, 153 (1969).

11) E. E. Gonzo and M. Boudart, *J. Catal.*, **52**, 462 (1978).

12) H. Conrad, *Surf. Sci.*, **43**, 462 (1974).