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# Temperature-Programmed Reduction Study on Calcination of Nano-Palladium

**Chi-Wei Chou,[†] Shou-Juan Chu,[‡] Hui-Jean Chiang,[§] Chien-Yu Huang,[§] Chiu-jung Lee,[†] Shyang-Roeng Sheen,[⊥] Tsong P. Perng,[‡] and Chuin-tih Yeh*[,†]**

*Department of Chemistry, Department of Material Science, and Material Science Center, National Tsinghua University, Hsinchu, Taiwan 30043, Republic of China, and Department of Science Education, Hsinchu Normal College, Hsinchu, Taiwan 30043, Republic of China*

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Effects of calcination treatment on samples of mono-metallic Pd and $Pd_{77}$-$Ag_{23}$ alloy with primary particles around 8 nm were studied with the temperature-programmed reduction technique. Temperature profiles of hydrogen consumption for calcined samples from a stream of 10% $H_2$ in $N_2$ were monitored by a thermal conductivity detector. Two distinct peaks, i.e., a consumption of hydrogen for PdO reduction and a subsequent desorption of hydrogen from bulk palladium hydride, were observed. The extent of palladium oxidation upon calcinations increased with the temperature of calcination ($T_o$): i.e., chemisorption of oxygen on particle surface upon calcination at $T_o < 373$ K, reconstruction into a surface PdO structure at 473 K and incorporation into sublayers to form bulk PdO structure at high $T_o$. Minimum temperature ($T_r$) required for reduction of oxidized palladium by the hydrogen stream was generally low ($150 \text{ K} < T_r < 320$ K) and increased with the extent of oxidation. A quantitative measurement of hydrogen desorbed from reduced samples suggested a formation of alloy phase in freshly prepared $Ag_{77}$−$Pd_{23}$ primary particles. The freshly prepared alloy was inhomogeneous in composition but became homogeneous upon calcination at $T_o > 673$ K.

## Introduction

Palladium metal permeates the hydrogen gas selectively.[1] In laboratories, hydrogen gas of ultrahigh purity is achieved by permeating low graded gas through palladium thimbles. Nevertheless, palladium membranes with high mechanical strengths are still sought by engineers to purify hydrogen in industrial scale for feedstock in petro-chemical processes.[2,3]

Currently, the preparative technology of palladium-coated stainless steel tubes[4] and other porous hollow supports[5] for purification of hydrogen in industrial quantity, is actively pursued. One of the palladium coating methods is to press palladium crystallites onto porous stainless steel substrate. A stainless steel plate pressed with crystallites of nano-palladium has recently been demonstrated to exhibit not only an excellent selectivity toward hydrogen permeation (99.99% relative to nitrogen), but also a decent stability against repeated treatments of hydrogen absorption.

An alloying of 23% silver to palladium may improve its diffusibility of hydrogen and its handicap of hydrogen embrittlement. Hence, a substitution of Pd nano-crystallites with Pd−Ag crystallites to coat the stainless steel tubing may be of an additional advantage. Nano-crystallites of Pd−Ag alloy for such a use have been successfully prepared with a wet-reduction technique.[6,7] TEM examination indicated that the prepared samples are aggregates formed from primary particles with a diameter of $d \sim 8$ nm.[6] An extensive characterization of this prepared nano-alloy becomes pertinent for further application.

A convenient technique for characterizing chemical environment of metal atoms in solid samples is the temperature-programmed reduction (TPR). This technique is especially talented toward probing oxidation states of noble metals. Samples of platinum dispersed on different porous supports have been recently studied.[8−10] Reductive phenomena of platinum depend heavily on the extent of sample oxidation and the property of support. From variations in the reduction temperature ($T_r$) and the amount of hydrogen consumption noticed in TPR traces, three stages of oxidation, i.e., the chemisorption, surface structures of PtO and $PtO_2$, have been successfully distinguished on increasing the oxidation temperature. The interest of this study is to study the effect of calcination on prepared Pd nano-metal and Pd−Ag nano-alloy with the TPR technique developed in our laboratory.

## Experimental Section

**Sample Preparations.** Powdered $Ag_2O$ was prepared by dehydration, at room temperature through evacuation of AgOH precipitated out from aqueous $AgNO_3$ by alkalizing with NaOH. A similar procedure was used to prepare PdO powders from $Pd(NO_3)_2$. Prepared oxides were used as standard samples for TPR characterization.

Nano-crystallites of mono-metallic Pd and bi-metallic $Pd_{77}$−$Ag_{23}$ were prepared with a wet reduction method described in the literature.[5] Briefly; research grade $Pd(NO_3)_2$ and $AgNO_3$ were dissolved in distilled water and mixed with excessive formaldehyde. Metal particles in the nanometer size were then precipitated by adding the mixed solution with a 3 M aqueous solution of NaOH until the solution became transparent. Obtained precipitates were sequentially washed with distilled water and acetone, and dried in a vacuum at the ambient temperature. Evacuated samples were stored in capped bottles as fresh samples. According to TEM characterization, the fresh samples are aggregates (∼100 nm in size) of primary particles

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* To whom correspondence should be addressed. Fax: 886-3-5711082. E-mail: ctyeh@mx.nthu.edu.tw.

[†] Department of Chemistry, National Tsinghua University.

[‡] Department of Material Science, National Tsinghua University.

[⊥] Material Science Center, National Tsinghua University.

[§] Department of Science Education, Hsinchu Normal College.

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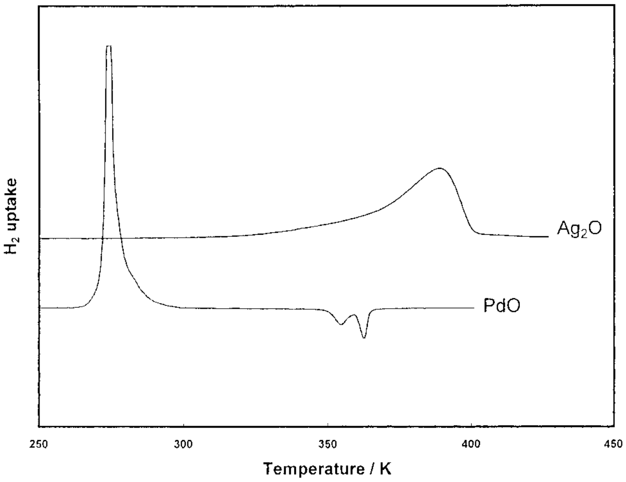

**Figure 1.** TPR traces for $Ag_2O$ and PdO prepared by calcination of hydroxide precipitates from alkalizing $AgNO_3$ and $Pd(NO_3)_2$ with NaOH.

which are spherical in shape and exhibit a homogeneous diameter of $d \sim 8$ nm.[6,7]

Prepared $Pd_{77}Ag_{23}$ bimetallic crystallites have been characterized with XRD. A single (111) peak around $2\theta = 40.0°$ was noticed from the diffraction spectrum. The peak position indicates an alloy phase was formed in the sample. The half-width ($B_{1/2} = 1.8°$) of peak confirms the nanosize nature (d ~ 8 nm) of primary particles found in TEM[7] for the freshly prepared sample. The peak retained at the same diffraction position, but its width was narrowed after the bimetallic sample was severely heated. The primary particles should have gradually sintered to large sizes upon the heating at $T_o > 673$ K.

**TPR Characterizations.** Each metallic sample was separated into several portions (~10 mg) and calcined for 1 h at different $T_o$ temperature in air. The effect of calcination on the sample was studied by TPR using a subambient-temperature routine (SATR). The SATR routine is a specially designed experimental procedure that we use in our laboratory to investigate reduction phenomena possibly occurring at subambient temperatures. This routine has been satisfactorily used to find the minimum temperature ($T_r$) required for reduction of oxygen species adsorbed on noble-metal crystallites of gold ($T_r \sim 200$ K),[11] rhodium (245 K),[12] and platinum (around 250 K)[8−10] dispersed on different substrates.

In the SATR routine, oxidized samples were inserted into a U-shape tubing of quartz and pre-cooled to 183 K in a nitrogen stream. At this temperature, the nitrogen stream was replaced with a flow of 10% hydrogen in nitrogen for TPR measurement. The thermal conductivity of the flow at downstream of the sample was subsequently monitored by a TCD (thermal conductivity detector). After 5 min of the baseline stabilization, the sample temperature was linearly raised from 183 to 500 K at a rate of 10 K min$^{-1}$. A positive peak generally indicates a consumption of hydrogen (a decrease in the thermal conductivity) by the sample, while a negative peak (an increase in the thermal conductivity) indicates a desorption of hydrogen from the sample.

## Results and Discussion

**Reduction of $Ag_2O$ and PdO.** Figure 1 depicts a series of TPR results obtained from the SATR routine on the prepared blank samples of $Ag_2O$ and PdO. Sample $Ag_2O$ exhibited a single hydrogen-consumption peak at 380 K. This peak may be assigned to a reaction of

$$H_2 + Ag_2O \rightarrow 2Ag + H_2O \qquad (1)$$

**TABLE 1: A Correlation between the $T_r$[a] Required for Complete Reduction of Metal Oxides with the $E^{o}$ [b] of Corresponding Metal Ions**

| | oxides | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $Au_2O$ | PtO | PdO | $Rh_2O_3$ | $Ag_2O$ | CuO | NiO | CoO |
| $T_r$/K | 200[11] | 250[10] | 280 | 380[12] | 380 | 500[16] | 600[17] | 650[18] |
| $E^o$/V | 1.50 | 1.20 | 0.99 | 0.80 | 0.80 | 0.34 | 0.23 | 0.28 |

[a] Minimum temperature. [b] Standard reductive potential.

Two peaks were noticed in TPR trace of PdO, i.e., a hydrogen-uptake peak at $T = 280$ K and a hydrogen-desorption peak at 360 K. The uptake peak may have resulted from a consumption of hydrogen on reduction of oxidized palladium:[13]

$$H_2 + PdO \rightarrow Pd + H_2O \qquad (2)$$

The palladium crystallites, thus reduced, may absorb hydrogen to form PdH (α or β) phase in hydrogen environments. The α-PdH phase contains less hydrogen (adsorbed only on the surface of crystallites) than the β-PdH phase (with hydrogen atoms absorbed into the bulk of palladium). Both phases are in fcc structure but with different lattice parameters (0.39 and 0.40 nm, respectively). The dominant phase of PdH depends on the pressure of hydrogen ($P_H$) and the system temperature.

According to the phase diagram of the Pd−$H_2$ system,[1] palladium crystallites tend to absorb hydrogen to form β-PdH at low temperatures under $P_{H_2} = 1.0 \times 10^4$ Pa (the partial pressure of hydrogen in $H_2$−$N_2$ flow of TPR system), i.e.,

$$yH_2 + 2Pd^b \Longleftrightarrow Pd^bH_y \qquad (3)$$

In reaction 3, superscript b denotes palladium atoms in the bulk of palladium crystallites reduced from reaction 2, and subscript $y$ is a temperature-dependent stoichiometry ($y \sim 0.51$ at T = 360 K).[1] On raising the temperature over 360 K, β-PdH in the flow of $H_2$−$N_2$ tends to desorb the hydrogen absorbed, and shift spontaneously to the α-phase (through the reversed reaction 3). The hydrogen-desorption peaks noticed in the TPR traces of PdO in Figure 1 are therefore attributed to the β-to-α phase transition.

Transition metals of groups VIII and IB in the periodic table are generally catalytically active toward hydrogenation reactions. Reduction of salts into metallic state with hydrogen is an essential step for activation of these metallic catalysts. However, the temperature selected for the reduction was regarded as an art in the preparation. A reduction at high temperatures generally causes sintering and therefore a loss in activity to the prepared crystallites. On the contrary, a reduction at low temperatures may be insufficient for the activation. A minimum temperature ($T_r$) required for a complete reduction varies with the inherent activity of the metal.

TPR is a talent method to characterize the $T_r$ of different metallic salts. Figure 1 indicates that $Ag_2O$ and PdO may be completely reduced at $T_r = 380$ and 280 K, respectively. In our laboratory the $T_r$s have been pursued for many oxides of transition metal. Table 1 lists $T_r$s accumulated thus far in our laboratory for reduction of several metal oxides prepared from dehydration of metal hydroxides. Following trend of increasing $T_r$ is noticed:

$$Au_2O < PtO < PdO < RhO, Ag_2O < CuO < NiO < CoO$$

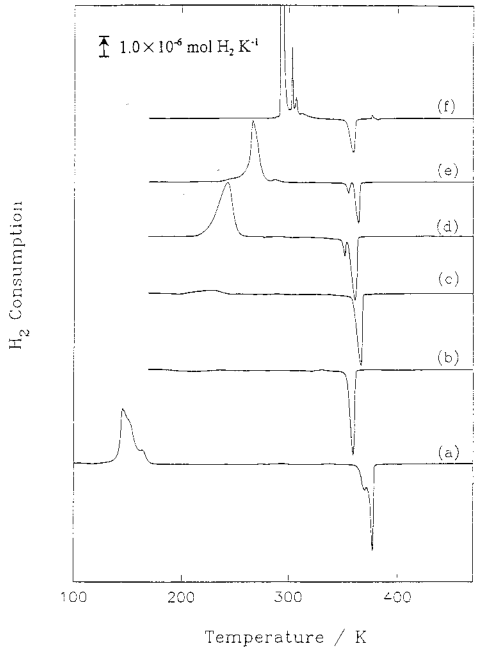

**Figure 2.** Variation of TPR traces (from SATR routine) of palladium nano-crystallites precalcined for 1 h at different $T_o$s: (a) 298 K (especially with ULTR routine); (b) 373 K; (c) 473 K; (d) 573 K; (e) 673 K; (f) 773 K. The vertical scale of traces e and f has been decreased to a factor of 1/2.

Noteworthy, this sequence agrees well with the standard reductive potential, $E°$, for their corresponding cations in aqueous solution,[13] i.e.,

$$M^{n+} + n\,e^{-} \rightarrow M \qquad (4)$$

Evidently, the $T_r$ required for reduction of these metal oxides increases with the potential $E°$ of the corresponding cations according to a linear equation of:

$$T_r/K = 600 - 280V \qquad (I)$$

**Calcination of Mono-metallic Palladium.** Figure 2 depicts a series of TPR results obtained from the SATR routine on a fresh sample of mono-metallic palladium preoxidized at increasing $T_o$. Two major peaks i.e., a hydrogen-uptake peak at $T \leq 300$ K and a hydrogen-desorption peak around 360 K, were noticed from these traces. According to a former assignment in Figure 1, the uptake peak came from a combination of reactions 2 and 3 and the desorption peak was resulted from the reverse of reaction 3.

Column 3 of Table 2 summarizes amounts of the desorbed hydrogen ($N_{H,d}$) found in TPR experiments from the nano-palladium sample preoxidized at increasing $T_o$. Calculated $N_{H,d}/N_{Pd}$ ratio stays very close to a value of 0.47 for samples calcined at $T_o < 573$ K. This ratio is slightly smaller than a ratio of 0.51 reported[1] for $\beta$-PdH at temperature 360 K. The difference between these two ratios may be attributed to the particle size of palladium sample. Our nano-palladium crystallites have a diameter $\phi \sim 8$ nm. A substantial fraction (11%) of palladium atoms was exposed to the surface of the nano-palladium. These atoms tended to chemisorb hydrogen atoms:

$$H_2 + 2Pd^{s} \rightarrow 2Pd^{s}H^{c} \qquad (5)$$

where $Pd^s$ and $H^c$ denote palladium atoms exposed to the surface of crystallites and hydrogen adsorbed on $Pd^s$, respectively. The adsorbed hydrogen has a higher bonding enthalpy ($\Delta H_{ad} \sim 60$ kJ mol$^{-1}$) than the absorbed hydrogen ($\Delta H_{ab} \sim 38$ kJ mol$^{-1}$).[14] Accordingly, the adsorbed hydrogen remained on the sample surface as the temperature of the TPR experiment was raised to 360 K.[15]

**TABLE 2: A Summary for TPR Results from the Mono-metallic Nano-palladium[a] Oxidized at Different Oxidation Temperatures ($T_o$)**

| $T_o$/K | $T_d$/K | $N_{H,d}/N_{Pd}$ | $T_r$/K | $N_{H,r}/N_{Pd}$ |
|---|---|---|---|---|
| 300 | 358 | 0.47 | 150[b] | 0.07[b] |
| 373 | 358 | 0.47 | nd[c] | nd[c] |
| 473 | 368 | 0.47 | 228 | 0.10 |
| 573 | 363 | 0.45 | 238 | 0.96 |
| 673 | 363 | 0.51 | 263 | 1.40 |
| 773 | 353 | 0.49 | 293 | 1.45 |

[a] $D = 11\%$. [b] Data from the sample precalcined at 300 K were observed from ULTR routine. Those from the sample precalcined at high temperatures were obtained from the normal SATR routine. [c] Not detected.

The amount of hydrogen desorbed ($N_{H,d}$) in the reverse of reaction 3 should therefore vary with the dispersion of palladium according to formula II,

$$N_{H,d} = 0.51(1 - D)N_{Pd} \qquad (II)$$

The third column of Table 2 indicates that calculated ratios of $N_{H,d}/N_{Pd}$ were ~0.47 in TPR traces of $T_o < 600$ K. The calculated ratio is in fair agreement to a value of 0.46 estimated from formula I (for $D_{Pd} = 0.11$).

The obtained $N_{H,d}/N_{Pd}$ ratio, however, increased slightly from 0.47 to 0.50 on increasing the $T_o$ of the oxidation treatment over 600 K. This increase in ratio may have resulted from sintering of primary particles of palladium during high-temperature oxidations. It is noteworthy that palladium metal has a melting point of $T_m = 1825$ K which indicates a Huttig temperature ($T_m/3$, a temperature over which surface atoms of solid become mobile) ~600 K.

Both the $T_r$ (column 4 in Table 2) required for a reduction of oxidized palladium and the amount of the hydrogen consumption ($N_{H,r}$ in the last column in Table 2) during the reduction are found in Figure 2 to increase with the oxidation temperature ($T_o$). This trend agrees well with our previous results on an oxidation of platinum dispersed on alumina.[8] Observed oxidation of the dispersed platinum was limited at the surface layer of platinum crystallite but led to different oxidized species. Oxygen atoms were chemisorbed (to a stoichiometry of $Pt^sO^c$) on the surface of dispersed platinum at a mild oxidation at $T_o = 300$ K. Upon a severe oxidation at $T_o > 373$ K, a surface structure of $Pt^sO$ was formed through a surface reconstruction. The temperature required for a reduction of oxygen in the chemisorbed $Pt^sO^c$ and in the $Pt^sO$ structure was found at $T_r = 300$ and 325 K, respectively. Conceivably, the temperature required for a reduction of oxidized palladium (reaction 1) should also vary with the extent of oxidation.

The last column of Table 2 lists the hydrogen consumption ($N_{H,\,r}$) in the reduction of nano-palladium oxidized at different $T_o$. Obviously, the oxidation was limited at the surface of nano-palladium upon $T_o < 473$ K but gradually extended into its bulk at high $T_o$ temperatures. However, the maximum $N_{H,r}/N_{Pd}$ ratio (1.45) found at $T_o = 773$ K is still smaller than a theoretically stoichiometric ratio of 2.0 for a complete conversion to PdO. Probably, a sintering of nano-palladium occurred during severe calcination and the expected penetration of oxygen into the inner core of sintered palladium might be kinetically hindered.

Oxygen atoms should have chemisorbed on the surface of the nano-palladium on the oxidation treatment at $T_o = 373$ K:

$$2Pd^s + xO_2 \rightarrow 2Pd^sO^c \qquad (6)$$

The $O^c$ in this equation denotes chemisorbed oxygen atoms. To our surprise, no reduction peak was found from the 373 K trace of Figure 2. There is scarce information available in the literature reporting on the $T_r$ required for a reduction of oxygen atoms chemisorbed on unsupported palladium by hydrogen, i.e.,

$$^3/_2H_2 + Pd^sO^c{}_x \rightarrow Pd^sH^c + xH_2O \qquad (7)$$

Speculatively, $O^c$ atoms might have been reduced by the $H_2-N_2$ flow at 183 K during stabilization the TCD baseline before raising the sample temperature for the TPR monitoring.

Accordingly, the $T_r$ of oxygen chemisorbed on the surface of nano-palladium was pursued on purpose in this study with a specially designed ultralow-temperature routing (ULTR). In this routine, a sample of palladium chemisorbed with oxygen (pretreated by a TPR reduction to 500 K and a subsequent oxidation in air at room temperature) was intentionally cooled to 110 K in a nitrogen stream before switching to the $H_2-N_2$ flow for the TPR measurement. The TPR trace (with $T_o = 298$ K in Figure 2) agreed well with our expectation. Besides the peak of hydrogen desorption at 360 K, a hydrogen consumption peak was indeed noticed at 150 K. The amount of hydrogen consumed in the reduction peak is slightly larger than that desorbed in the peak at 360 K (by an amount of $0.07N_{Pd}$). Apparently, the 150 K peak should be contributed to a combination of reactions 7 and 3. The amount of hydrogen consumed in reaction 7 was therefore $0.07N_{Pd}$.

The fourth column of Table 2 lists variation of $T_r$ with $T_o$ of oxidation treatment. Observed $T_r$ generally increased with the extent of oxidation, i.e., $T_r$ remained less than 230 K for oxygen chemisorbed on palladium surface and gradually increased to 290 K for oxygen in PdO structure. Conceivably, PdO reduction with hydrogen is a thermodynamically favored reaction ($\Delta G° \sim -28$ kJ mol$^{-1}$). The rate of reduction depends on the structure of PdO produced in calcination treatment. Oxygen chemisorbed on a palladium surface at mild calcination is thermodynamically possible and kinetically easy. However, an energy barrier for reconstruction of crystallite becomes necessary to reduce oxygen ions in the rigid PdO lattice formed at severe calcinations.

Figure 3 schematically illustrates the physical change of nano-palladium on increasing $T_o$ of calcination treatment. The aggregated nano-palladium (represented by big circles) chemisorbed oxygen atoms (small dots) on surface at light calcination at $T_o < 373$ K. Upon raising the $T_o$ over 473 K, a layer of PdO was formed. The thickness of the layer gradually increased with $T_o$ and a sintering of PdO became evident when $T_o$ was raised over 873 K.

**Calcination of Pd−Ag Bi-metallic Crystallites.** Figure 4 presents a series of TPR traces obtained from a $Pd_{77}Ag_{23}$ (in atomic ratio) sample preoxidized at different $T_o$s. Similar to TPR results from the sample of nano-palladium (Figure 2), each trace in Figure 4 also exhibits a reduction peak (at low temperature) as well as a hydrogen-desorption peak (at $T_d > 380$ K). However, the expected reduction peak was absent in trace a of this figure for the sample calcined at $T_o = 373$ K. The absence may, similar to the case of monometallic palladium, be attributed also to a low $T_r$ (<183 K) for this sample. The chemisorbed oxygen should have been reduced at 183 K, during stabilizing the baseline of trace a, by the $H_2-N_2$ flow before raising the system temperature.

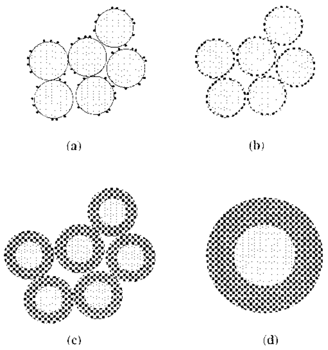

**Figure 3.** Schematic diagram for consecutive changes of 8 nm palladium during calcination in air on raising the temperature: (a) $T_o < 373$ K, adsorption of oxygen on surface; (b) $T_o = 473$ K, formation of a surface layer of PdO; (c) $T_o = 573$ K, incorporation of oxygen into sublayers; and (d) $T_o > 673$ K, sintering of the primary particles.

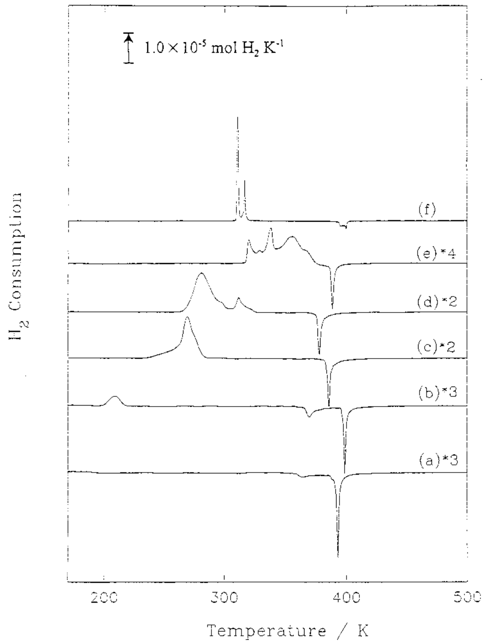

**Figure 4.** Variation of TPR traces from samples of nano-$Pd_{77}Ag_{23}$ precalcined for 1 h at different $T_o$s: (a) 373 K; (b) 473 K; (c) 573 K; (d) 673 K; (e) 773 K; and (f) 873 K.

Since reduced Pd−Ag alloys also have the ability of absorbing hydrogen into bulk, the hydrogen-desorption peaks in traces of Figure 4 should come from the $\beta$-to-$\alpha$ phase transition of bimetallic crystallites. However, a bimetallic alloy of Pd with Ag slightly raised the transition temperature to $T_d = 380$ K instead of 360 K noticed in Figure 2 for mono-metallic Pd. A slight shift of equilibrium of reaction 3 toward right by alloy palladium with silver is indicated.

A ratio of $N_{H,d}/N_{Pd} = 0.31$ was noticed in the third column in Table 3 for the fresh sample. This ratio is significantly smaller than the 0.51 of the nano-palladium. The difference may be attributed to a decrease in the amount of hydrogen absorbed into bulk palladium by alloying with silver. A ratio of $N_{H,d}/N_{Pd} = 0.25$ has been reported for bulk $Pd_{74}Ag_{26}$ alloy at a transition temperature of 300 K.[1] This ratio is smaller than the 0.31 observed in the present study for $Pd_{77}Ag_{23}$. The discrepancy suggests that the composition in the alloy of freshly prepared $Pd_{77}Ag_{23}$ was inhomogeneous.

The $N_{H,d}/N_{Pd}$ ratio of the bimetallic sample was decreased from 0.31 to 0.20 after a calcination at $T_o > 673$ K. Obviously, the composition of bimetallic sample became homogenized due to an inter-diffusion of constituent components upon severe

**TABLE 3: A Summary for TPR Results from Pd−Ag Bimetallic Crystallites[a] Preoxidized at Different Oxidation Temperatures ($T_o$)**

| $T_o$/K | $T_d$/K | $N_{H,d}/N_{Pd}$ | $T_r$/K | $N_{H,r}/N_{Pd}$ |
|---|---|---|---|---|
| 373 | 400 | 0.31 | nd[b] | nd[b] |
| 473 | 393 | 0.26 | 210 | 0.12 |
| 573 | 390 | 0.31 | 273 | 1.08 |
| 673 | 380 | 0.31 | 280 | 1.47 |
| 773 | 390 | 0.20 | >310 | 2.96 |
| 873 | 400 | 0.18 | 300 | 2.85 |

[a] $D_{Pd}$ = 11%. [b] Not detected.

oxidation treatments. However, silver was slightly segregated toward the external surface of the crystallites during the diffusion because XPS study indicated that the surface of calcined sample was enriched with Ag (40%).[7] Observed segregation probably reflected the difference in the surface energy between Ag and Pd (0.39 and 1.50 J m$^{-2}$, respectively).

The extent of oxidation on these bimetallic crystallites also increased with the calcination temperature. The oxidation was limited to surface (chemisorption) for $T_o < 373$ K but extended to sublayers at high temperatures. At $T_o > 773$ K, a hydrogen consumption ratio of $N_{H,r}/N_{Pd} = 2.7$ was reached for reaction 1. This ratio suggested not only that silver atoms in the alloy had oxidized to $Ag_2O$, but also that the oxidation had extended to the center of crystallites.

Similar to the reduction of calcined nano-palladium (Figure 2), the $T_r$ found in Figure 4 for a complete reduction of Ag−Pd nano-alloy increased with calcination temperature. A comparison of $T_r$s found in Tables 2 and 3 indicates that an alloy of silver to palladium does not significantly alter the $T_r$ of oxidized palladium. The absence of a 400 K peak, assigned to a reduction of $Ag_2O$ (reaction 1), suggests that hydrogen was effectively spiltover from reduced palladium to $Ag_2O$ during the reduction of PdO in bimetallic sample.

## Conclusions

Effects of calcination on nanocrystallite samples of monometallic palladium and bimetallic Pd−Ag have been carefully studied with TPR technique. Two peaks, a hydrogen-consumption at low temperature and a hydrogen-desorption at high temperature, were observed from obtained TPR traces. The following features can been concluded from variations in the area and temperature of these two peaks:

1. The extent of oxidation on both samples increases with the calcination temperature, i.e., adsorption of oxygen on the surface of primary particles at $T_o < 373$ K, formation of surface oxide at 473 K, and incorporation of oxygen into sublayers at $T_o > 573$ K.
2. The temperature required for a reduction of oxidized palladium by hydrogen is generally low. $T_r = 150$ K for oxygen chemisorbed on nano-palladium but raised over 260 K for oxide anions in the PdO structure.
3. Primary particles of nano-palladium retain their size of 8 nm upon calcination at $T_o < 673$ K but dramatically sinter under severe calcination at high temperatures.
4. Pd−Ag bimetallic crystallites freshly prepared are inhomogeneous in composition. However, the composition gradually homogenized because of inter-diffusion upon calcination at $T_o > 673$ K.
5. Incorporation of oxygen into sublayers of palladium crystallites is promoted by alloy with silver.

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