Effect of Pd Dispersion on Methanol Decomposition over Supported Pd Catalysts

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The turnover frequency (TF) for the methanol decomposition over various supported Pd catalysts is dependent upon both supporting materials and Pd crystallite sizes. On the other hand, the apparent activity (gas evolution rate per g-catalyst) is roughly proportional to the degree of Pd dispersion. This variation in the apparent activity is related to starting materials for the preparation of supports as well as to properties of supports. The highest dispersion of Pd was obtained with TiO_2 prepared from $Ti[OCH(CH_3)_2]_4$ or $TiCl_4$, but at an elevated temperature (above 773 K) in the reduction treatment applied, it showed a suppressed activity. Pd particles on ZrO_2 support gave a high value of TF when the Pd/ZrO_2 catalyst was calcined in air at an elevated temperature (873—1073 K). The findings about the influence of heat treatment suggest that thermal stabilization of the ZrO_2 support would play an important role in the development of catalytic properties of Pd. TF curves for the methanol decomposition over TiO_2- and ZrO_2-supported Pd catalysts change discontinously at about 10 Å of Pd particle size. In the case of Al_2O_3 support, characteristic behavior of TF curve are significantly different from those observed in the case of TiO_2 and ZrO_2 supports.

Metal catalysts highly dispersed on supporting materials are widely used in various fields such as petrochemical industry. This is due to the fact that supported catalysts have larger surface area and are stabler against heating than unsupported ones. Effects of crystallite size and the degree of metal dispersion have been extensively discussed upon the catalytic activity and selectivity of supported transition metal catalysts for many reactions.[1-5] It is interesting to clarify whether those effects resulting in variation of specific catalytic activity and selectivity are different or not, in connection with the nature of supporting materials.

With highly dispersed metal catalysts, the effects of metal–support interaction (MSI) and metal crystallite size on catalytic activity and reducibility have been known well to be related closely to each other. Therefore, separate discussions on these phenomena will not be effective for essential clarification of this complex relationship.[6] MSI is enhanced with increasing degree of metal dispersion, i.e., this MSI results in strong MSI (SMSI). This resulting SMSI phenomenon gives rise to depression of uptake in chemisorption and suppression of catalytic activity, and drastic decrease in catalytic activity has been observed in the case of such supports as TiO_2 and Nb_2O_5, which oxides are reducible at elevated temperatures in prereduction treatment of supported catalysts.[6] In contrast, these phenomena are not found in the case of such nonreducible oxide supports as Al_2O_3, MgO, and ZrO_2.[6]

It has also been known that different methods for preparing supported metal catalysts and different reagents employed as starting materials affect considerably the degree of metal dispersion and catalytic activity.[3,7] There has been a study on supported metal catalysts comprising investigations for the effect of metal crystallite size and nature of the support upon catalytic activity. Such a standard method as provides a series of catalysts with a particular mean crystallite size is convenient in examining the influence of metal crystallite size, but it gives an additional problem[3] that supported catalysts with highly dispersed metal are likely to cause variation in specific catalytic activity, and that atomically dispersed metals on supports may behave like an SMSI caused by metal-support electron transfer.

The present work describes characteristics of palladium catalysts obtained via impregnation of different supports (TiO_2, ZrO_2, and Al_2O_3) with palladium ammine complex and also presents detailed effects of support area, metal content, reduction conditions, heat pretreatment of support, etc. upon Pd dispersion and other characteristic properties.

Experimental

Supports. The supports (anatase-type TiO_2, ZrO_2, and γ-Al_2O_3) used in this work, their pretreatment conditions, and their sources are summarized in Table 1. For the preparation of the metal oxides as supporting materials, commercially available oxides, sulfates, chlorides, alkoxides, and nitrates, etc. from Wako Pure Chemical Industries were used as starting materials. These materials, except commercially available oxides, were first hydrolyzed by addition of 28% aqueous ammonia into their solution with vigorous stirring at pH 7—8. After aging overnight, the resulting precipitates were washed with deionized water until no negative ions were detected, and dried. The dried precipitates were calcined at 823 K in air for 4 h into oxides. Prior to impregnation with Pd ion, the TiO_2 samples were evacuated at 773 K for 4 h in Pyrex glass tubes. Subsequently, ammonia solution was poured onto them out of contact with air in order to facilitate the surface-ion-exchange reaction between NH_4^+ ion and the cation of Pd ammine complex.

Table 1. Preparation Conditions for the Supported Pd Catalysts and Their Characteristics Estimated by H_2 Chemisorption

Support (Symbol)	No.	Starting material	Pretreatment process	Pd content/ wt%	Calcn. temp./K	Surface area[f]/ m^2 g-cat^{-1}	H_2 uptake/ μmol g-cat^{-1}	Dispersion (H/Pd)
TiO_2	1	Commercial	EV[b]-dry	1.0	823	19	2.1	0.05
(T)	2	JRC-TID-1[a]	EV[b]-dry	1.0	823	32	18.8	0.36
	3	$Ti(SO_4)_2$	HY[c]-EV[b]-dry	1.0	823	47	22.4	0.48
	4	$Ti[OCH(CH_3)_2]_4$	HY[c]-EV[b]-dry	1.0	823	82	31.4	0.67
	5	$Ti[OCH(CH_3)_2]_4$	RC[d]-HY[c]-EV[b]-dry	1.0	823	84	35.3	0.75
	6	$TiCl_4$	HY[c]-EV[b]-dry	1.0	823	57	38.0	0.80
	7	$TiCl_4$	HY[c]-heat (773 K)	1.0	823	37	11.2	0.24
	8	$TiCl_4$	HY[c]-dry	1.0	823	44	36.9	0.78
ZrO_2	1	Commercial (1)	No	1.0	973	27	6.8	0.15
(Z)	2	Commercial (2)	No	1.0	973	12	2.8	0.06
	3	$ZrO(NO_3)_2$	HY[c]-dry	1.0	973	33	16.5	0.35
	4	$Zr(OH)_4$	No	1.0	973	27	30.8	0.66
	5	$Zr(SO_4)_2$	HY[c]-dry	1.0	973	27	31.1	0.66
	6—1	$ZrOCl_2$	HY[c]-dry	0.1	973	33	5.3	1.00
	6—2	$ZrOCl_2$	HY[c]-dry	0.25	973	27	12.4	1.00
	6—3	$ZrOCl_2$	HY[c]-dry	0.50	973	30	15.3	0.65
	6—4	$ZrOCl_2$	HY[c]-dry	1.00	973	32	13.9	0.30
	6—5	$ZrOCl_2$	HY[c]-dry	1.50	973	28	10.2	0.15
	6—6	$ZrOCl_2$	HY[c]-dry	1.0	673	52	16.4	0.35
	6—7	$ZrOCl_2$	HY[c]-dry	1.0	773	46	15.6	0.34
	6—8	$ZrOCl_2$	HY[c]-dry	1.0	823	43	6.0	0.13
	6—9	$ZrOCl_2$	HY[c]-dry	1.0	873	36	5.2	0.11
	6—10	$ZrOCl_2$	HY[c]-dry	1.0	1073	16	8.6	0.18
Al_2O_3	1	Commercial	EV[b]-dry	3.0	823	144	19.9	0.14
(A)	2	$Al[CH(CH_3)_2O]_3$	DS[e]-HY[c]-EV[b]-dry	0.5	823	193	6.5	0.27
	3	$Al[CH(CH_3)_2O]_3$	DS[e]-HY[c]-EV[b]-dry	1.0	823	248	12.5	0.26
	4	$Al[CH(CH_3)_2O]_3$	DS[e]-HY[c]-dry	1.0	823	197	10.8	0.23

a) The mark indicates the TiO_2 sample which has been supplied from the Committee of Reference-Catalysts in Japan. b) The symbol EV indicates that the oxide was treated with ammoniacal solution after evacuation at 823 K. c) The symbol HY indicates that the solution was hydrolyzed by ammonia under neutralization. d) The symbol RC indicates recrystallization in 2-propanol solvent repeated three times. e) The symbol DS indicates distillation at 523 K and 0.01 Torr. f) The data were obtained from the used catalysts in the activity tests.

Catalysts. The supports were impregnated overnight with a hot ammoniacal solution of $PdCl_2$. Subsequently, the solution was evaporated at 323—353 K and then the catalyst was dried at ca. 373 K for ca. 14 h in an air oven. Finally, the powdered sample was calcined in an electric furnace at the prescribed temperature for 4 h. Reduction of the catalysts was carried out in a glass reactor in a stream of high-purity hydrogen (commercial 99.9%) at the prescribed temperature for 4 h. For adsorption measurement, the hydrogen used for the reduction of catalyst was further purified by passing it successively through a Pd-asbestos bed, a Molecular Sieve (MS 13X) trap, and a liquid nitrogen cold trap. The effect of the evacuation of support on catalytic activity was examined for the series of Pd/TiO_2 catalysts.

Activity Test. CH_3OH decomposition was chosen as the test reaction for comparison of activities of various Pd catalysts in a flow system at atmospheric pressure using N_2 as a carrier gas. A fresh catalyst sample (1.0 g) was charged in a glass U-tube (i.d. 6 mm) reactor, and then activated in a hydrogen stream (40 ml min^{-1}) for 4 h. The nitrogen used as the carrier gas was purified by successive passage through reduced copper chips at ca. 573 K and MS 13X trap at ca. 273 K. CH_3OH conversion was measured in a steady state at 673 K and a space velocity of ca. 10000 h^{-1}. Reactants and products in catalytic tests were analyzed by gas chromatography (TCD cell) at 353 K. An additional column packed with PEG-1000 (2 m long and 3 mm in i.d.) was used for analysis of liquid products. For analysis of gaseous products condensed in a methanol–Dry Ice trap, an activated carbon column (1 m long and 3 mm in i.d.) was used.

Catalyst Characterization. The degree of dispersion, surface area, and the particle size of Pd were evaluated by measuring the amount of hydrogen adsorbed in a modified BET-type apparatus. One gram of catalyst was reduced at 673 K for 3 h after evacuation, and then the purified hydrogen gas was introduced to the catalyst at 423 K. The adsorption pressure was up to 150 Torr (1 Torr≈133.322 Pa). The adsorbed amount of hydrogen, v, was measured at a given pressure, p, after it had reached a constant value. Additional doses of hydrogen were successively admitted onto the sample and a hydrogen isotherm was thereby obtained. The saturated monolayer volume, v_m, was obtained from Langmuir plots in which p/v vs. p plots satisfied a fairly good linear relationship. The amount of hydrogen adsorption on the support was found to be negligibly small at room temperature, and therefore, no correction was made for the hydrogen adsorption on the support. By assuming a hemispherical crystallite for the Pd metal particles, the average diameter of crystallite, D_s, is given by[8,9]

$$D_s = 5/(\rho S_m), \quad (1)$$

where S_m is the surface area per gram of metal, and ρ is the density of Pd. Turnover frequency (TF), which is considered to give the qualitative catalytic activity per metal atom, was calculated from

$$TF[h^{-1}] = G[\text{mol } h^{-1}\text{ g-cat}^{-1}]/\{Pd[\text{mol g-cat}^{-1}](H/Pd)\}, \quad (2)$$

where G is the gas evolution rate, and (H/Pd) is the degree of dispersion of Pd. In the present work, G is considered to be the reaction rate index of methanol because the conversion of methanol is approximately proportional to time factor in the range of 10000 h^{-1} (SV). XRD experimnents were conducted to estimate the crystallographic structure change of the supports, by using a Nihondenshi (JEOL) Model DX-GE50S diffractometer with Cu $K\alpha$ radiation. The surface area of catalyst was determined by applying the BET equation to the adsorption isotherm of N_2 at the liquid nitrogen temperature. The change in size and shape of catalysts with reduction was followed by a Hitachi H-600 transmission electron microscope.

Results and Discussion

Effect of Support Preparation on Catalytic Activity. Hydrogen and carbon monoxide were observed as the primary products in all the catalytic tests, and occasionally trace amounts of methane, carbon dioxide, and water were detected. Methanol conversions and product distributions obtained at 673 K are given in Tables 2 and 3. Figure 1 shows correlations between the catalytic activity (total gas evolution rate) and the dispersion of Pd. The activity of the Pd/TiO_2 catalysts which were prepared from various starting materials or in different manners of pretreatment, was found to be approximately proportional to the degree of Pd dispersion. From Fig. 1, it is obvious that the highly dispersed Pd on the TiO_2 support having a large surface area leads to an increase in catalytic activity. For the Pd/TiO_2 catalysts prepared from $TiCl_4$ through the pretreatment with evacuation of TiO_2, the observed results indicate that both the surface area and catalytic activity are increased by 30% and 18%,

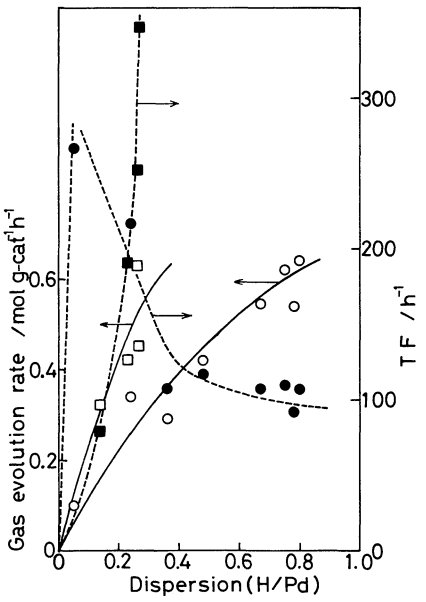

Fig. 1. Relationships between the apparent catalytic activities or the turnover frequency (TF) and the degree of Pd dispersion of Pd/TiO_2 (or Al_2O_3) catalysts. Reaction temperature; 673 K, Pre-reduction temperature; 673 K, Plots for TiO_2; (○, ●), for Al_2O_3; (□, ■).

Table 2. Catalytic Activities and Selectivities of Various Supported Pd Catalysts (Reduction Temp.=673 K, Reaction Temp.=673 K, SV=10000 h^{-1}, and Catalytic Data were Obtained at about 1 h after the Start of Activity Test)

Support (Symbol)	No.	Pd wt%	Total conv.[a]/ mol%	Gas evolution rate/mol g-cat^{-1} h^{-1}	Selectivity[b] to CO+H_2/%	Pd particle size/Å	Turnover frequency (TF)/h^{-1}
TiO_2	1	1.0	11	0.10	98.4	167	267
(T)	2	1.0	70	0.29	77.2	23	107
	3	1.0	84	0.42	85.0	17	117
	4	1.0	83	0.54	98.8	12	107
	5	1.0	95	0.62	98.5	11	110
	6	1.0	93	0.64	98.1	10	107
	7	1.0	70	0.34	95.8	34	217
	8	1.0	85	0.54	—	10	92
ZrO_2	1	1.0	38	0.35	98.5	55	201
(Z)	2	1.0	36	0.33	97.8	139	283
	3	1.0	51	0.32	99.4	23	79
	4	1.0	60	0.38	99.5	12	50
	5	1.0	78	0.48	99.4	12	63
	6-1	0.10	48	0.30	99.6	7	231
	6-2	0.25	59	0.37	99.7	8	128
	6-3	0.50	62	0.38	99.6	13	101
	6-4	1.00	81	0.51	96.1	27	147
	6-5	1.50	69	0.43	99.7	55	165
Al_2O_3	1	3.0	71	0.32	97.9	59	79
(A)	2	0.5	86	0.45	97.1	30	347
	3	1.0	90	0.62	96.2	32	252
	4	1.0	86	0.42	96.4	36	190

a) Conversion of CH_3OH. b) Corresponding to CO+H_2/(CO+H_2+CH_4+CO_2).

Table 3. Effects of Calcination Temperature and Reduction Temperature on Catalytic Activity and Products Distribution [Pd(1 wt%)/ZrO_2 Catalysts] (Reaction Temp.=673 K and SV=10000 h^{-1})

Reduction temp./K	Calcination temp./K	Surface area/ m^2 $g\text{-}cat^{-1}$	Gas evolution rate/ mol $g\text{-}cat^{-1}$ h^{-1}	Total conv./ mol%	Conversion/%				Selectivity to CO/%	TF/h^{-1}
					CO	CH_4	CO_2	H_2O		
473	673	47	0.469	68.3	60.5	1.1	1.3	4.4	88.7	—
	823	42	0.462	74.6	70.7	1.0	1.0	1.3	94.7	—
	873	36	0.428	85.4	80.4	0.3	1.3	3.2	94.2	—
	973	29	0.584	84.0	81.7	0.9	0.9	0.5	97.2	—
	1073	16	0.461	84.0	81.2	1.2	1.1	0.3	96.7	—
673	673	52	0.113	32.4	14.8	0.5	0.5	14.1	45.8	29
	773	46	0.232	51.4	39.6	0.3	0.6	10.0	78.4	59
	823	43	0.426	80.3	78.0	1.0	1.1	0.2	97.2	282
	873	36	0.415	80.9	78.9	0.2	0.5	1.0	97.5	325
	973	27	0.427	83.7	81.4	0.9	0.9	0.4	97.2	263
	1073	16	0.520	89.3	87.1	0.4	0.4	1.2	96.4	249
773	673	—	0.044	19.5	2.5	0.2	0.1	11.7	13.0	—
	873	37	0.149	40.1	19.0	0.6	0.6	14.6	47.4	—
	973	—	0.471	55.7	53.6	0.6	1.0	0.1	96.3	—
	1073	—	0.359	55.0	51.8	1.3	1.0	1.0	94.1	—

respectively, over those of the unpretreated catalysts, as seen in Tables 1 and 2 (comparison of T-6 with T-8). For the Pd/Al_2O_3 catalysts, the pretreatment with evacuation of Al_2O_3 gave rise to significant increases in the surface area (26%), the dispersion (17%), and the catalytic activity (46%). For both the Al_2O_3 and ZrO_2 supports, though featured by relatively lower Pd dispersions, they displayed higher activities, as seen from Fig. 1. The present study and other ones[10,11] suggest that this primitive procedure (evacuation of support), particularly in the case of TiO_2 support, is capable of enhancement of the surface area and high Pd dispersion.

Figure 2 illustrates the change in the total conversion of methanol and selectivity to CO with reduction temperature for the Pd/TiO_2 catalysts. Figure 2 shows that the reduction at higher temperatures (above 773 K) gives rise to a significant decrease in the activity, and that the selectivity to CO is strikingly suppressed at 773 K and above in the reduction in such a way that it varies from 95% at 773 K or below to 53% at 873 K. Since Tauster et al.[12] presented definitive evidence for losses of chemisorptive capacity for H_2 and CO caused when various metal oxide-supported transition metal catalysts, including Pd/TiO_2, were pretreated at high temperatures, many discussions have been made in recent literatures on the influence of MSI on chemisorption and catalytic properties of transition metals. X-Ray diffraction patterns have revealed that a small amount of an intermetallic compound, given the formula Ti_2Pd on the basis of a powder diffraction file,[13] is formed at high reduction temperatures. This finding suggests, therefore, that the serious decline in activity may be due to the metal coalescence which would lead to a metal–support electron transfer. Similar results were reported by Bracey et al.[14] However, the present knowledge about the interaction of Pd with TiO_2 is insufficient for satisfactory understanding of the influence of metal oxide

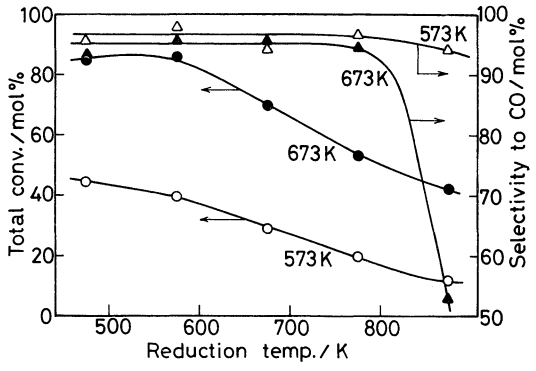

Fig. 2. Influences of reduction temperature upon the catalytic activity of Pd/TiO_2 (from $TiCl_4$) and selectivity to CO. Calcination temperature; 823 K. Total conversion; (○, ●), selectivity; (△, ▲). Reaction temperatures; 573 K, 673 K.

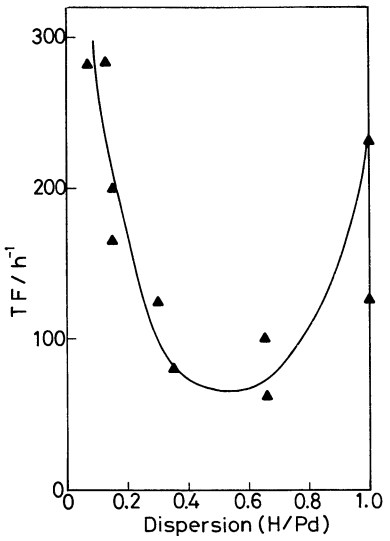

Fig. 3. Influences of Pd dispersion in Pd/ZrO_2 catalysts upon the turnover frequency (TF). Catalyst calcination temperature; 973 K. ZrO_2 support was prepared from the various starting materials.

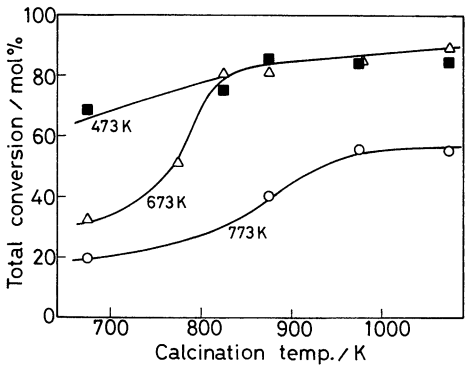

Fig. 4. Influences of calcination temperature on the activity (total conversion) of Pd/ZrO_2 catalysts. Reaction temperature; 673 K. Reduction temperatures; 473 K (■), 673 K (△), and 773 K (○). ZrO_2 support was prepared from $ZrOCl_2$.

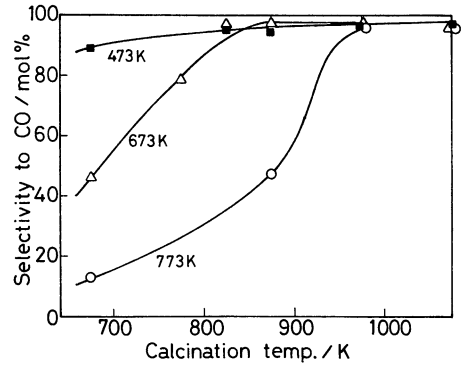

Fig. 5. Influences of calcination temperature on the selectivity of Pd/ZrO_2 catalysts. Reaction temperature; 673 K. Reduction temperatures; 473 K (■), 673 K (△), and 773 K (○). ZrO_2 support was prepared from $ZrOCl_2$.

support upon the activity of Pd catalysts, because of experimental failures, for example, to conduct some reduction–oxidation experiment using Pd/TiO_2 catalysts.

Catalytic Activity and Dispersion for the Pd/ZrO_2 System. In the case of the Pd/ZrO_2 catalysts, no simple relation between the degree of Pd dispersion and the value of TF was found, as seen from Fig. 3. The value of TF is not proportional to the degree of Pd dispersion.

The elevated calcination temperature for the ZrO_2 prepared from $ZrOCl_2$ depressed the dispersion slightly, while the catalytic activity of Pd/ZrO_2 was not proportionally lowered. The surface area of the Pd/ZrO_2 catalyst (Pd 1 wt%, with ZrO_2 prepared from $ZrOCl_2$) was gradually decreased as the calcination temperature was increased, e.g., in such a way that an increase in temperature from 673 K to 1073 K decreased the surface area from 52 to 16 m^2 $g\text{-}cat^{-1}$ (Table 3), and remarkable crystallization of ZrO_2 above 973 K was found by the XRD measurement. It may be speculated, therefore, that the catalytic activity of Pd/ZrO_2 is preferentially affected by the thermal stability of ZrO_2 crystallite rather than by the dispersion of Pd or by the surface area of ZrO_2 support. Figures 4 and 5 show the changes in the catalytic activity and the selectivity to CO for the Pd/ZrO_2 catalyst, respectively, as a function of calcination temperature. In this case, the Pd/ZrO_2 catalyst was pretreated at the different reduction temperatures indicated as parameter in Figs. 4 and 5. Both the catalytic activity and the selectivity declined at the higher reduction temperature (773 K), in particular in the case of lower calcination temperature, while the selectivity to CO was not changed with reduction temperature in the case of higher calcination temperatures (above 923 K). On the other hand, in the case of the lower reduction temperature (473 K), they were little affected by the change in the calcination temperature, as shown in Figs. 4 and 5.

As shown in Fig. 6 in which the reduction temperature is 673 K, the degree of Pd dispersion exhibits a notable decline at the calcination temperatures near 823 K, while the catalysts calcined above 823 K show no definite change in the degree of Pd dispersion. ZrO_2 support has been known to crystallize in a stable monoclinic system at 873 K and above.[15] Thus, the favorable reduction of Pd precursor without particle coalescence may be effected because of the loading of Pd on the thermally stabilized ZrO_2 support, with subsequent development of the essential catalytic activity. And, no more remarkable decrease in the Pd dispersion rather than the decrease in the activity was found in the case of elevated calcination temperature. The value of TF also was seriously changed by varying

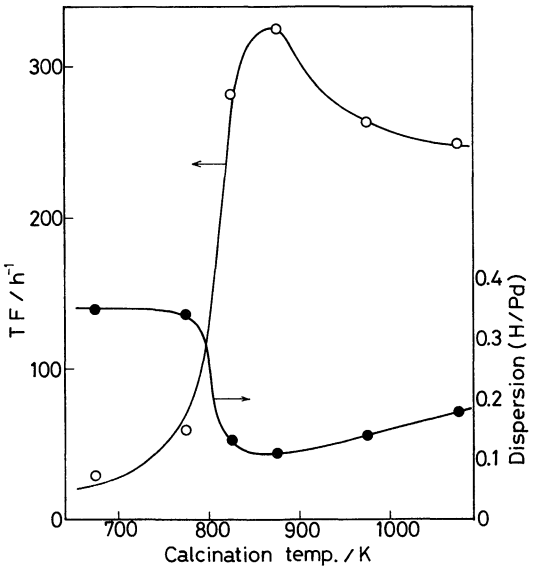

Fig. 6. Changes in turnover frequency and Pd dispersion with calcination temperature of Pd/ZrO_2 catalysts. Reduction temperature; 673 K.

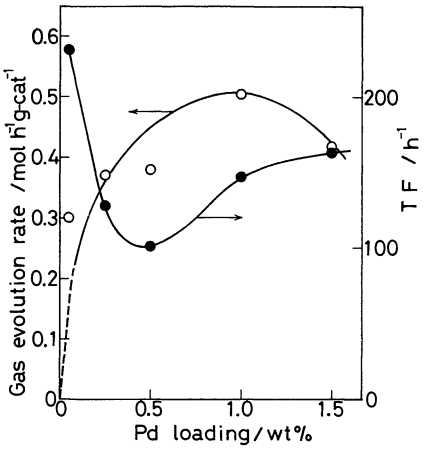

Fig. 7. Influences of Pd loading upon the apparent activity and turnover frequency of Pd/ZrO_2 catalysts prepared from $ZrOCl_2$.

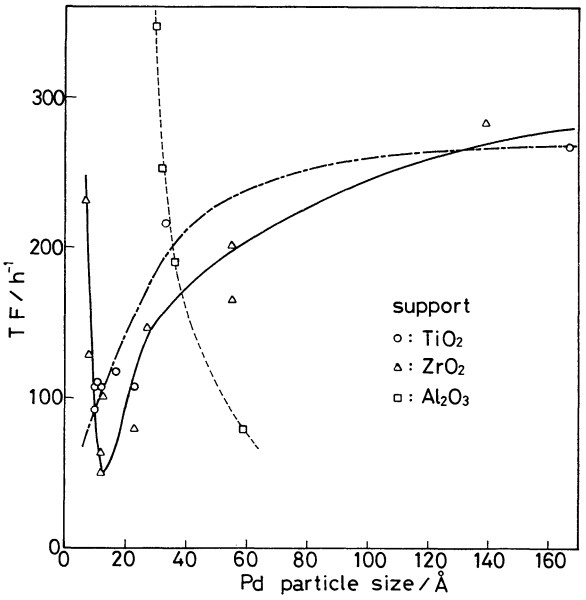

Fig. 8. Changes in turnover frequency with Pd particle size of various supported Pd catalysts.

the amount of Pd loading or the material for ZrO_2 support (Fig. 3). These results suggest that the size or number of Pd particles as estimated from hydrogen adsorption measurements may affect the catalytic activity. Therefore, it can be speculated that the value of TF is caused to change at a certain size of Pd particle, especially in the region of high Pd dispersion, because the catalytic activity was not proportional directly to the surface area or the degree of Pd dispersion.

Influence of Pd Loading on Catalytic Activity of the Pd/ZrO_2 System. The activity tests of the Pd/ZrO_2 catalysts which were prepared from $ZrOCl_2$ with different Pd contents were carried out in order to know the effect of Pd particle size on catalytic activity. We had expected that the degree of Pd dispersion would vary with loaded Pd content. However, the catalytic activity was not varied in parallel with the change in the degree of Pd dispersion, as shown in Fig. 3. Although the maximum catalytic activity per gram catalyst was attained near 1 wt% Pd content, the value of TF calculated as the catalytic activity per Pd atom seemed to be increased from 0.5 wt% as seen in Fig. 7. It is significant to note from these findings that the specific activity for the methanol decomposition would vary with properties of Pd surface in the region where the magnitude of metal dispersion might be diminished and that the value of TF would be influenced significantly by the nature of surface metal. It can be assumed that various solid phase processes such as coalescence, migration,[9] and aggregation of Pd crystallites might occur on ZrO_2 support when the Pd loading is relatively large. In addition, it has been considered that the change in intrinsic catalytic activity may be attributed to the particle size of Pd for the Pd/ZrO_2 catalysts employed here.

Average Size of Pd Particles and Its Distribution. Figure 8 shows the relation between the mean particle size of Pd and the value of TF calculated from both the data of the H_2 adsorption and activity tests. In Fig. 8, the TF vs. particle size plots include all of the data of the TiO_2-, ZrO_2-, and Al_2O_3-supported Pd catalysts which were reduced for 3 h at 673 K before being subjected to catalytic activity tests. It can be seen from Fig. 8 that a drastic change in TF takes place near a mean Pd particle size of 10 Å in the case of the TiO_2 and ZrO_2 supports. The TF curve for the Al_2O_3 support seems to be distinct from those for the TiO_2 or ZrO_2 supports, although we cannot definitely eluci-

date the influence of particle size upon specific activity, because experimental data are not enough to draw a definite conclusion. As additional information, Fig. 8 suggests that, in the case of the ZrO_2 and TiO_2 supports, there is a critical particle size of Pd so that minimum value of TF is given. It has already been pointed out that, when a supported metal catalyst retains the critical mean particle size of the order of 15—20 Å, the metallic properties including electronic properties of the catalyst may discontinuously vary at the particular metal size.[16]

It has also been known that highly dispersed metal or very small metal particles on oxide supports may allow the occurrence of SMSI when reduced at such a high temperature that, for instance, metal-support electron transfer may be caused.[14,17] However, the explanation based on the SMSI effects cannot be used for the present work because we have not yet investigated in detail whether the dispersion of Pd and the adsorption of hydrogen are affected by the elevation of reduction temperature. It is possible to say that the catalytic activity of the surface of Pd particles dispersed on supports prepared in different manners, is sensitive to the particle size in the range 5—160 Å of mean particle size. Vannice et al.[18] have reported that the turnover frequency in methanation of CO over a TiO_2-supported Pd catalyst is independent of Pd crystallite size, at least over the range 30—300 Å of particle size. If the SMSI effect on catalytic activity works in our case of supported Pd catalysts, the critical Pd particle size is about 10 Å. However, no intrinsic correlation between the Pd dispersion and the particle size effect upon the catalytic activity has yet been definitely established, and the clarification needs investigations in the future.

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