

## PRIORITY COMMUNICATION

Evidence for the Role of Colloidal Palladium in the Catalytic Formation of H<sub>2</sub>O<sub>2</sub> from H<sub>2</sub> and O<sub>2</sub>Dhammike P. Dissanayake<sup>1</sup> and Jack H. Lunsford<sup>2</sup>*Department of Chemistry, Texas A&M University, College Station, Texas 77842-3012*

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The direct production of H<sub>2</sub>O<sub>2</sub> from H<sub>2</sub> and O<sub>2</sub> (O<sub>2</sub>/H<sub>2</sub> = 2) at 25°C and 760 Torr occurs in an aqueous phase over colloidal palladium that may be introduced either via PdCl<sub>2</sub> or via Pd supported on silica gel (Pd/SiO<sub>2</sub>). In the latter case, aqueous HCl facilitates the dissolution of the supported Pd. The presence of colloidal palladium was confirmed by electron microscopy. When the solution was either 0.1 M or 1.0 M in HCl, removal of the silica, along with any remaining supported Pd, did not affect the rate of H<sub>2</sub>O<sub>2</sub> formation because the amount of active colloidal Pd remained unchanged. The specific activity of the supported Pd is only 3% of that for colloidal Pd, probably because of transport limitations within the pores of the silica. © 2002 Elsevier Science (USA)

**Key Words:** palladium colloid; hydrogen peroxide; palladium/silica; supported palladium catalyst.

## INTRODUCTION

For environmental reasons, hydrogen peroxide has become a substitute for chlorine as a bleach in the pulp and paper industry and as an oxidant in wastewater treatment (1). Moreover, it has recently been proposed as a reagent for the removal of residual aromatic sulfur compounds in fuels (2). The current method for the commercial production of H<sub>2</sub>O<sub>2</sub> is a circuitous process that involves the catalytic hydrogenation of an alkylanthroquinone to the corresponding hydroquinone, followed by its treatment with O<sub>2</sub> to produce H<sub>2</sub>O<sub>2</sub> and the original anthroquinone (1). In the quest for a less expensive route, attention has been given to the direct production of H<sub>2</sub>O<sub>2</sub> from the reaction of H<sub>2</sub> and O<sub>2</sub> over a supported palladium catalyst, and a number of patents have resulted from the work at duPont and other companies (3–6). A fundamental study of a catalyst containing hafnium phosphate and viologen phosphonate with supported Pd has recently been reported by Thompson and

co-workers (7). More typical supports include silica, silicic acid, carbon and alumina. The reaction is usually carried out at elevated pressures in an aqueous slurry that contains HCl or HBr. The presence of protons is known to inhibit the decomposition of H<sub>2</sub>O<sub>2</sub> (8); however, the role of the halide has not previously been established. The results reported here demonstrate the importance of colloidal palladium in the catalytic conversion of H<sub>2</sub> and O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub>, even when one begins with palladium supported on silica. The presence of HCl facilitates the dissolution of metallic Pd as PdCl<sub>4</sub><sup>2-</sup>, which is an intermediate in the colloid formation.

## EXPERIMENTAL

The catalytic reactions were carried out at 760 Torr and 25°C in a 22-mm-i.d. Pyrex reactor so that changes in the system could be observed visually. The gases, oxygen (20 mL min<sup>-1</sup>) and hydrogen (10 mL min<sup>-1</sup>), were allowed to flow through a fine glass frit at the bottom of the reactor. The reactor was open at the top. Note that this is a potentially explosive mixture and appropriate precautions should be taken. For example, if a supported palladium catalyst is used, there should be no dry catalyst on the walls of the reactor.

Palladium was introduced to 10 mL of an aqueous phase either as PdCl<sub>2</sub> or via a Pd/SiO<sub>2</sub> material. Before addition of the Pd, the water was acidified with HCl and saturated with the H<sub>2</sub>/O<sub>2</sub> mixture. The Pd/SiO<sub>2</sub> material consisted of 5 wt% Pd on Davison grade 57 silica gel that had been reduced in H<sub>2</sub> at 300°C (9). After the Pd was added to the aqueous phase, the solution or slurry was rapidly stirred with an overhead stirrer (~500 rpm). Small aliquots of the liquid phase were removed from the reactor, and the H<sub>2</sub>O<sub>2</sub> formed was analyzed by colorimetry after complexation with a TiOSO<sub>4</sub>/H<sub>2</sub>SO<sub>4</sub> reagent (10).

The amount of colloid present in solution was determined by first analyzing for the amount of Pd<sup>2+</sup>, using the method of Onishi (11). Then the colloid was oxidized by exposing the solution to air for 12 h, and the solution was again

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analyzed for  $\text{Pd}^{2+}$ . The difference between the amounts of  $\text{Pd}^{2+}$  is taken to be the amount of colloidal Pd.

Samples for electron microscopy were prepared by removing aliquots of liquid after 1 h of reaction from the solution that originally contained  $1.0 \times 10^{-3}$  M  $\text{PdCl}_4^{2-}$ . This was neutralized with NaOH, deposited on a carbon-coated copper grid, dried, and analyzed with a Zeiss 10C transmission electron microscope.

## RESULTS AND DISCUSSION

The formation of  $\text{H}_2\text{O}_2$  in aqueous solutions that initially contained  $1.0 \times 10^{-3}$  or  $1.0 \times 10^{-4}$  M  $\text{PdCl}_4^{2-}$  in 1.0 M HCl is depicted in Fig. 1. Although it is not evident from this figure, there was generally a brief induction period during which almost no  $\text{H}_2\text{O}_2$  was formed. After this period the rate of  $\text{H}_2\text{O}_2$  formation was essentially constant for several hours and then began to decrease. During the course of the reaction the yellow color that results from  $\text{PdCl}_4^{2-}$  began to decrease in intensity and the solution eventually became colorless. The electron micrograph of Fig. 2 shows the presence of colloidal Pd with a broad distribution of particle sizes but with an average diameter of about 6 nm. Henglein (12) has previously reported the formation of Pd colloids by reduction of  $\text{PdCl}_4^{2-}$  by hydrogen; however, sodium citrate was used as a stabilizer, which resulted in a narrow size distribution and an average particle size of about 4 nm. From the data of Fig. 1 it was established that after 1 h, for the nominally  $1 \times 10^{-4}$  M  $\text{PdCl}_4^{2-}$  solution, the rate of  $\text{H}_2\text{O}_2$  formation was  $1 \times 10^{-4}$  M  $\text{min}^{-1}$  and the colloid concen-

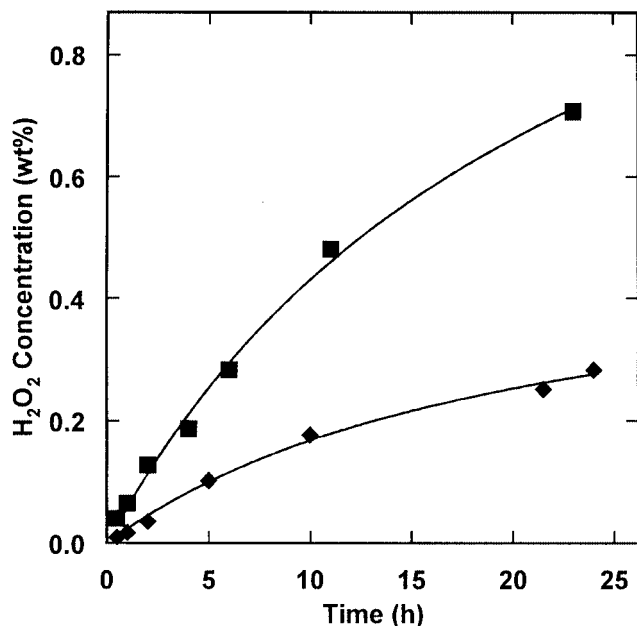


FIG. 1. Catalytic formation of  $\text{H}_2\text{O}_2$  at  $25^\circ\text{C}$  in an aqueous solution that was 1 M in HCl and originally (◆)  $1.0 \times 10^{-4}$  M or (■)  $1.0 \times 10^{-3}$  M in  $\text{PdCl}_4^{2-}$ .

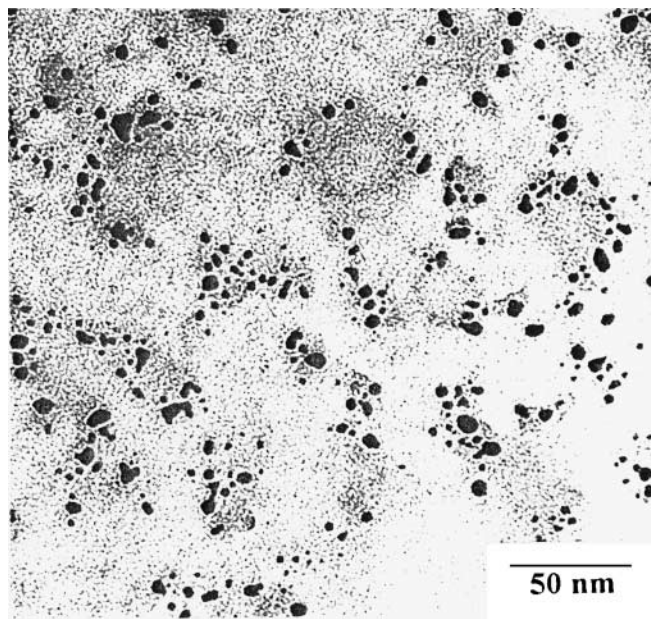


FIG. 2. Electron micrograph of a Pd colloid obtained after exposure of a  $1.0 \times 10^{-3}$  M  $\text{PdCl}_4^{2-}$  solution to  $\text{H}_2/\text{O}_2$  for 1 h at  $25^\circ\text{C}$ .

tration was  $2 \times 10^{-5}$  M. For the nominally  $1 \times 10^{-3}$  M  $\text{PdCl}_4^{2-}$  solution, the rate was  $3 \times 10^{-4}$  M  $\text{min}^{-1}$  and the colloid concentration was  $5 \times 10^{-5}$  M. Thus, the rates are approximately proportional to the colloid concentration. The specific rate was ca.  $50$  mmole  $\text{H}_2\text{O}_2$   $\text{g}^{-1}$  colloidal Pd  $\text{min}^{-1}$ .

As shown in Fig. 1, the rates of  $\text{H}_2\text{O}_2$  formation are nearly constant for 3–5 h, but thereafter the rates, as well as the colloid concentrations, continuously decrease. After 24 h, for example, the rate of  $\text{H}_2\text{O}_2$  formation and the Pd colloid concentration were  $7 \times 10^{-5}$  M  $\text{min}^{-1}$  and  $7 \times 10^{-6}$  M, respectively, for the nominally  $1 \times 10^{-3}$  M solution. The lower colloid concentration is approaching the limit of detection; nevertheless, it is apparent that the colloid is disappearing from the aqueous phase. Meanwhile the frit became dark as a result of the deposition of palladium. The  $\text{PdCl}_4^{2-}$  is not a factor since it has decreased below a detectable level even after 1–2 h on stream. Neither is the decomposition of  $\text{H}_2\text{O}_2$  a factor in the decreasing rates under the conditions of these experiments; although, at smaller  $\text{H}^+$  concentrations and/or at larger wt%  $\text{H}_2\text{O}_2$ , the decomposition reaction becomes significant, particularly in the presence of Pd/SiO<sub>2</sub>.

One may speculate as to why the palladium prefers to reside on the frit. The answer may be found in the local concentration of  $\text{H}_2$  that exists at the frit where the gases are introduced. At  $25^\circ\text{C}$  the concentration of  $\text{H}_2$  in the gas phase is approximately 50 times that found in the aqueous phase, and the  $\text{Pd}^{2+}$  ions may preferentially be reduced at the gas–liquid film on the frit where the  $\text{H}_2$  concentration is the largest. Attempts were made to stabilize the colloid with sodium citrate or poly (vinyl alcohol), but without success. The palladium metal on the frit exhibited very little catalytic activity, probably as a result of its small surface area. It

may be largely digested back into solution as PdCl<sub>4</sub><sup>2-</sup> by passing only O<sub>2</sub> through the frit. Then upon addition of the H<sub>2</sub>/O<sub>2</sub> mixture, the aqueous phase again becomes active. In general, the formation of the colloid appears to be autocatalytic, as has been noted previously for Pt colloids (13), and to achieve reproducible results it was necessary that a small amount of Pd remain on the frit from one experiment to the next. When the frit was rigorously cleaned with nitric acid, long induction periods were observed, and the palladium in the form of PdCl<sub>4</sub><sup>2-</sup> was extensively reduced on the frit, without the formation of a significant amount of colloid.

In the range of conditions described here, colloidal palladium also plays a major role as a catalyst even when Pd/SiO<sub>2</sub> is present in the system. The formation of H<sub>2</sub>O<sub>2</sub> over 2.2 mg of Pd/SiO<sub>2</sub> in the slurry was followed as a function of time at three different HCl concentrations. The amount of Pd on the silica is equivalent to that present in 10 mL of a 1 × 10<sup>-4</sup> M solution. As shown in Fig. 3, the reaction was characterized by a brief induction period, during which time the aqueous phase became yellow and then clear again for the systems containing 0.1 M and 1 M HCl. Analysis of the yellow solution by UV/vis spectroscopy indicated that PdCl<sub>4</sub><sup>2-</sup> was formed. After 60 min on stream the solid phase was rapidly removed by centrifuging, and the reaction was continued only in the liquid phase. Surprisingly, the rate of H<sub>2</sub>O<sub>2</sub> formation (ca. 5 × 10<sup>-5</sup> M min<sup>-1</sup>) was essentially the same after the solid phase had been removed

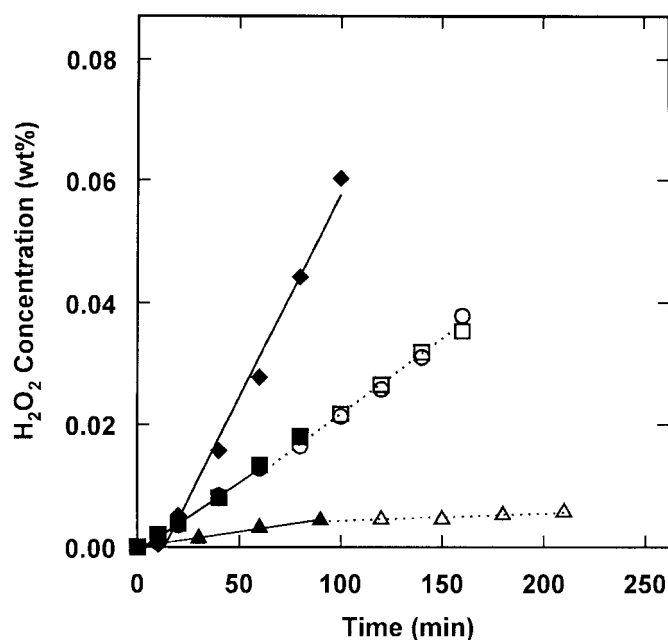


FIG. 3. Catalytic formation of H<sub>2</sub>O<sub>2</sub> in an aqueous phase before and after the removal of 2.2 mg of 5 wt% Pd/SiO<sub>2</sub>: (■) before and (□) after the removal of the solid phase from a 1 M HCl solution; (●) before and (○) after the removal of the solid phase from an 0.1 M HCl solution; (▲) before and (△) after the removal of the solid phase from an 0.01 M HCl solution. Peroxide formation in a nominally 1.0 × 10<sup>-4</sup> M PdCl<sub>4</sub><sup>2-</sup> solution containing 1 M HCl is depicted by (◆).

TABLE 1

Rates of H<sub>2</sub>O<sub>2</sub> Formation and Pd Colloid Concentrations in Several Catalytic Systems

System	Rate (M min <sup>-1</sup> )	Colloid concentration (M)
Nominally 1 × 10 <sup>-4</sup> M PdCl <sub>4</sub> <sup>2-</sup> in 1 M HCl solution	1.5 × 10 <sup>-4</sup>	2.9 × 10 <sup>-5a</sup>
After removal of 2.2 mg Pd/SiO <sub>2</sub> from 1 M or 0.1 M HCl solution	5.1 × 10 <sup>-5</sup>	1.8 × 10 <sup>-5</sup>
Prior to removal of Pd/SiO <sub>2</sub> from 0.01 M HCl solution	1.5 × 10 <sup>-5</sup>	n.a. <sup>b</sup>

<sup>a</sup> The estimated error in the rates is ±10% and the estimated error in the colloid concentrations is ±3 × 10<sup>-6</sup> M.

<sup>b</sup> The colloid concentration after removal of the Pd/SiO<sub>2</sub> was <3 × 10<sup>-6</sup> M.

from the solutions that contained the larger acid concentrations. These results confirm that the reaction was catalyzed by a form of palladium in the liquid phase, i.e., colloidal palladium. Obviously, the palladium remaining on the silica gel, as well as that on the frit, contributed very little to the activity. The smaller rate that was observed after the solid phase was removed from the 0.01 M HCl solution may result, in part, from the partial loss of colloidal palladium. Although this loss of colloidal palladium may take place at all three acid concentrations, it is most apparent when the colloid concentration is small, which occurs when the acid strength is low. For comparison with the results obtained with the Pd/SiO<sub>2</sub> slurry, the catalytic properties of 1.0 × 10<sup>-4</sup> M PdCl<sub>4</sub><sup>2-</sup> in 1.0 M HCl were determined over the same time on stream, and the results are shown in Fig. 3. The rates of H<sub>2</sub>O<sub>2</sub> formation and the respective Pd colloid concentrations are summarized in Table 1. Within the limits of uncertainty, the rates are again found to be proportional to the colloid concentration. When the solutions were 1.0 or 0.1 M HCl, 40% of the palladium remained on the silica or was deposited on the frit. In the 0.01 M solution, the palladium remained largely on the silica. The rate obtained for the Pd/SiO<sub>2</sub> in the 0.01 M solution was 1.5 × 10<sup>-5</sup> M<sup>-1</sup>, which is only 10% of the value found for the nominally 1.0 × 10<sup>-4</sup> M aqueous phase. If one makes the comparison based on the amount of colloid present in the latter system, the activity of the colloid is about 50 mmol H<sub>2</sub>O<sub>2</sub> g<sup>-1</sup> Pd min<sup>-1</sup>, whereas the activity of the Pd/SiO<sub>2</sub> is only 1.4 mmol H<sub>2</sub>O<sub>2</sub> g<sup>-1</sup> Pd min<sup>-1</sup>. At H<sub>2</sub>O<sub>2</sub> concentrations <0.01 wt%, the decomposition of H<sub>2</sub>O<sub>2</sub>, even at 0.01 M HCl, is not a factor.

The question arises as to why the Pd/SiO<sub>2</sub> itself is so inactive for H<sub>2</sub>O<sub>2</sub> production. As pointed out above, the concentration of H<sub>2</sub> in the gas phase is much greater than in the aqueous phase, and, as a consequence, H<sub>2</sub>O<sub>2</sub> may be formed mainly at the interface between a gas bubble and a colloidal Pd particle (i.e., in a region where the reagent concentration is the largest). The absence of this interface

in the pores of the silica gel would result in the small activity of the Pd/SiO<sub>2</sub> phase, even though the Pd particle size in this phase, at least initially, was about 6 nm (9). In this three-phase system, transport of H<sub>2</sub> across the liquid film between a bubble and a colloidal particle may be the rate-limiting factor in the formation of H<sub>2</sub>O<sub>2</sub>, similar to that found in the partial hydrogenation of benzene to cyclohexene over a supported ruthenium catalyst (14). Thompson and co-workers(7) have addressed the issue of mass transfer in the context of H<sub>2</sub>O<sub>2</sub> formation; however, their focus was on the transport of hydrogen, the limiting reagent, from the gas bubble into the liquid phase. This aspect of mass transfer was not a limiting factor in the results reported here since the rates were proportional to the amount of Pd present as the colloid, which would not be expected if the global transfer of the gases into the liquid phase were rate limiting.

In conclusion, the catalytic conversion of H<sub>2</sub> and O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> occurs over colloidal Pd in the aqueous phase. This colloidal Pd may be derived from the hydrogen reduction of PdCl<sub>4</sub><sup>2-</sup> that is introduced either directly or indirectly via the oxidation of metallic Pd in contact with an aqueous HCl solution. A solid consisting of reduced Pd supported on silica gel may serve as one source of palladium. Indirect evidence suggests that the transfer of reagents from small bubbles within the liquid phase to the colloid may be the rate limiting step in the reaction.

## ACKNOWLEDGMENT

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