

Effect of Palladium Size on Chemistry Activity

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ABSTRACT

Palladium clusters with an average size (d_{pd}) ranging from 10 nm to subnanometer (< 1 nm) were dispersed on silica support. Chemical interaction between the dispersed nanopalladium and hydrogen gas was calorimetrically studied as a function of hydrogen uptake. Measured profiles of interaction energy vary with the d_{pd} of studied samples and change drastically as the d_{pd} approaches subnanometer. The size of dispersed metallic clusters affects not only their chemical activity but also their application in technologies of fuel cell, gas sensor and heterogeneous catalysis.

Keywords: Nanoparticle; palladium; hydrogen; chemisorption; potential energy.

1 INTRODUCTION

The molecular wire has been selected as the major breakthrough of science in year 2001. A practical application of molecular wires and other nano-materials relies profoundly on the advance on their preparation and their physical and chemical properties. Many physical properties of nanomaterials, i.e., mechanic strength [1], melting point [2], absorption spectra [3], magnetic susceptibility [4], quantum confinement effect [5], as well as electronic structure [6] have been reported to vary with size. Since the chemical property of a material depends heavily on its electronic energy in the valence state, it is expected that the **chemical activity** of nanoparticles should also vary with their size. In this report, we want to communicate the effect of size on the absorption of hydrogen into nanopalladium and on the chemical activities of nano-metals.

The **absorption of hydrogen** is a technology to store a large amount of hydrogen at ambient temperature and pressure. Different solid materials have been tried as hosts of the storage. An extensive research attention has been on absorption in palladium because the absorption is also used to refine samples of crude hydrogen into the research quality.

Palladium powders with primary particles in a size of $d_{pd} \sim 8$ nm can be prepared by the **reductive precipitation** of palladium ions in an aqueous solution [7]. However, the primary particles prepared in the precipitation are thermally unstable and tend to aggregate into secondary particles and subsequently coalesce into large particles upon filtration and other treatments. In practice, the aggregation of primary particles may be suppressed by dispersion them on porous supports of large surface area. Different dispersing

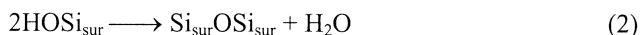
methods have been used in the literature. The **incipient wetness (IW)** is a physical method that disperses the primary particles on a vast surface of porous support, such as SiO_2 . The impregnation is a convenient method and has been widely used for preparation of metallic catalysts.

The dispersion of metal particles on supported samples may be chemically enhanced by **ion exchange (IE)** method. The affinity of palladium cations to silica surface is increased significantly by a formation of ionic bonds through



Where the symbol of Si_{sur} indicates silicon atoms exposed to the surface of silica. The extent of bond formation varies with the pH value of the impregnating solution. Pd/SiO₂ samples with an average palladium size of $d_{pd} \sim 3$ nm have been prepared by reaction 1 at pH = 9 [8].

The extent of reaction 1 may also be enhanced by an increase in density of siloxy groups (HOSi_{sur}) pendent on the surface of silica. The density varies significantly on the history of silica preparation. A freshly prepared silica gel generally has a maximum density. However, it diminishes upon a formation of inert siloxane bonds through the following dehydration:



during subsequently processes of drying and calcination. Accordingly, Pd/SiO₂ samples with palladium dispersed in very small size may be prepared by a **sol-gel (SG)** method (9) that allows reaction 1 to proceed at the stage of gel formation before the extent of reaction 2 becomes extensive.

2 EXPERIMENTAL

Table 1 lists palladium **samples prepared** for the present study. A sample of pure palladium powders was prepared by the precipitative reduction of PdCl_2 [7]. Supported Pd/SiO₂ samples were prepared by three techniques, i.e., IW, IE, and sol-gel SG, described above. The support used in the samples of IW and IE was commercial SiO₂ crystallites (Cab-o-sil M-5, SA = 200 m² g⁻¹). The IW samples were prepared by impregnating this support with an aqueous solution of H_2PdCl_4 . The IE samples were prepared by suspension the Cab-o-sil in an aqueous solution of $\text{Pd}(\text{NO}_3)_2$ (Strem) and NH_4OH at pH = 9.0. Silica support used in the SG samples was homely prepared from

Table 1: Physical properties characterized for samples prepared in this study.

Catalyst	Pd wt%	T_c (K)	T_r (K)	Pretreatment		Characterization	
				D_{Pd} (%)	Q_{Hi} (kJ mol ⁻¹)	Q_{Hab} (kJ mol ⁻¹)	Q_{O_i} (kJ mol ⁻¹)
Pd powder	100	383	323	7	94	39	-
20Pd/SiO ₂ (IW)	1.86	723	573	18	92	37	272
10Pd/SiO ₂ (IW)	0.87	723	573	20	93	37	272
05Pd/SiO ₂ (IW)	0.45	723	573	21	95	38	280
20Pd/SiO ₂ (IE)	1.84	773	573	29	107	42	324
20Pd/SiO ₂ (IE)	1.80	573	573	34	113	44	320
20Pd/SiO ₂ (SG)	2.05	723	573	57	120	43	321
10Pd/SiO ₂ (SG)	0.95	573	573	60	115	48	335
10Pd/SiO ₂ (SG)	0.94	723	573	75	131	45	377
10Pd/SiO ₂ (SG)	0.98	873	573	81	149	70	369
05Pd/SiO ₂ (SG)	0.47	723	573	85	183	65	376

tetraethoxysilane (TEOS) (Acros). After refluxing TEOS with ethanol at 353 K, a gelation was formed upon adding an aqueous solution of PdCl₂ (Merck) and NH₄OH. All of the Pd/SiO₂ samples prepared by methods described above were subsequently dried at 373 K, calcined at 723 K and stored as fresh samples of IW, IE and SG, respectively. Table 1.

The dispersion, i.e., fraction of atoms exposed to surface of crystallites, of palladium (D_{Pd}) on the fresh samples was determined from isotherms of hydrogen chemisorption at 313 K. Freshly samples were inserted into an adsorption cell connected to a **volumetric system** schematically depicted in Fig. 1. Prior to an isotherm measurement, each sample was pretreated with a reduction in flowing hydrogen (30 ml/min) for 1 h and an evacuation at 10⁻³ Pa for 2 h in the sample cell. Supported Pd samples were generally pretreated at 573 K. A mild pretreatment at 373 K was specially selected for the Pd powders to prevent severe coalescence. Controlled doses of hydrogen gases were sequentially introduced to an evacuated sample to pursue its isotherm of hydrogen uptake (N_H). Increments of hydrogen uptake (ΔN_H) upon the doses were calculated from the pressure changes monitored by a Texas pressure gauge (with a resolution of 1 Pa). Heats evolved on these uptakes were measured by a Setaram C-80 differential microcalorimeter embracing the sample cell.

3 RESULTS AND DISCUSSIONS

Figure 2A compares **isotherms of hydrogen uptake** volumetrically monitored for five samples. Each isotherm showed three consecutive stages of hydrogen uptake (N_H) on increasing P_{H_2} :

1. Steep increase of N_H at very low overpressure ($P_{H_2} < 100$ Pa).
2. Mild increase of N_H between 0.1 and 3 kPa.
3. Additional increase of N_H between 3 and 5 kPa .

The contribution of these three stages in isotherms of Fig. 1 varies with the method of sample preparation. Stage 1 is obscure for the Pd powers (isotherm a) while stages 2 and 3 becomes negligible for the SG samples.

Hydrogen uptake at the first stage has been assigned to chemisorption on palladium surface [10]. The dispersion of palladium in each sample can be estimated from the uptake in this stage (N_{Hc} , i.e., N_H at $P_H = 100$ Pa) and the number of palladium atoms in sample (N_{Pd}) through:

$$D_{Pd} = N_{Hc}/N_{Pd} \quad (I)$$

Column 5 of Table 1 lists the D_{Pd} estimated for all of the samples freshly prepared in this study. The unsupported palladium powders exhibited a low dispersion of $D_{Pd} < 10$ %. High dispersions were found from supported Pd/SiO₂ samples. Estimated D_{Pd} for the supported samples varied significantly with the techniques of preparation and showed a trend of IW < IE < SG.

Among supported samples prepared by a same dispersing method, D_{Pd} slightly decreased on increasing the loading of palladium.

The uptake of hydrogen on palladium is an exothermic process. Figure 2B presents a sequence of heat flow monitored by the Setaram C-80 calorimeter during the isotherm measurement for Pd powders. The system temperature was held at 313.00 ± 0.01 K for the whole 5 h of monitoring period (a steady system temperature has been found essential for maintaining a decent DSC baseline). Twelve doses of hydrogen were sequentially introduced to the powders and each dose caused an exothermic peak that returned to the baseline in 1 x 10³ s. Heat (q) evolved in each dose may be integrated from its peak area. **Differential heats of hydrogen uptake (Q_H)** may be calculated from the q and the increment of hydrogen uptake (ΔN_H), monitored from the volumetric measurement, according to

$$Q_H = q/\Delta N_H \quad (II)$$

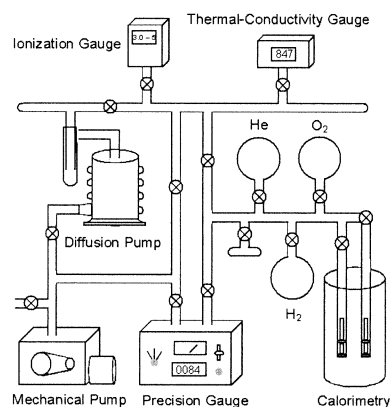


Figure 1: A schematic diagram for the coupled calorimetry-volumetry system used in this study.

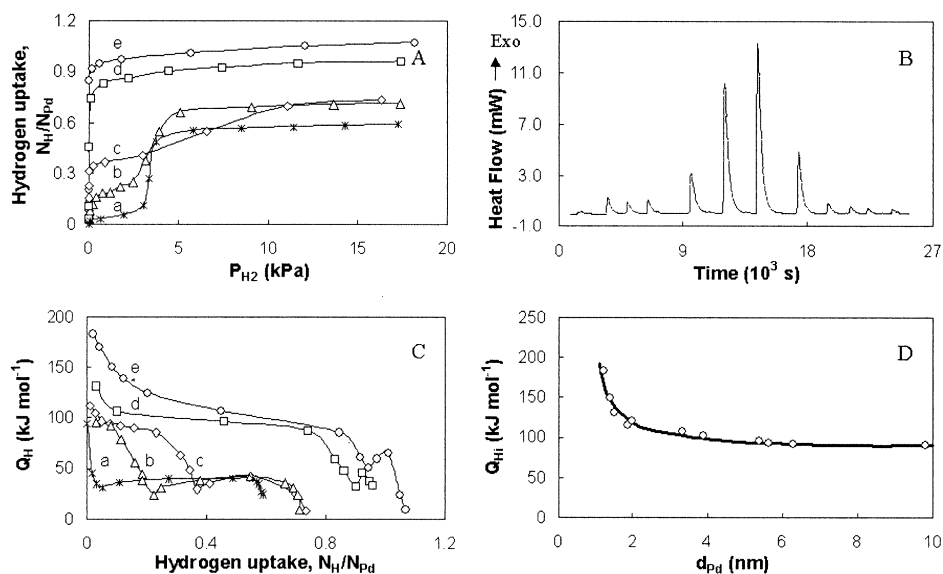


Figure 2: Detailed experimental results on measurement of adsorption heat: (A). Adsorption isotherms of hydrogen uptake at 313 K for different palladium samples: (a) Pd powder; (b) 20Pd/SiO₂(IW); (c) 20Pd/SiO₂(IE); (d) 10Pd/SiO₂(SG); and (e) 05Pd/SiO₂(SG). (B). Experimental heat flow monitored from Setaram C-80 DSC on introduction of 12 consecutive doses of hydrogen into palladium powders (see isotherm (a) in Fig. 2). (C). Differential heat of hydrogen uptake for hydrogen chemisorption on samples of: (a) Pd powder; (b) 20Pd/SiO₂(IW); (c) 20Pd/SiO₂(IE); (d) 10Pd/SiO₂(SG); and (e) 05Pd/SiO₂(SG). (D). Effect of the average particle size of nano-palladium (d_{Pd}) on the initial heat of hydrogen chemisorption (Q_{Hi}).

Calculated Q_H generally varied with the accumulated uptake of hydrogen (N_H). Fig. 2C compares uptake profiles of calculated Q_H for the five samples illustrated in Fig. 2A. Each profile again exhibited **three stages** on increasing N_H :

- Initial stage: Q_H decreases from an initial value (Q_{Hi} , which is shown in Fig. 2D to increase with the D_{Pd} of sample) to a level-off value of $Q_H \sim 90$ kJ (mole H_2)⁻¹ on increasing N_H . This decline feature is not prominent in the profiles a and b. They come from samples of low D_{Pd} and showed a short stage A with a constant $Q_H \sim 90$ kJ (mol H_2)⁻¹.
- Second stage: Q_H decreases from 90 kJ (mole H_2)⁻¹ to an energy valley with $Q_H \sim 25$ kJ (mole H_2)⁻¹; and
- Third stage: A small peak is found at the end of profiles. The width of this peak is broad for the sample of palladium powders (curve a) but narrows on increasing the D_{Pd} (curves b to e) of samples.

Behm et al. proposed from their results of a temperature programmed desorption study [11] that hydrogen in absorption systems may stay in four different environments, i.e., molecules in the gaseous phase (H_g), atoms dissociatively chemisorbed on surface (H_c), atoms incorporated at the sub-surface of palladium crystallites (H_s) and atoms dissolved to the bulk of palladium in the form of homogeneous hydride (H_h).

The features observed in Figs. 2A and 2C may be correlated to absorption of H_g to different environments. Upon collision on palladium crystallites, hydrogen gases initially introduced to the system may be chemisorbed

dissociatively on their surface through a fast equilibrium of



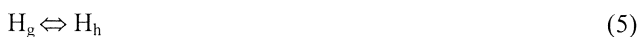
The chemisorption is an exothermic step [$Q_c > 90$ kJ (mol H_2)⁻¹] that does not require significant activation energy. The uptake in the chemisorption is generally described as strong adsorption.

After the surface was saturated with a layer of chemisorbed hydrogen, the uptake increases only gently on raising P_{H_2} and the accompanied heat decreases to $Q_H = 25$ kJ (mol H_2)⁻¹ in a P_{H_2} region between 10 and 3×10^3 Pa. The uptake in this stage results from a penetration of gaseous hydrogen into the subsurface layer of palladium crystallites [10],



LEED studies suggested that a reconstruction of surface palladium occurred during the penetration [12].

In isotherms a, b and c (from samples with low D_{Pd}) in Fig. 2A, the uptake increases abruptly again on raising P_{H_2} over 3 kPa and levels off around 5 kPa. The additional uptake in this stage reflects an absorption of hydrogen into bulk palladium to form palladium hydride, i.e.,



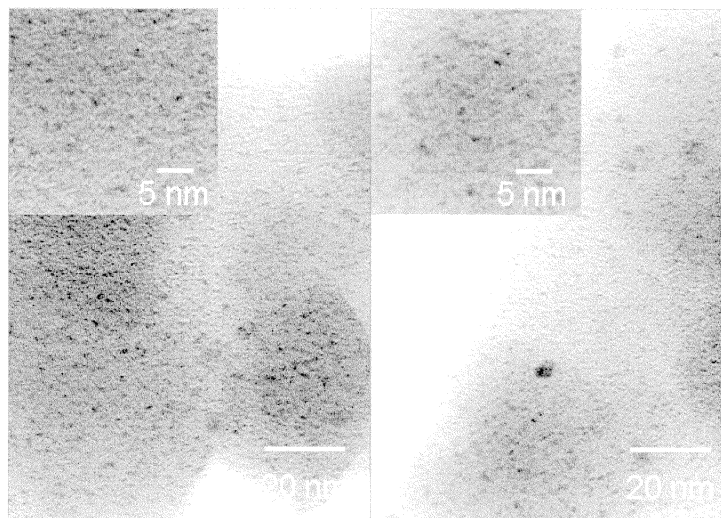


Figure 3: Transmission electron micrograph for 05Pd/SiO₂ reduced by hydrogen at 573 K.

For samples of crystalline palladium, PdH_n is a homogeneously bulk hydride with an enthalpy of formation $\sim -38 \text{ kJ (mol H}_2\text{)}^{-1}$ [13].

Equations 3 to 5 describe the elementary steps occurred in the absorption process of hydrogen into palladium. These steps explain the three stages observed in the isotherms of Fig. 2A and correlate well with the three stages distinguished from the calorimetric profiles of Fig. 2C. Noteworthy, the average size of palladium (d_{pd} , estimated from $1.1 \text{ nm}/D_{pd}$) significantly affects the phenomena of the absorption.

Figure 2D correlates effects of the d_{pd} on the Q_{Hi} (the initial heat of hydrogen chemisorption found in Fig. 2C) for the samples prepared in this study. Evidently, the Q_{Hi} remains at 90 kJ mol^{-1} for samples with $d_{pd} > 10 \text{ nm}$, raises mildly on decreasing d and abruptly as $d < 1.5 \text{ nm}$. A two-fold increase in the Q_{Hi} (from 90 to 183 kJ mol^{-1}) is noticed on decreasing the d_{pd} from 10 nm to subnanometer.

Figure 3 presents transmission electron micrograph for a sample ($D_{pd} = 90 \%$) prepared by SG method. A small fraction of palladium particles in the micrograph showed a size larger than 1 nm. However, the majority (over 90 % in number) of palladium particles have a size less than 1 nm. The size of the subnanometer palladiums is so tiny that the contrast difference between them and the background of silica can be barely distinguished in this micrograph. Since the radius of a palladium atom is $\sim 0.13 \text{ nm}$, a maximum of three atoms can lineup along a diameter of these **subnanometer palladiums**. In other words, the number of atoms in a tiny particle of subnano-palladium is generally less twelve.

4 CONCLUSIONS

In conclusion, Pd/SiO₂ samples with different sizes of palladium have been prepared. The potential diagram of hydrogen absorption and the enthalpies of chemisorption obtained from the prepared samples vary significantly with

the size of palladium particles dispersed. A 100 kJ mol^{-1} increment in the enthalpy of chemisorption was generally noticed on decrease the size from 10 nm to sub-nanometer. Such enthalpy change affects chemical activity of dispersed nanometals. Dispersed nanometals have been widely used as catalysts in chemical industry, pollution abatement, fuel cell and sensor technology. The activity of metallic catalysts may be tailored with many parameters, i.e., the kind transition metal, its alloy formation and nature of dispersing support. It is the theme of this report that the activity may also be modified by another parameter, i.e., the size of metal cluster. The effect is most prominent on decrease the size down to subnanometer.

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