Dispersion Stability of Supported Palladium Crystallites

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The dispersion stability of supported Pd has been studied over a range of temperatures. The results of this study demonstrated that the initial dispersion of Pd crystallites on Al_2O_3 was much larger than on SiO_2 or on $\text{SiO}_2/\text{Al}_2\text{O}_3$ when prepared by wet impregnation method. The metal on the Al_2O_3 support was more resistant to thermal sintering in vacuum. These differences were due to the chemical interactions of the support with the reduced Pd metal or the Pd salt used in the catalyst preparation. The degree of thermal sintering of $\text{Pd}/\text{Al}_2\text{O}_3$ in vacuum was found to depend on the fractional surface coverage of the carrier with Pd (FSC). The small crystallites were stabilized at low FSC, i.e., on a carrier with a high surface area and low Pd loading.

The degree of the crystallite growth of Pd in hydrogen or in oxygen atmosphere was similar to that in vacuum. On the other hand, the pronounced crystallite growth of Pd was observed in the presence of acetic acid/oxygen mixtures at considerably lower temperatures. The aggregation of Pd under such conditions was associated with the formation of palladous acetate and its migration on the surface of catalysts.

1. Introduction

Loss in the metal surface area of supported catalysts due to thermal sintering remains a problem of considerable importance in catalyst technology. While the subject has received a great deal of attention in the past, the development of surface-reactive methods for metal surface area determination by surface titration of the chemisorbed oxygen by either hydrogen¹⁾ or carbon monoxide^{2),3)} provides the opportunity for quantitative measurements, especially at high levels of metal dispersion where alternate experimental techniques with supported metal catalysts are more difficult.

With supported Pt-catalysts^{4)~15)} the temperature and gaseous environments have a profound influence on the rate of sintering. In addition, the type of insulator support employed, the metal weight loading, the method of catalyst preparation and the length of exposure to elevated temperatures affect the crystallite size distribution attained on the catalyst.

For supported Pd-catalysts fewer data are available^{17)~20)}. By means of the surface titration of the chemisorbed oxygen with CO, reported earlier for Pt²⁾ and Pd³⁾, a detailed sintering study was

undertaken in order to further the development of thermally stable Pd metal dispersion.

2. Experimental Details

The catalysts were prepared by conventional wet impregnation technique. A number of Al_2O_3 , SiO_2 and $\text{SiO}_2/\text{Al}_2\text{O}_3$ supports were impregnated with an aqueous solution of sodium tetrachloropalladate to yield the desired weight loading of the metal. After evaporation to dryness on a steam bath, the samples were reduced with an alkaline solution of hydrazine hydrate (5 wt% N_2H_4 , 1-N NaOH solution), washed with distilled water until free of Cl^- ion, then dried under reduced pressure (20 torr) at 60°C for 10 hours.

All carriers were obtained from commercial sources (Table 1). Preceding the surface area determination, the supported Pd-catalysts were crushed and screened (14~20 mesh).

The surface area of each carrier was measured by means of the BET method (Kr). Pore volume distribution was determined by high pressure mercury porosimetry. Analogous to the earlier work, the Pd surface area was determined by "surface titration" involving the interaction of oxygen adatoms on Pd-sites with gaseous carbon monoxide, and quantitative determination of the mass of carbon dioxide produced ($\text{O(s)} + 2\text{CO} \rightarrow \text{CO(s)} + \text{CO}_2$)^{2),3)}. The measurements were carried out in an electrically heated quartz reactor into which the sample under study could be introduced and exposed to various temperatures for various time

Received April 11, 1979.

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Table 1 Physical Structure of Catalyst Support

Carrier No.	S. A. (m ² /g)	Pore Volume (cc/g)	Pore Size Distribution (Å)*	Source
Al ₂ O ₃ (I)	150	—	<100	Mallinckrodt Chem. Co.
Al ₂ O ₃ (II)	82	0.35	120~160	Mizusawa Chem. Co.
Al ₂ O ₃ (III)	23	0.30	200~500	Mizusawa Chem. Co.
Al ₂ O ₃ (IV)	9	—	broad	Mallinckrodt Chem. Co.
Al ₂ O ₃ (V)	9	0.29	600~1,500	Shokubai Kasei Co.
Al ₂ O ₃ (VI)	8	0.27	1,400~1,700	Mizusawa Chem. Co.
SiO ₂ (I)	96	0.61	37.5~300	Nikki Chem. Co.
SiO ₂ (II)	105	1.09	100~300	Nikki Chem. Co.
SiO ₂ (III)	25	—	37.5~700	Nikki Chem. Co.
SiO ₂ ·Al ₂ O ₃	250	—	broad	Nikka Seiko Co.

* 80% of total pore volume.

Catalyst : Pd 1.0wt%-Al₂O₃(III)
Thermal aging in vacuum : ○ 250°C, ● 600°C

Fig. 1 Effect of Temperature on Sintering

periods. The reactor, an integral part of the apparatus employed for surface-area measurement, could be evacuated ($P < 10^{-6}$ torr) and filled with different gases at any desired pressures. Following such treatment the catalyst sample could be subjected to the surface-area titration without the intervening exposure to room air. The mean crystallite size was calculated from the Pd surface area and Pd content⁽¹¹⁾.

3. Results

3.1 Sintering in Vacuum

The role of the catalyst support on the sintering of Pd-crystallites was investigated in a series of experiments in which individual samples were exposed to elevated temperatures for fixed periods of time in vacuum ($P < 10^{-6}$ torr). At any prescribed time interval the surface area of the sample was determined. A representative example of the sintering behavior of the Pd/Al₂O₃(III) catalyst at several temperatures is shown in **Fig. 1**. To obtain information of the effect of different Al₂O₃ support materials on the sintering process the data summarized in **Fig. 2** were collected. In each of these samples the Pd-content was 1 wt%. On varying the weight loading of Pd from 1.0 to 0.1

Catalyst : Pd 1.0 wt%-Al₂O₃
△ Al₂O₃(I), ○ Al₂O₃(II), ▲ Al₂O₃(III),
▼ Al₂O₃(IV), ● Al₂O₃(V), ■ Al₂O₃(VI).
Heat treatment : 600°C in vacuumFig. 2 Effect of Carrier Type (Al₂O₃) on Sintering

wt% on Al₂O₃(IV) a marked decrease in sintering rate was observed (**Table 2**). At the lowest Pd-loading (0.1 wt%) no change in the total metal surface area was observed after exposure to vacuum at 600°C for 17 hours (**Fig. 3**).

With silica and silica-alumina supports, the initial Pd dispersion was found to be much smaller than that observed for the aluminas (cf. **Tables 2** and **3**). Also on these carriers the metal appeared to be less resistant to sintering.

3.2 Sintering in Chemically Reactive Atmospheres

In extending the studies on thermal sintering in vacuum, the effect of chemically reactive gases, hydrogen, oxygen and acetic acid (in air), on the stability of the Pd-dispersion was examined. The results, summarized in **Table 5**, demonstrate a relatively small contribution of H₂ or O₂ to crystal-

Table 2 Effect of Palladium Content on Thermal Sintering at 600°C

Carrier		Pd Content (wt%)	Heat Treatment (hr)	S . A . (m ² /g Pd)	Pd Crystal Size (Å)*1)	Fractional Surface*2) Coverage of Carrier with Pd (%)
No.	S . A . (m ² /g)					
Al ₂ O ₃ (II)	82	1.0	0	79	63	0.24
			3.5	71.5	70	0.22
			15.5	70	71.5	0.21
		5.0	0	59	85	0.90
			3	37	135	0.57
			16	34	147	0.53
Al ₂ O ₃ (V)	9	0.3	0	61	82	0.51
			3	56	89	0.46
			10	54	92.5	0.45
		1.0	0	40	125	1.1
			3	36	139	1.0
			10	36	139	1.0
Al ₂ O ₃ (IV)	9	0.1	0	97.5	51	0.271
			17	99	50.5	0.275
		0.3	0	99	50.5	0.825
2.5	69		72.5	0.575		
		1.0	0	78	64	2.2
			3	43	116	1.2
			16	44	114	1.2
Al ₂ O ₃ (VI)	8	0.3	0	91	55	0.85
			3	74.5	67	0.70
			17	63	79.5	0.59
		1.0	0	65	77	2.0
			13	32	156	1.0
			17	29	173	0.9

*1) Pd crystallite size (Å)=10,000/2S (where S represents Pd surface area m²/g Pd)
*2) Fractional surface coverage of carrier with Pd (%)
$$= \frac{1/4 \times \text{Pd S.A. (m}^2/\text{g cat.)}}{\text{Al}_2\text{O}_3 \text{ S.A. (m}^2/\text{g)}} \times 100 \quad (1/4 \times \text{Pd S.A.} = \text{Section area of Pd crystallite})$$

Fig. 3 Effect of Palladium Content on Sintering

lite growth (Table 5), as most of the decrease in the surface area may be accounted for in terms of thermal sintering. However, the pronounced crys-

tallite growth of Pd was observed in the presence of acetic acid/oxygen mixtures at considerably lower temperatures. To obtain further information on the role of the support in chemical sintering, catalyst samples on different supports were exposed to acetic acid/oxygen environments (Table 6). The SiO₂-supported catalyst retained its Pd-metal dispersion while the Al₂O₃-supported samples sintered readily by comparison.

4. Discussion

For the interpretation of the experimental results on thermal sintering in vacuum, two aspects must be considered. One deals with the role of the support in controlling the initial dispersion of Pd, the other concerns with the influence of the support on crystallite growth by thermal aging in vacuum.

By comparing the initial surface area of the Al₂O₃-supported samples and that of the SiO₂- or SiO₂/Al₂O₃-supported catalysts, it is noted that the latter materials yield much lower Pd-dispersion, an effect noted previously^{7),17)}. The cause for this

Table 3 Effect of Carrier Type and Palladium Concentration of Thermal Sintering at 600°C

Carrier			Pd Content (wt%)	Treatment (hr)	Pd S.A. (m ² /g)	Pd Crystal Size (Å)	Fractional Surface Coverage of Carrier with Pd (%) ^{*2)}
No.	S.A. (m ² /g)	Pore Size ^{*1)} (Å)					
SiO ₂ (I)	96	30~300	1.0	0	52	96	0.14
				4.5	35	143	0.093
				11	24	208	0.063
SiO ₂ (II)	105	100~300	1.0	0	55	91	0.16
				3	27	185	0.075
				22	26	192	0.075
SiO ₂ (III)	25	100~700	0.5	0	32	156	0.16
				2	27	185	0.14
			1.0	16	25	200	0.125
				0	23	218	0.23
SiO ₂ ·Al ₂ O ₃	250	broad	1.0	16	15	334	0.15
				0	15	334	0.015
				21.5	14	356	0.014

^{*1)} 80% of total pore volume of a carrier.
Pd crystallite size (Å) = 10,000/2S (where S represent Pd surface area m²/g_{Pd})
^{*2)} Fractional surface coverage of carrier with Pd (%) given in Table 2.

Table 4 Number of Palladium Crystallites and Interparticle Distance*

Carrier		Pd Content (wt%)	Mean Crystallite Size (Å)	Number of Crystallites per g·cat	Critical Distance of Crystallites (Å)
No.	(m ² /g)				
(I)	150	1.0	56	9.0	1,290
(II)	82	5.0	147.5	2.5	1,820
		1.0	71.5	4.4	1,370
(III)	23	1.0	93	2.0	1,080
(IV)	9	0.3	92.5	0.63	1,300
		1.0	139	0.59	1,240
(V)	9	0.1	50.5	1.23	860
		0.3	68	1.59	752
		1.0	114	1.07	920
(VI)	8	0.3	79.5	1.00	880
		1.0	173	0.37	1,490

* Average equilibrium distance between palladium crystallites after sintering.

difference does not appear to be associated with the pore structure or surface area of the supports. Rather it could be the result of the chemical interaction between the Pd-salt and the support and the bonding of the metal after reduction. In studies reported by Echigoya et al.,¹⁷⁾ the mass of Pd-salt adsorbed by various Al₂O₃, SiO₂ and SiO₂/Al₂O₃ supports was found to be a function of the type of Pd-complex salt used. These authors found that Pd complexed as an anion, such as in (PdCl₄)²⁻, shows little adsorptive affinity for SiO₂ or SiO₂/Al₂O₃ in comparison with Al₂O₃; on the other hand, when Pd is present in the cationic form ([Pd(NH₃)_m]²⁺), just the opposite effect is observed. Pd crystallites on SiO₂ and SiO₂/Al₂O₃ were less resistant to sintering than on Al₂O₃. Weller

et al.¹⁵⁾ observed a similar phenomenon on supported platinum catalysts. These results suggest that interaction takes place between alumina and the metal (or an oxide coated metal crystallite), similar to the interaction between Pd salt and alumina described above. In fact, some workers have indicated the evidence of the formation of a Pt-alumina complex which stabilized the platinum crystallites^{15),16)}. The sintering curve of Pd/Al₂O₃ catalysts (**Figs. 1 and 3**) can be divided into two stages, i.e., labile state and steady state. The rate of sintering during the labile state and the existence of a limiting crystallite size beyond which no further change occurs in metal surface area appear to be related to the fractional surface coverage of the carrier

Physical data on supports given in Table 2
Catalyst : Pd content (wt%)
□ 0.1, △ 0.3, ○ 1.0, × 5.0

Fig. 4 Effect of Fractional Surface Coverage of Carrier with Palladium on Sintering

Table 5 Dispersion Stability of Pd/Al₂O₃ Catalysts in Reactive Environment

Catalyst	Exposure				Pd Surface Area (m ² /g Pd)
	Gas	Pressure (torr)	Temp. (°C)	Time (hr)	
Pd(1.0 wt%)/ θ -Al ₂ O ₃	—	<10 ⁻⁶	—	—	92±3 ^{*1}
	—	<10 ⁻⁶	600	3	83±3
	H ₂	380	600	3	95±5
	O ₂	40	600	3	90±3 ^{*2}
Pd(1.0 wt%)/ α -Al ₂ O ₃	—	<10 ⁻⁶	—	—	120±4
	—	<10 ⁻⁶	600	3	71±2
	—	<10 ⁻⁶	600	16	62±2
	H ₂	380	600	3	78±3
	O ₂	380	500	4	70±3
	AcOH ^{*2} /Air	115/645	200	22	18±3

^{*1}) Initial surface area.
^{*2}) Following the exposure to oxygen or AcOH/air the sample was exposed to hydrogen at 200 torr and 200°C, for 2.5 hr, then to vacuume (P<10⁻⁶ torr) at 300°C for 12 hrs. (AcOH=CH₃COOH).

with Pd (FSC), i.e., the surface area ratio of Pd to the support material (Table 2). The small crystallites can be stabilized at low FSC as they occur on a carrier having high surface area and low Pd content (Fig. 4). The distance between the particles at steady state was estimated from the average metal crystallite size computed on the basis of cubic shape and of contact with the carrier at one face. The results of these calculations (Table 4) indicate that on alumina the Pd crystallites cease to grow when the distance between particles reaches from 750 to 1,500 Å.

Regarding the effect of chemically reactive atmospheres on Pd sintering, a remarkable crystal-

Table 6 Effect of Catalyst Support on Palladium Sintering during Exposure to Acetic Acid/Oxygen Mixtures^{*1})

Catalyst	Exposure		Pd Surface Area (m ² /g Pd)	
	Temp. (°C)	Time (hr)	Initial	Final
Pd(1.0 wt%)/Al ₂ O ₃ ^{*2})	200	22	120±4	18±3
Pd(1.0 wt%)/Al ₂ O ₃	135	16	120±4	39±3
Pd(1.0 wt%)/SiO ₂	135	16	52±2	55±2

^{*1}) 115 torr CH₃COOH, 130 torr O₂, 515 torr N₂.
^{*2}) α -Al₂O₃, source as in Table 5.

lite growth of Pd was observed in the presence of acetic acid/oxygen mixtures at considerably lower temperatures while the degree of crystallite growth of Pd in hydrogen or oxygen was similar to that in vacuum. The aggregation of Pd in acetic acid/oxygen environments may result from the formation of Pd(OCOCH₃)₂ and its migration, as reported previously²¹). The cause for the difference in the degree of Pd aggregation between the SiO₂-supported catalyst and the Al₂O₃-supported catalysts (Table 6) has not been established. It may point to the existence of some Pd-cations on the surface of alumina supports and predominantly Pd-metal on the surface of silica supports.

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要 旨

担持パラジウム結晶粒子の熱安定性

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含浸法により調製した Pd 触媒に関し、真空ならびに種々のガスふん囲気下における Pd 結晶粒子の熱安定性について検討した。Pd の結晶粒子径は CO 滴定法により測定した^{2),3)}。

(1) 真空下での Pd の熱安定性

調製した Pd の分散性は担体の種類により異なり、 $\text{Al}_2\text{O}_3 > \text{SiO}_2, \text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ であった。また、熱安定性に関しても、 Al_2O_3 に担持させた Pd がとくにすぐれていた (Tables 2, 3 との比較)。

表面積ならびに細孔径分布の異なる 5 種の Al_2O_3 担体 (Table 1) について、Pd を担体に対し 0.1~5 wt% 担持させ、それらの熱安定性を比較した (Figs. 1~3)。いずれの触媒も熱処理の初期に Pd の結晶粒子の成長がおこるが、数時間後に成長はとまり、Pd 結晶粒子は一定の値 ($D_{\text{limit. Pd}}$) となって安定化した。各触媒について、Pd の結晶粒子径から担体表面上の Pd の被覆率 (触媒 g 当りの Pd 結晶粒子の総断面積/触媒 g 当りの担体の表面積 $\times 100$) を算出した結果、Pd の被覆率と $D_{\text{limit. Pd}}$ との間に直線関係が成立し (Fig. 4)、Pd の被覆率の小さい触媒ほど $D_{\text{limit. Pd}}$ は小となることが示唆された。これより、熱安定性のよい触媒をつくるには、Pd の被覆

率を小さくする、換言すれば、表面積の大きい担体を用いるまたは Pd の担持量を少なくすることが必要であることがわかる。Pd の結晶粒子の成長がとまり、安定化した時点での結晶粒子の間隔は 750~1,500 Å と算出された (Table 4)。

(2) 種々のガスふん囲気下における Pd の熱安定性

酸素、水素ならびに (酢酸+酸素) の 3 種のガスについて、それぞれのガスふん囲気下で Pd/ Al_2O_3 触媒を加熱処理し、Pd 結晶粒子の成長の度合を調べた。酸素および水素のガスふん囲気中での熱安定性 (600°C) は、真空下での場合とほぼ同様であるのに対し、(酢酸+酸素) ガスで熱処理した場合には、低温下 (200°C) において Pd 結晶粒子の顕著な成長が認められた (Table 5)。このような処理条件下では Pd 触媒上に Pd (OCOCH_3)₂ が生成すること²¹⁾ から、この場合の Pd 結晶粒子の成長機構は真空下の場合と異なり、Pd (OCOCH_3)₂ を経由しておこるもの²¹⁾ と推定された。上記と同様の処理条件 (ただし、135°C) で Pd/ SiO_2 と Pd/ Al_2O_3 の熱安定性を比較したが、 SiO_2 担体上では Al_2O_3 担体の場合にみられるような Pd 結晶粒子の成長はおこらなかった (Table 5)。この相異は現在明らかでないが、おそらくは SiO_2 担体上では Pd^{2+} が生成し難いことによるものであろう。

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Keyword

Dispersion, Palladium, Sintering