

Effect of Oxidation–Reduction Cycling on C₂H₆ Hydrogenolysis: Comparison of Ru, Rh, Ir, Ni, Pt, and Pd on SiO₂¹

S. GAO AND L. D. SCHMIDT

Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455

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Activities of C₂H₆ hydrogenolysis on 5% Ru, Rh, Ni, Ir, Pt and Pd supported on SiO₂ are compared as functions of oxidation and reduction treatments. It is shown that activities after oxidation and low-temperature reduction vary by a factor of ~10⁶ between metals in the order Ru > Rh > Ir ~ Ni > Pt > Pd. Annealing at high temperatures causes all rates to decrease, with the largest changes (~10³) on Ru and Rh and smaller changes (3 to 30) on other metals. Most rates do not change significantly with reaction time, but Ir rapidly deactivates due to carbon formation. These results correlate with the ability of each metal to retain the high-activity, low-coordination sites produced by oxidation and low-temperature reduction and, for Pt, the inability to form the oxide. Thus, Ni and Pd exhibit small changes because the metal surfaces anneal by 200°C, and the more refractory Ru, Rh, and Ir can be retained in the high-activity state during hydrogenolysis. © 1989 Academic Press, Inc.

INTRODUCTION

It is well known that supported metal catalysts can exhibit drastically different performances depending on conditions of preparation and treatment (1–17). Alkane hydrogenolysis has been well documented to exhibit large variations, beginning with the classic work of Sinfelt *et al.* (3–5) who found a large dependence of activity of Rh on Al₂O₃ on loading. More recent investigations have focused on effects of pretreatment (11, 12, 18), and several studies using different metals and supports have demonstrated that treatment of a given catalyst in O₂ followed by low-temperature reduction generally produces a higher activity than that after high-temperature annealing in H₂.

We have recently examined the effects of O₂ and H₂ treatment on C₂H₆, C₃H₈, and C₄H₁₀ hydrogenolysis activities on Rh supported on SiO₂ (19–21). We observed variations of up to a factor of 10⁴ and find that

these are reversible in that low- and high-activity states on a given catalyst can be obtained repeatedly. We also showed that the selectivity of C₄H₁₀ hydrogenolysis was affected by treatment with the low-activity state producing less CH₄ and more C₃H₈.

We also showed (19) by TEM that annealing produces ~200 Å polyhedra exposing predominantly low-index planes while oxidation followed by low-temperature annealing produces clusters of 10- to 20-Å particles which only sinter into polyhedra upon heating above 500°C. XPS showed that particles are totally reduced in H₂ at low temperatures, while H₂ chemisorption showed that total surface areas were not altered significantly by these treatments.

We interpreted these results as arising from creation of metastable, high-activity, low-coordination sites by oxidation and low-temperature reduction. The ability to create such sites obviously depends on their formation by oxidation and low-temperature reduction and the ability to avoid sintering which will cause the surface to revert back to its original low-activity state.

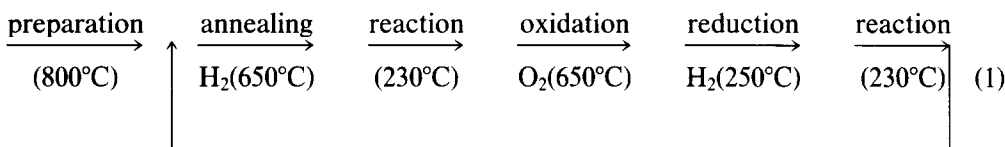
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EXPERIMENTAL

All samples were prepared by impregnation of aqueous metal chlorides on Cab-O-Sil SiO₂ to form 5 wt% catalysts. Samples were then dried in air and calcined in air at 800°C for 4 hr to form low-dispersion particles. This treatment also assured that subsequent treatments at lower temperatures would not produce extensive sintering.

21), rates were measured in a flow reactor using 3 mol% of C₂H₆ and 21 mole% of H₂ in He at atmospheric pressure. High-purity H₂ was further purified by passing through a liquid nitrogen trap to remove traces of H₂O which were previously found to significantly increase the activity of the annealed state.

All samples were subjected to the same temperature and gas treatments



As described in detail previously (20, All treatments were for 4 hr in pure flowing H₂ or air at temperatures indicated. Samples were allowed to cool to the next temperature in each gas before switching to other treatments or reaction. We shall refer to the situation after treatment in H₂ at 650°C as "annealed" and that after oxidation and low-temperature treatment in H₂ as "oxidized." However, we have shown previously using XPS (19, 22, 23) that Rh, Ni, Pd, and Ir particle surfaces are totally oxidized by heating in O₂ at 500°C (TEM shows that no unreduced metal cores remain in ~200 Å particles), and particles are totally reduced to their zero-valent states upon subsequent heating in H₂ at 250°C (no oxide diffraction lines remain).

Hydrogen chemisorption was measured by the flow desorption method. In the standard procedure, the oxidized sample was first reduced in flowing hydrogen at 250°C for 4 hr, and the annealed sample was heated in flowing nitrogen at 650°C for 2 hr to desorb hydrogen and then exposed to hydrogen at 250°C for 4 hr. Then it was cooled in hydrogen and kept at 0°C for 20 min, and flow was switched to nitrogen for 30 min to purge remaining gaseous hydrogen. The reactor was then heated to 650°C to flash de-

sorbed hydrogen into the gas chromatograph (GC) where the amount of hydrogen desorbed was determined. We also measured the amount of hydrogen uptake directly after annealing the sample at 650°C in hydrogen as indicated in the tables.

For TEM of Ru, substrates were prepared as described in detail previously (19, 23). A thick layer of Si was vacuum deposited on a gold microscopy grid, which was then heated in air to form SiO₂. An aqueous solution of RuCl₃ was then deposited on the SiO₂-covered grid at a concentration calculated to yield the desired metal loading and particle size. Samples were treated in a furnace in flowing H₂ or O₂ for 4 hr and the same region was examined repeatedly after the gas and heat treatment indicated to observe the microstructure evolution of a single set of particles.

RESULTS

Hydrogenolysis Rates

Figure 1 shows rates of ethane hydrogenolysis on the six metals on SiO₂, all for 5% loading. It is seen that the rates vary by a factor of 10⁶ from the most active (oxidized Ru) to the least active (annealed Pd). Flow rates and sample sizes were adjusted as

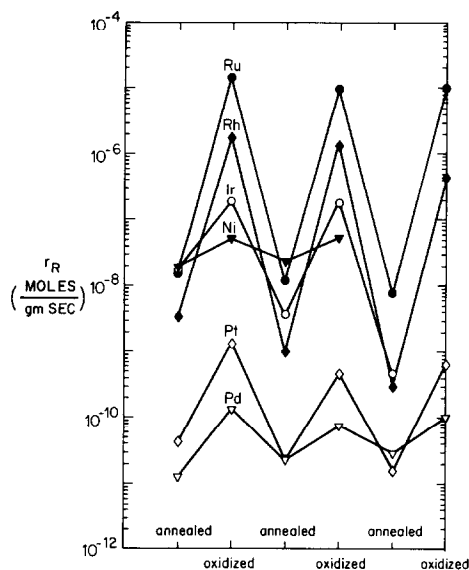


FIG. 1. Reaction rates of C_2H_6 hydrogenolysis at $230^\circ C$ in a 7:1 $C_2H_6:H_2$ mixture on the six metals at 5% loading on SiO_2 in oxidized and annealed states for treatments described in Eq. (1); rates are in units of moles of C_2H_6 converted per gram of catalyst per second. Each sequence shows three cycles of treatment of a single sample. Some irreversible sintering is evident, but changes caused by oxidation and annealing are nearly reversible.

necessary to maintain lower conversions for accurate GC analysis without significant reactant depletion. Rates shown are in moles of C_2H_6 converted per gram of catalyst per second.

It is seen that rates are generally reversible with treatment in that activities can be restored to within a factor of approximately 2 by repeated cycling, although all rates exhibit a generally monotonic decrease in both oxidized and annealed states. This is expected from irreversible sintering of particles (disappearance of small particles by coalescence with larger ones) caused by repeated high-temperature heat treatments.

The variations between oxidized and annealed states are factors of $\sim 10^3$ for Ru and Rh, a factor of ~ 10 for Ir, Pt, and Pd, and a factor of ~ 2 for Ni. Rates for Rh agree fairly well with those reported previously

(19) for comparable metal loading and heat treatment.

The rates in the annealed states were generally less reproducible than those in the oxidized states. As discussed previously (19–21), this arises from the effects of H_2O in H_2 during or after the annealing treatments and because the rates are fairly sensitive to treatment temperature. The variation in activity arises from partial oxidation of particles by reaction with water. The high activity rates should therefore be regarded as fairly accurate, while the annealed rates will depend more strongly on treatment conditions.

Figure 2 shows Arrhenius plots of rates versus temperature for five metals in oxidized states (solid lines) and annealed states (dashed lines). It is seen that all metals exhibit reasonably straight lines and the range of values in Table 1 indicates lowest and highest activation energies in three

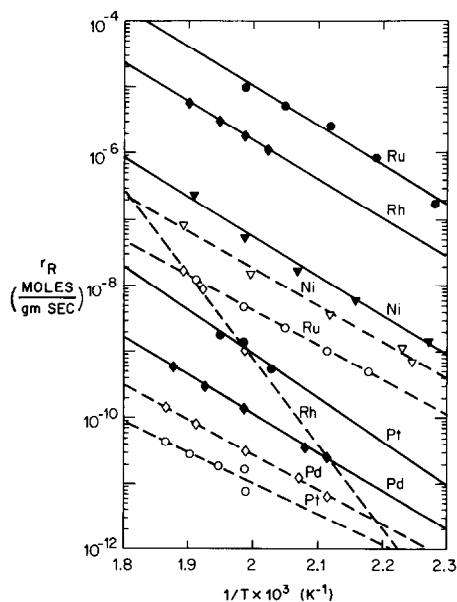


FIG. 2. Arrhenius plots of rates on all metals except Ir in oxidized states (solid lines) and in annealed states (dashed lines). Apparent activation energies are shown in Table 1. Arrhenius plots could not be obtained for Ir because of severe deactivation in both oxidized and annealed states.

TABLE 1
Ethane Hydrogenolysis Rates

Metal	H ₂ uptake at 250°C (μmole/g catalyst)		Average particle size (Å)	Rates at 230°C (μmole/g catalyst sec)		TOF at 230°C (1/sec)		E (kcal/mole)	
	Oxidized	Annealed		Oxidized	Annealed	Oxidized	Annealed	Oxidized	Annealed
Ru	8.6	6.6	320	1.1×10^{-5}	1.0×10^{-8}	1.28	1.5×10^{-3}	28 ± 1.5	24 ± 2.0
Rh	6.1	3.2	640	1.8×10^{-6}	1.1×10^{-9}	0.30	3.4×10^{-4}	27 ± 2.0	50 ± 3.0
Ni	4.8	3.5	940	5.5×10^{-8}	2.3×10^{-8}	1.1×10^{-2}	6.6×10^{-3}	28 ± 0.6	25 ± 0.5
Pt	3.9	4.9	230	8.0×10^{-10}	2.6×10^{-11}	2.1×10^{-4}	5.3×10^{-5}	28 ± 2.5	20.3
Pd	24	26	500 ^a	1.4×10^{-10}	3.4×10^{-11}	2.0×10^{-5a}	8.5×10^{-6a}	27 ± 3.0	26 ± 3.5
Ir	8.0	7.8	140	1.8×10^{-7} (7×10^{-10})	4.0×10^{-9} (4×10^{-10})	2.2×10^{-2} (8.7×10^{-5})	5.1×10^{-4} (5.1×10^{-5})		

^a Calculated from hydrogen uptake at 0°C.

to eight experiments for each metal. For Ir the rate change with time was too large to obtain an accurate Arrhenius plot. For other metals rates did not decrease by more than a factor of approximately 2 over a period of several hours, and no significant deactivation occurred during an Arrhenius plot determination.

Table 1 shows rates at 230°C (from Fig. 1) and activation energies (from Fig. 2) for oxidized and annealed states for each metal. It is seen that activation energies do not differ significantly between metals or between oxidized and annealed states. The exception is the annealed state of Rh which exhibits a much higher activation energy than any other system. We repeated the Rh activation energy measurement several times and on several different samples with good reproducibility. We have no explanation for the difference in the apparent activation energy of Rh compared to those of the other metals.

Hydrogen Chemisorption

Hydrogen chemisorption amounts measured on the six metals using the procedure described previously are shown in Table 1. These values are fairly similar on all metals, with Pd giving anomalously high values because of bulk solution. The average particle sizes, calculated from hydrogen chemisorption on the annealed surfaces assuming cubes with five planes exposed to the gas

phase and one hydrogen atom per surface metal atom, are also shown in Table 1. Turnover frequencies (TOF) are also shown in Table 1, obtained from the metal areas calculated for oxidized and annealed states.

Chemisorption amounts shown were generally reproducible to within ~20% for successive measurements, although very high or low values would occasionally be obtained. Chemisorption amounts were also very sensitive to temperature. Table 2 shows a comparison of hydrogen uptakes at 250 and 650°C on the annealed surfaces and at 250°C on the oxidized surfaces. It is seen that uptake at 650°C on the annealed surfaces is significantly higher than that at

TABLE 2
Hydrogen Uptake (μmole/g · cat.)

Metal	Annealed		Oxidized 250°C	Average particle size (Å) ^a
	250°C	650°C		
Ru	6.6	18	8.6	320
Rh	3.2	10	6.1	640
Ni	3.5	15.4	4.8	940
Pt	4.9	6.4	3.9	230
Pd	26	130	24	500 ^b
Ir	7.8	12	8.0	140

^a Calculated from uptake at 250°C on annealed catalyst.

^b Calculated from uptake at 0°C on annealed catalyst.

250°C on all metals, while on the oxidized surfaces at 250°C the uptake is only slightly higher than that on the annealed surfaces.

We conclude that hydrogen chemisorption indicates that metal surface areas on these samples are comparable ($\sim 6 \mu\text{mole/g} \cdot \text{catalyst}$) on all metals and that areas do not change by large factors (typically a factor of 2) by oxidation and low-temperature annealing. The variability with treatment suggests that caution should be used in attempting to interpret hydrogen chemisorption results more quantitatively, but these results confirm our contention that metal surface areas are roughly comparable and that areas are not altered significantly (much less than a factor of 10) by oxygen and hydrogen treatments.

Deactivation

On most metals the rates were essentially independent of time. For Rh, the most extensively examined system, the rate decreased by only a factor of 2 while the catalyst was maintained under reaction conditions over a period of many hours. For all of the other metals except Ir, rates shown in figures and tables were stable for periods of many minutes, and no long-term deactivation processes were evident. The deactivation process appeared to be faster at higher temperatures, but the steady-state rate attained appeared to be independent of the reaction treatment temperature.

Ir exhibited considerable deactivation in hydrogenolysis activity. The rate decreased by a factor of approximately 10 in the first few minutes and then decreased by another factor of approximately 5 over several hours. Similar deactivation processes occurred in oxidized and annealed states. Rates shown for Ir in Fig. 1 and Table 1 are the initial rates, and steady-state rates would be at least a factor of 10 less than these values.

We attribute these deactivation processes to carbon buildup on the Ir surface. Hydrogen titration of surface carbon to form methane indicated a progressive

buildup of carbon which appeared to cease as the rate attained a steady value. Iridium is a very active catalyst for cracking alkanes, and it evidently dehydrogenates these fragments efficiently to form inactive carbon. All rates were measured at a hydrogen-to-ethane ratio of 7 to 1, and no attempt was made to determine the dependence of the rate or deactivation on reactant composition. For most metals the hydrogen pressure was evidently high enough to prevent formation of multilayers of carbon, but a higher hydrogen ratio would presumably be necessary to prevent carbon buildup on Ir.

Ruthenium Particle Microstructures

For all metals except Ru, we have previously shown (19, 22–24) using TEM that particles form polyhedra upon annealing in H_2 at 650°C and that all but Pt forms smaller clusters of metal particles by treating in O_2 and then reducing in H_2 at low temperatures. Figure 3 shows TEM micrographs of Ru on a SiO_2 substrate for treatment conditions indicated. The region shown is near the edge of a curved SiO_2 region which is curved so that the shapes of metal particles perpendicular to the substrate can be observed. There is no evidence of oxidation after heating to 300°C, by 500°C a thin layer ($\sim 40 \text{ \AA}$ thick) is evident, and after heating to 650°C all particles are totally oxidized. Electron diffraction confirmed the formation of Ru_2O_3 and the disappearance of Ru metal by this temperature.

Figure 3e shows that low-temperature reduction of the oxidized particles (Fig. 3d) causes the breakup of the oxide into clusters of 10- to 30- \AA particles, and electron diffraction confirms the presence of only metallic hcp Ru. Only after heating to above 600°C do particles sinter into the large particles shown in Fig. 3a. Thus, Ru on SiO_2 behaves essentially identically to Rh and Ir which were examined previously (19, 23). In a later paper we will compare the shapes of Rh and Ir by examining the particles on the edge of SiO_2 and Al_2O_3 similar to the micrographs of Fig. 3.

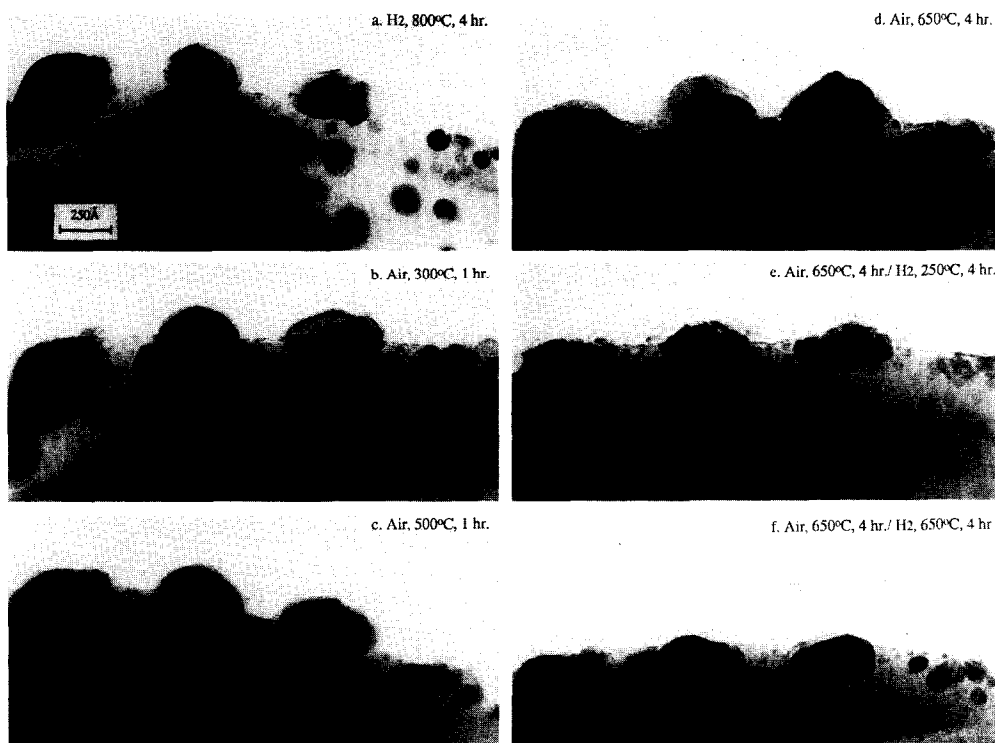


FIG. 3. Transmission electron micrographs of Ru particles near the edge of a curved region SiO₂ showing the evolution of microstructure with oxidation and subsequent treatment in H₂. Micrograph (a) is after annealing in H₂ at 800°C, while (b), (c), and (d) are after heating in air at 300, 500, and 650°C, respectively. Subsequent heating in H₂ at 250°C (micrograph (e)) produces a breakup into smaller clusters which are annealed only after heating to 650°C (micrograph (f)).

DISCUSSION

For all six metals examined, the hydrogenolysis rates can be altered significantly by oxidation and reduction treatments.

Several possible explanations are possible to account for these variations. Among them are the following:

(i) variations in fractions of particular crystal planes produced by these treatments,

(ii) variations in metal surface area,

(iii) different metal-support interactions,

(iv) different levels of contamination produced by exposures to particular gases and temperature, and

(v) partially oxidized metals remaining after oxidation and low-temperature reduction.

Surface area changes are far too small to account for the observed activity changes, and H₂ chemisorption area changes are consistent with metal surface area changes inferred from TEM. Strong metal-support interactions with SiO₂ have not been reported, and it would be surprising that all metals would behave so similarly with SMSI. Also, particles are so large (200 to 1000 Å in diameter) that chemical interactions with the SiO₂ seem unlikely. Crystallites are 10 to 50 Å diameter in the freshly oxidized states, and there could be some type of electronic size effect occurring. However, these particles are still large compared to atomic dimensions, and such effects appear unlikely to cause the observed order-of-magnitude variations.

We have been very concerned that con-

tamination may occur during high-temperature gas and heat treatments. We purified gases very carefully and observed good reproducibility between different experiments and between different catalyst samples, especially in oxidation treatment. Our greatest concern was carbon contamination in the H₂ during high-temperature annealing. When carbon was intentionally deposited by decomposing a hydrocarbon at high temperatures, it could easily be removed by reaction with H₂ to form CH₄ which was analyzed by GC. Thus, in all experiments reported here, there was no more than a monolayer of any carbonaceous species which could be removed by H₂ titration.

Our overall interpretation of the observed rate variations is therefore that the surface crystal planes exposed are altered by these treatments, with high-temperature annealing producing mostly high-coordination, low-free-energy planes (the (111) and (100) planes of fcc metals) and oxidation followed by low-temperature reduction producing a large fraction of low-coordination, high-free-energy crystal planes.

There is considerable data on rates of reactions on single-crystal surfaces (10, 17, 25–32) which shows significant crystallographic anisotropies in many reactions. For example, cyclopropane, methylcyclopropane, and ethylene hydrogenolysis and hydrogenation reactions exhibit differences by factors of 2 to 10 on different planes of Ir (27, 28), Ni (29), and Pt (30, 31) in steady-state flow reactor experiments at reactant partial pressures of approximately 1 Torr, the pressure range in these experiments. Larger crystallographic variations would in fact be difficult to detect in such experiments because it is difficult to prepare single-crystal surfaces sufficiently free of defects to have exclusively the low-index surfaces. It is clear from such experiments, however, that the low-Miller-index planes of most metals are less reactive than low-coordination, high-index surfaces. These variations have been speculated to be associated with different levels of reactive car-

bon which form in the reactive gases (25–32).

We have shown using XPS for Rh, Ir, and Ni that particle surfaces (>10-Å-thick layers) are totally oxidized by heating in O₂ at 500°C and that these oxides are totally reduced to their metallic states by heating in H₂ at 150°C. For Ru and Pd the XPS experiments have not been performed, although these conditions will almost certainly produce oxidation and reduction of these surfaces also. For Pt, XPS shows no evidence of oxidation by heating in O₂ at any temperature. Thus we conclude that all metals in these experiments are completely in their *metallic* states under conditions of hydrogenolysis measurements.

We have used TEM to examine microstructures of all these metals on SiO₂. Upon oxidation and reduction of Ru (Fig. 3), Rh and Ir (19, 23), the original 200-Å-diameter crystallites are broken up into clusters of 10- to 20-Å particles which only coalesce into their original sizes and shapes upon heating to 600 and 800°C, respectively. Ni also forms clusters (22) upon oxidation and reduction, but these are never as small as those for Rh or Ir. Pd forms PdO₂ readily, but reduction and partial coalescence occur in H₂ even at 25°C, so that it is impossible to trap Pd as very small clusters.

Pt exhibits no morphological or phase changes upon heating in O₂ at 500°C. However, we have shown that annealing Pt particles in H₂ at 600°C produces predominantly cube-shaped particles exposing mostly (100) planes, while heating cubes in N₂ at 500 to 600°C for several hours causes the shapes to change to spheres which expose all planes (24). Heating the spherical particles in H₂ causes shapes to revert to cubes.

The observations of microstructural changes thus appear to correlate activities and their variations with treatment very well. As summarized in Table 3, high maximum activity correlates with the ability to form small clusters which are stable under reaction temperatures (<300°C) as ob-

TABLE 3
Summary of Rate Variations and Causes

Metal	Maximum rate	Variation with treatment	Cause	Temperature (°C)
Ru	High	High	Forms 10-Å particles	600
Rh	High	High	Forms 10-Å particles	600
Ir	Moderate	Moderate	Forms 10-Å particles, deactivates by C formation	800
Ni	Moderate	Small	Forms 50-Å particles	300
Pt	Low	Moderate	Changes from cubes to spheres	600
Pd	Low	Moderate	Particles coalesce readily	25

served for Ru, Rh, and Ir. Ni and Pd begin to revert back to their annealed microstructures by 300°C, while Pt particles do not change size but change shape only upon heating in different gases.

SUMMARY

The large variation in hydrogenolysis activity of supported metals with gas and temperature treatment appears to be a general phenomenon, and the variation in maximum activity with metals and the differences between high- and low-activity states appears to be correlated with the ability to prepare and decompose the various oxides and the ability to maintain the low-coordination, high-reactivity sites formed by oxidation and low-temperature reduction.

In a subsequent paper we shall show that comparable variations in reaction rate with treatment occur in olefin hydrogenation and CO hydrogenation.

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