The direct formation of H_2O_2 from H_2 and O_2 over colloidal palladium

Dhammike P. Dissanayake [1] and Jack H. Lunsford [*]

Department of Chemistry, Texas A&M University, College Station, TX 77842-3 12, USA

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Abstract

Additional evidence is presented for the catalytic role of aqueous colloidal palladium in the direct conversion of H_2 and O_2 to H_2O_2. Reactions typically were carried out at an O_2/H_2 ratio of 2, and 25 °C, by introducing the gases at 1 atm through a frit into the aqueous slurry. The source of palladium was either $PdCl_2$ or reduced palladium supported on silica gel. During the course of the reaction the palladium is distributed among $PdCl_4^{2-}$, colloidal palladium, palladium deposited on the frit, and Pd/SiO_2 when SiO_2 is present. Although the amount of colloidal palladium differs, depending on its source and the time on stream, the rate of H_2O_2 formation is proportional to the amount of colloid present at a particular time. Maximum rates were observed for colloids prepared from Pd/SiO_2; however, the largest H_2O_2 concentration of 0.7 wt% was attained when $PdCl_2$ was the source of colloidal palladium. The ultimate steady-state concentration of H_2O_2 is, in part, affected by the rate of H_2O_2 decomposition, which is relatively large over the Pd/SiO_2 sample that was tested. The rate of decomposition also is determined by the H^+ concentration. Results obtained with a mixture of $^{16}O_2/^{18}O_2$ confirm that oxygen remains undissociated during the formation of H_2O_2, which may explain why palladium is uniquely suited as a catalyst for this reaction.
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1. Introduction

The increasing utilization of hydrogen peroxide as a bleach in the pulp and paper industry, as an oxidant in wastewater treatment, and as a source of oxygen for epoxidation reactions has resulted in renewed interest in the direct formation of H_2O_2 from H_2 and O_2. The current commercial method for the production of H_2O_2 is a circuitous process that involves the use of alkylanthroquinone and hydroquinone intermediates [1]. The raw product mixture contains only about 2 wt% H_2O_2. Although recent advances in the direct formation of H_2O_2 have been reported in the patent literature [2–5], the fundamental studies that have been carried out on this reaction are limited in both scope and number. Most notable is the work of Thompson and coworkers [6], who investigated the reaction over a catalyst containing hafnium phosphate and viologen phosphonate with supported Pd. This group reported that 13 wt% H_2O_2 could be attained by carrying out the reaction at atmospheric pressure in anhydrous methanol. A paper by Choudhary et al. [7], in which they describe a novel membrane reactor, also is of interest because such a reactor would enable one to avoid potentially explosive mixtures of H_2 and O_2 while maintaining the most efficient ratio of these reagents in the liquid phase.

In a recent paper, we reported on the direct formation of H_2O_2 at atmospheric pressure, with the unexpected conclusion that the reaction was mainly catalyzed by *colloidal* palladium [8]. Palladium metal is unique in its ability to catalyze this reaction to any significant extent, and it is usually introduced in a supported form. Typical supports include silica, silicic acid, carbon, and alumina. Generally, the reaction is carried out in an aqueous slurry that also contains an acid such as HCl or HBr. In the presence of HCl, supported Pd^0 initially is oxidized, with the formation of $PdCl_4^{2-}$ ions in solution. The palladium ions then are reduced back to Pd metal by H_2, and some of the metal is present as a colloid. Evidence for the predominant role of the colloid in the catalytic reaction principally came from two observations: (1) after a period of reaction, the rate of H_2O_2 formation remained essentially the same after the remaining Pd/SiO_2 had been removed from the slurry, and (2) even larger rates of reaction were observed when the source of palladium was $PdCl_2$; i.e., no SiO_2 support was present in the system.

* Corresponding author.
E-mail address: lunsford@mail.chem.tamu.edu (J.H. Lunsford).
[1] On leave from the Department of Chemistry, University of Colombo, Colombo 3, Sri Lanka.

Moreover, electron microscopy confirmed the presence of a colloid in the aqueous phase.

To determine whether the predominant role of colloidal palladium in the formation of H_2O_2 is a more general phenomenon, the influence of other factors on colloid concentrations and reaction rates has been explored. These factors include types of silica, acid concentration and reaction time. In addition, experiments involving $^{16}O_2/^{18}O_2$ mixtures provide insight into the reaction mechanism.

2. Experimental

Most of the reactions reported here were carried out at 760 Torr and 25 °C in a Pyrex reactor, shown in Fig. 1, that was 22 mm id. The oxygen and hydrogen gases were allowed to flow through a Kimax 20F fine glass frit that was located 100 mm below the top of the open reactor. The flow rates, unless noted otherwise, were maintained at 20 mL min^{-1} for O_2 and 10 mL min^{-1} for H_2 using Scott mass flow controllers. Note that this is a potentially explosive mixture and appropriate precautions should be taken, some of which are described below.

Palladium was introduced as $PdCl_2$ or via a Pd/SiO_2 material to 10 or 20 mL of an aqueous phase. Prior to adding the catalyst, the O_2/H_2 mixture was allowed to pass for
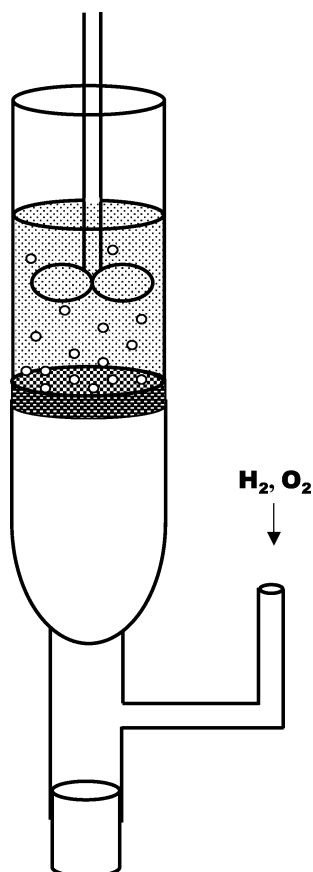

Fig. 1. Schematic of the reactor.

10–15 min through the solution that was usually acidified with HCl. The Pd/SiO_2 materials consisted of 5 wt% Pd supported on either Davison grade 57 silica or grade 03 silica. The resulting materials are referred to as $Pd/SiO_2(57)$ and $Pd/SiO_2(03)$, respectively. The surface areas and pore diameters of grade 57 silica are ca. 300 m^2 g^{-1} and 15 nm, respectively; whereas, those of the grade 03 silica are 625 m^2 g^{-1} and 3 nm, respectively. The preparation of the materials, which included as a final step reduction in H_2, has been described previously [9]. After addition of the Pd to the aqueous phase, the solution or slurry was rapidly stirred with an overhead stirrer ($\sim$ 500 rpm) that had a glass impeller. For longer duration runs, parafilm was loosely placed over the top of the reactor to inhibit evaporation. After different times on stream, small aliquots of the liquid phase were removed from the reactor, and the H_2O_2 formed was analyzed by colorimetry after complexation with a $TiOSO_4/H_2SO_4$ reagent. The estimated error in the analysis of H_2O_2 is $\pm 2 \times 10^{-4}$ wt% ($\pm 5 \times 10^{-5}$ M).

Contact of the 2:1 O_2/H_2 mixture with a *dry* Pd/SiO_2 catalyst may result in an explosion. After several hours on stream a small amount of Pd/SiO_2 is deposited on the reactor wall above the liquid phase. This deposited material usually has a water film, but to ensure that it did not become dry, the stirring occasionally was stopped, the reactor was lowered, and the slurry was swirled so as to remove the solid from the wall. More recently we have found that the initial introduction of Pd/SiO_2 into the solution can result in an explosion because the dry catalyst contacts the exiting O_2/H_2 gas mixture. To avoid this problem, ca. 15 mL of the aqueous solution was removed and slurried with the Pd/SiO_2. This slurry was then introduced into the remaining aqueous phase.

The selectivity for H_2O_2 formation was obtained by converting the single-pass reactor to a recycle reactor which made it possible to follow the loss of H_2 and O_2 during the reaction. The gas-phase ratio, which initially was 2:1 for O_2/H_2, was followed by gas chromatography. The reaction was carried out for 1 h. From the reactions

$$yH_2 + yO_2 \rightarrow yH_2O_2, \tag{1}$$

$$2xH_2 + xO_2 \rightarrow 2xH_2O, \tag{2}$$

it follows, that the H_2 selectivity to H_2O_2 is given by

$$S_{H_2O_2} = \left[y/(y + 2x) \right] \times 100. \tag{3}$$

The values of x and y were determined from the O_2/H_2 ratios before and after reaction, the volume of the system, the initial and final total pressures, and the amount of H_2O_2 formed.

The amount of colloid that was formed in the aqueous phase during the reaction was determined by first analyzing for the amount of Pd^{2+}, using the method of Onishi [10]. Then the colloid was oxidized by exposing the solution to air for 12 h, and the solution was again analyzed for Pd^{2+}.

The difference between the amounts of Pd^{2+} is taken to be the amount of colloidal Pd. The estimated error in the colloid concentrations is $\pm 3 \times 10^{-6}$ M.

Electron micrographs of the colloidal palladium were obtained with a Zeiss 10C TEM instrument operating at 100 kV. After 1 h on stream an aliquot of liquid was removed from the aqueous phase and deposited on either a carbon-coated copper or gold grid. The liquid was rapidly dried in a vacuum oven at ca. 80 °C.

The oxygen isotope distribution in the hydrogen peroxide that forms from the reaction of H_2 with an $^{16}O_2/^{18}O_2$ mixture was determined by Raman spectroscopy. A Holo-probe Raman spectrometer (Kaiser Optical) system that was equipped with a Nd: YAG laser was used for this purpose. Hydrogen peroxide in concentrations as small as 0.05 wt% could be detected. The isotopically labeled H_2O_2 was pre-pared by reacting $^{18}O_2$ (340 Torr) and $^{16}O_2$ (400 Torr) with H_2 (400 Torr) in a catalyst derived from 5 mg of $Pd/SiO_2(57)$ in 10 mL of 1 M HCl. The reaction was car-ried out in a closed 100-mL Pyrex round-bottom flask. The slurry was stirred for 8 h with a magnetic stirrer, and dur-ing this period 0.4 wt% H_2O_2 was produced. The H_2O_2 was concentrated by pumping on the system for 0.5 h with the solution at 30 °C.

3. Results

3.1. Kinetic results

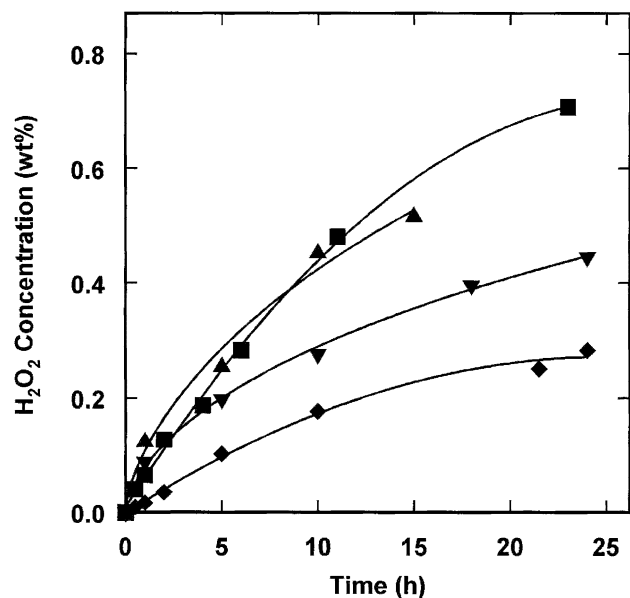The formation of H_2O_2 as a function of time on stream for four different catalyst systems is depicted in Fig. 2.

The systems prepared from 10^{-3} M $PdCl_2$, 44 mg of $Pd/SiO_2(57)$, or 44 mg of $Pd/SiO_2(03)$ all contained 2.2 mg of Pd; whereas, the system prepared for 10^{-4} M $PdCl_2$ contained 0.22 mg of Pd. The liquid volume was 20 mL. It will be shown subsequently that Pd was distributed among the colloid, the frit, and the SiO_2 when it was present. At shorter times on stream (e.g., 2 h) the activity follows the sequence $Pd/SiO_2(57) > Pd/SiO_2(03) > 10^{-3}$ M $PdCl_2 > 10^{-4}$ M $PdCl_2$, but as the reaction proceeded, the system derived from 10^{-3} M $PdCl_2$ maintained the largest activity. Selectivities for H_2O_2 formation, based on H_2 consumption, were 61 and 66% for the $Pd/SiO_2(57)$ and 10^{-3} M $PdCl_2$ systems, respectively.

The variation in activity for the $Pd/SiO_2(57)$ and $Pd/SiO_2(03)$ systems is shown in Fig. 3. When 22 mg $Pd/SiO_2(03)$ was introduced into the 10 mL of 1 M HCl so-lution, there was an induction period of about 5 min, during which time only a small amount of the colloid was formed and, correspondingly, the rate of H_2O_2 formation was low. After about 15 min, the colloid concentration and the rate of H_2O_2 formation reached a maximum and thereafter both slowly declined. By contrast, with the $Pd/SiO_2(57)$ cata-lyst, the formation of the colloid was rapid, and no induc-tion period was observed. But, with this system as well, the decrease in the colloid concentration at times greater than 15 min was accompanied by a decrease in activity.

In a separate experiment, the amount of Pd present in the colloid, on the silica, and, by difference, on the frit was determined for a $Pd/SiO_2(57)$ system after 10 and 24 h of reaction in 1 M HCl. Of the 2 mg Pd in the system, after 10 h there was 0.2 mg as the colloid, 0.8 mg as Pd/SiO_2, and 1 mg on the frit; whereas, after 24 h there was 0.08 mg as the colloid, 0.3 mg as Pd/SiO_2 and 1.6 mg on the frit. The frit became dark as a result of the Pd deposit. In the presence of the 2:1 O_2 to H_2 ratio, the amount of palladium
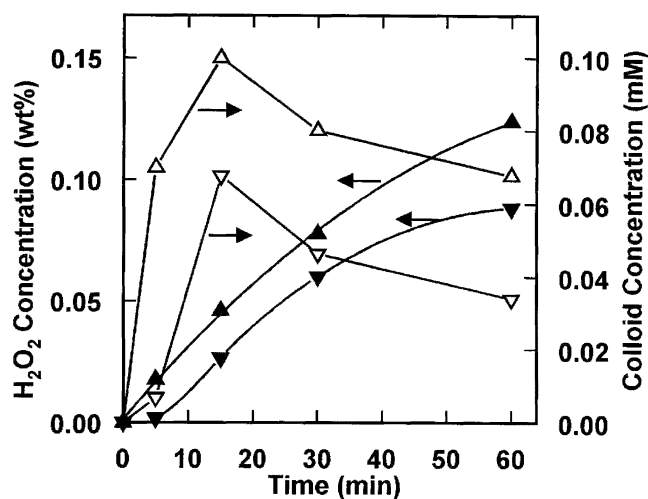

Fig. 2. Comparison of H_2O_2 production over palladium derived from different sources: ■, 10^{-3} M $PdCl_2$; ◆, 10^{-4} M $PdCl_2$; ▲, 5 wt% $Pd/SiO_2(57)$; ▼, 5 wt% $Pd/SiO_2(03)$.

Fig. 3. Formation of H_2O_2 and variation in colloid concentration during the reaction of H_2 and O_2 in aqueous slurries of (▲, △) $Pd/SiO_2(57)$ and (▼, ▽) $Pd/SiO_2(03)$.

as $PdCl_4{}^{2-}$ was small after an initial induction period. Most of the Pd resides on the frit for times on stream greater than about 10 h, but the catalytic activity of this form of Pd is relatively small. After allowing the palladium to form on the frit for 5 h during the reaction of H_2 and O_2 in a system derived from 10^{-3} M $PdCl_2$, the solution with the colloid was replaced by a fresh 1 M HCl solution, and the rate was determined. The rate of H_2O_2 formation was 1.4×10^{-5} M min^{-1}, which may be compared to the original rate of 1.9×10^{-4} M min^{-1}. Thus, the activity of the Pd on the frit was more than an order of magnitude less than that of the colloid in solution. Even this value for the Pd/frit is an upper limit since a small amount of the Pd was reintroduced into the solution as a colloid.

The rates of H_2O_2 formation for the systems derived from the two supported catalysts and from $PdCl_2$ have been determined, and the results are shown in Fig. 4 as a function of the colloid concentration. Within experimental error, there is a linear relationship between the rate and the colloid concentration, which further supports the predominant catalytic role of the colloidal palladium. A specific activity of 80 mmol H_2O_2 g^{-1} Pd min^{-1} was determined from the linear relationship of Fig. 4. The earlier catalytic results, which were obtained with 2.2 mg Pd/SiO$_2$(57), indicated that the specific activity of the solid catalyst itself was only about 3% of the specific activity of colloidal palladium [8].

The role of the HCl in the formation of H_2O_2 also was of interest, and in order to avert the complications introduced by the dissolution of palladium from Pd/SiO$_2$, $PdCl_2$ was used to form the colloid. The results of Fig. 5A show that at 0.1 and 0.01 M HCl concentrations, the initial activities were slightly larger than that of the 1.0 M HCl solution, but
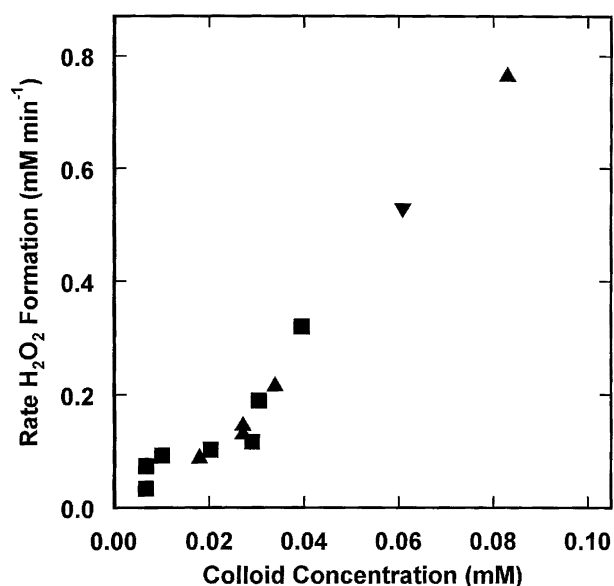
activities at the lower acid concentrations were not as stable with respect to time on stream. Even the neutral solution was active after an induction period of several minutes. In this case, as well as with the 0.01 M HCl solution, there was a decrease in activity that resulted from H_2O_2 decomposition at the lower proton concentrations. Pospelova and Kobozev [11] have shown that the decomposition of H_2O_2 is strongly inhibited by protons in similar catalytic systems. This interpretation for the decrease in net H_2O_2 formation as depicted in Fig. 5A is confirmed by the results of Fig. 5B. After the steady state was reached, H_2O_2 was added to a level of about 0.04 wt%, and it was observed that decomposition of this added H_2O_2 rapidly occurred, down to the level of the original steady-state concentration. Subsequent acidification of the solution to 1 M HCl caused a net formation of H_2O_2 at a rate comparable to that found for the original 1 M HCl solution (Fig. 5A).

The question arises as to whether the decrease in activity of the 0.1 M solution also resulted from the approach to steady state (i.e., the more rapid decomposition of H_2O_2) or whether colloidal Pd was less stable in the 0.1 M solution. In a separate experiment, the reaction was carried out for 7 h, during which time the rate had decreased significantly. Then 0.1 mg Pd was added as $PdCl_2$ (the same amount of $PdCl_2$ as was originally present) and the rate increased to the original value that is indicated in Fig. 5A. This result confirms that in the 0.1 M solution, the decrease in net rate results mainly from the loss of palladium rather than the decomposition of H_2O_2.

The potential influence of the decomposition reaction on the net formation of H_2O_2 was determined for solutions that
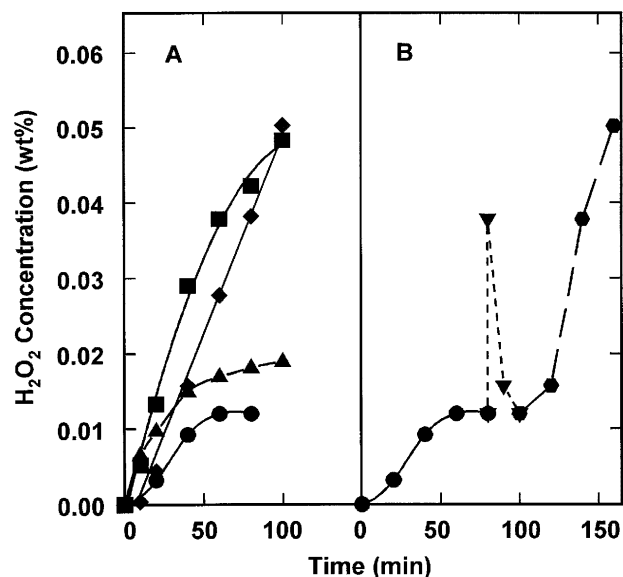

Fig. 4. Variation in catalytic activity for H_2O_2 formation as a function of colloid concentration with the colloid being derived from: ■, 10^{-3} M $PdCl_2$; ▲, 5 wt% Pd/SiO$_2$(57); ▼, 5 wt% Pd/SiO$_2$(03).

Fig. 5. (A). Formation of H_2O_2 in aqueous colloids derived from 10^{-4} M $PdCl_2$ at different HCl concentrations: ◆, 1.0 M HCl; ■, 10^{-1} M HCl; ▲, 10^{-2} M HCl; ●, no HCl added. (B) After 80 min H_2O_2 was added to give 0.04 wt%; after 100 min the solution was acidified to 1 M HCl.

Table 1
Hydrogen peroxide decomposition[a]

System	Decomposition rate[a] (M min^{-1})
200 mg 5 wt% Pd/SiO$_2$(57)	2×10^{-3}
20 mg 5 wt% Pd/SiO$_2$(57)	3×10^{-4} [b]
Pd/Frit	4×10^{-5}
1×10^{-3} M PdCl$_2$ [c]	-8×10^{-5} [d]

[a] Decomposition of 2 wt% H$_2$O$_2$ in 1 M HCl in the presence of flowing O$_2$ and H$_2$.

[b] The H$_2$O$_2$ formation rate over this catalyst was 1.6×10^{-4} M min^{-1} after 5 h.

[c] The solution remained yellow, indicating that Pd^{2+} was not extensively reduced.

[d] A net formation of H$_2$O$_2$ occurred.

contained a catalyst and a significantly larger H$_2$O$_2$ concentration of 2 wt%. The experiments were carried out in 10 mL of 1 M HCl with palladium in one of the relevant forms, as well as O$_2$ and H$_2$ in a 2:1 ratio. The results are given in Table 1. The rate of decomposition was approximately proportional to the amount of Pd/SiO$_2$(57) catalyst. Over 20 mg Pd/SiO$_2$(57), the rate of H$_2$O$_2$ decomposition was comparable to the net rate of formation that was observed when the level of H$_2$O$_2$ was much less. The palladium on the frit was about an order of magnitude less active, and the colloid derived from 10^{-3} M PdCl$_2$ actually resulted in the net formation of H$_2$O$_2$. These results, together with those that demonstrate the loss of palladium to the frit, indicate that at the lower concentrations of H$_2$O$_2$ attained in the previous experiments (e.g., those described in Fig. 2) and in 1 M HCl the H$_2$O$_2$ concentration is limited more by the stability of the colloid than by the decomposition of H$_2$O$_2$, especially for the systems that did not contain Pd/SiO$_2$.

The effect of O$_2$ and H$_2$ concentration on the reaction rate was studied in a reactor similar to that described above except that the top was closed and the gases exited through tubing. The glass stirrer passed through a gas tight seal. The total flow rate was kept constant by using argon as a diluent. Each reaction rate was determined in a separate experiment, during which the rate was constant for approximately 3 h after an initial transition period. The palladium was introduced to the system as Pd/SiO$_2$(57). The results of Fig. 6 show that there is a positive order with respect to both O$_2$ and H$_2$ up to a certain partial pressure, but at higher pressures the order approaches zero. Here, the concept of a reaction order needs to be understood in view of the fact that the concentration of the colloid is also affected by the O$_2$ and H$_2$ partial pressures. At the higher O$_2$:H$_2$ ratios, e.g., [12], the palladium was present in solution mainly as PdCl$_4$$^{2-}$. The yellow color of PdCl$_4$$^{2-}$ was clearly evident. The plateau at the larger O$_2$ partial pressures may reflect the steady state between colloidal Pd and PdCl$_4$$^{2-}$; namely, most of the palladium is in the form of PdCl$_4$$^{2-}$. The plateau at the larger H$_2$ partial pressures is more difficult to interpret, although it may result from a saturation coverage of hydrogen on the surface. The linear region of both curves
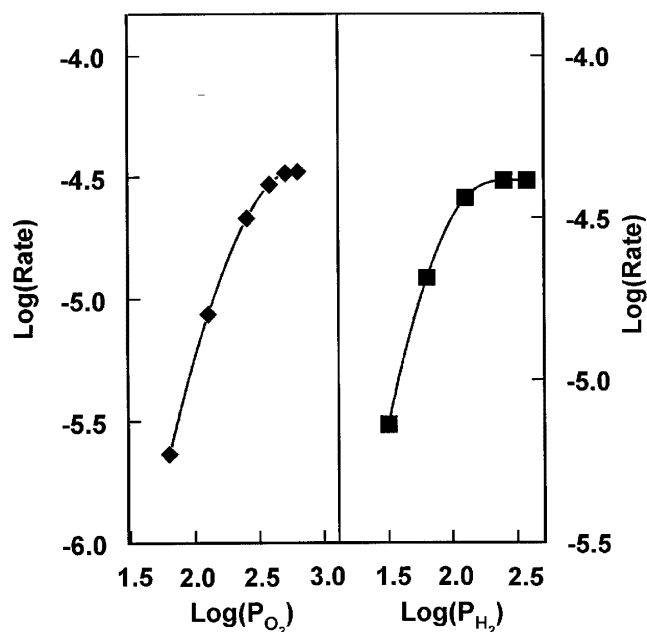

Fig. 6. Variation in H$_2$O$_2$ formation rate as a function of (♦) O$_2$ or (■) H$_2$ partial pressure in a slurry derived from 2.2 mg of 5 wt% Pd/SiO$_2$(57) in 10 mL of 1 M HCl. Rates are expressed in M min^{-1} and pressures are in Torr. For the variation in O$_2$ pressure, the smallest and largest ratios were O$_2$:H$_2$:Ar = 5:10:45 and 50:10:0, respectively; for the variation in H$_2$ pressures the smallest and largest ratios were O$_2$:H$_2$:Ar = 30:2.5:27.5 and 30:30:0, respectively.

corresponds to an apparent reaction order of 0.8, although for the reasons stated above, no fundamental significance concerning the mechanism can be attached to this value.

3.2. Electron microscopy

The electron micrographs shown in Fig. 7 confirm the presence of colloidal palladium in the aqueous phase. For the colloid formed from PdCl$_4$$^{2-}$ in the 0.01 M HCl solutions (Fig. 7A), a broad distribution in particle size was apparent, with an average diameter of ca. 3 nm. For the colloid formed from Pd/SiO$_2$(57) in 0.1 M HCl, the average diameter was ca. 6 nm (Fig. 7B). In the latter case, the particles are more clustered. These results may be compared with those reported by Henglein [12], who observed the formation of Pd colloids following the reduction of an aqueous PdCl$_4$$^{2-}$ solution with H$_2$. The colloid was stabilized by sodium citrate, and a narrow size distribution centered at about 4 nm was observed.

3.3. Oxygen isotope results

Experiments using a mixture of ^{16}O$_2$ and ^{18}O$_2$ were carried out to determine whether a dissociated form of oxygen is involved in the formation of H$_2$O$_2$. If, indeed, a dissociated form of oxygen were involved or if oxygen dissociated and rapidly recombined to produce a diatomic species which was then hydrogenated, one would expect to observe a scrambling of oxygen isotopes, and H$_2$^{16}O^{18}O
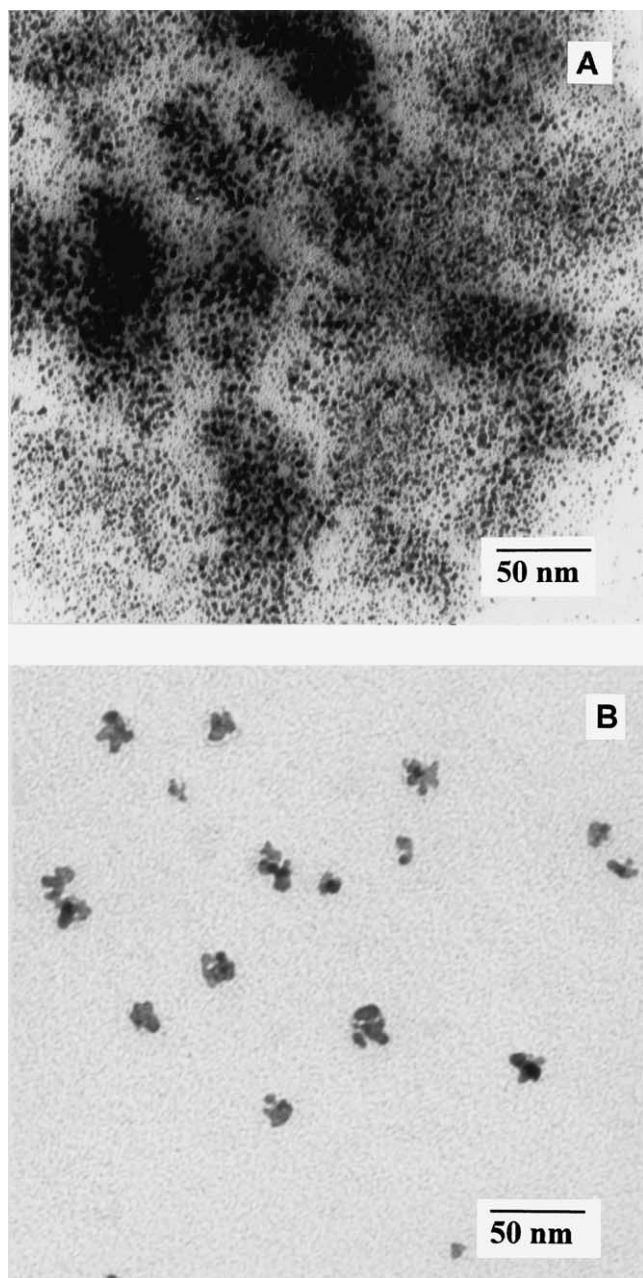
Fig. 7. Electron micrographs of palladium colloids obtained (A) after exposure of a 10^{-3} M $PdCl_4^{2-}$ solution, 0.01 M in HCl, to O_2/H_2 for 1 h at 25 °C or (B) from the aqueous phase over 22 mg $Pd/SiO_2(57)$ in 10 mL 0.1 M HCl, after exposure to O_2/H_2 for 1 h at 25°C.

Fig. 8. Raman spectra of H_2O_2 after reacting H_2 with (A) an $^{16}O_2{}^{18}O_2$ mixture and with (B) $^{16}O_2$.

4. Discussion

4.1. Additional evidence for the role of colloidal palladium

As noted in the introduction, previous results indicated that colloidal palladium may be the predominant active phase during the catalytic conversion of H_2 and O_2 to H_2O_2 [8]. Changes in the rate of H_2O_2 formation, deduced from the slopes of the H_2O concentration curves in Fig. 3, support this conclusion since they correlate well with the temporal changes in the colloid concentration. This is particularly evident for the $Pd/SiO_2(03)$ catalyst, for which there is a distinct induction period. Moreover, as shown in Fig. 4, there is a linear relationship between the rate of H_2O_2 formation and the colloid concentration for three different catalysts, including the one derived from $PdCl_2$. The fact that the results for the $PdCl_2$-derived system are approximately on a common curve with those from the two Pd/SiO_2 sources indicates that the colloid can be formed from all three sources, though not with equal efficiency.

The electron micrographs of Fig. 7 independently validate the presence of the colloids in the aqueous phase. The average diameters and the particle size distributions may not, however, reflect the actual state of the aqueous phase since the colloids were not stabilized and agglomeration of particles may occur during preparation of the samples. Fortuitously, the average particle diameter of 6 nm for the colloid derived from $Pd/SiO_2(57)$ is the same as that reported previously for the supported palladium [9]. The agreement is unexpected because the Pd first enters the aqueous phase as $PdCl_4^{2-}$ and then is reduced to the colloidal palladium.

The palladium is believed to be distributed between its several states according to Scheme 1. Even in a 2:1 oxygen-to-hydrogen gas mixture, palladium on the frit is the dominant final state, but in the presence of pure O_2, almost all of the palladium reenters the solution as $PdCl_4^{2-}$. Variations in the state of palladium, according to Scheme 1,

would be a major product. Raman spectroscopy was used to determine the isotopic distribution in the product, and the results of Fig. 8 show that only $H_2{}^{16}O_2$ with a peak at 879 cm^{-1} and $H_2{}^{18}O$ with a peak at 830 cm^{-1} were present. The Raman shift of 49 cm^{-1} is in good agreement with the calculated value based on isotopic masses. No significant peak was detected at about 852 cm^{-1}, which is the position expected for $H_2{}^{16}O^{18}O$. Clearly, H_2O_2 is derived from a diatomic form of oxygen that presumably is adsorbed on the palladium.
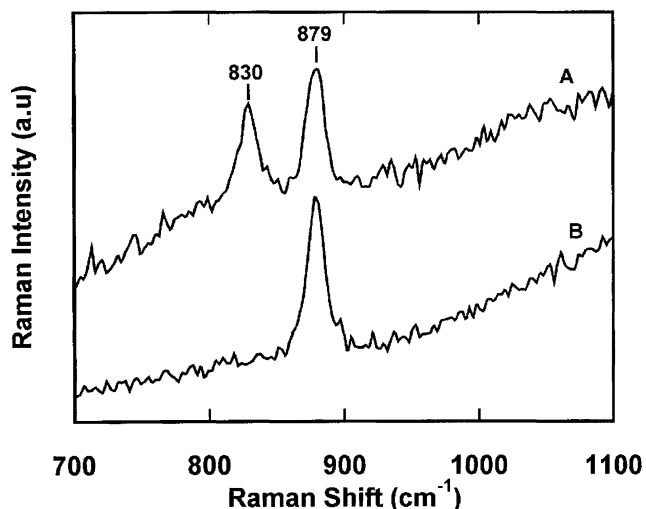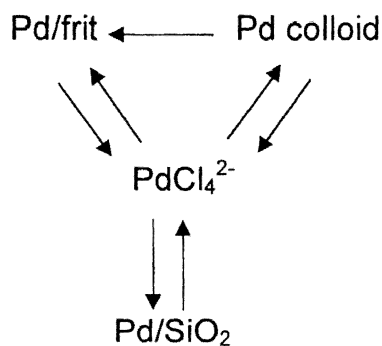
Pd/frit ← Pd colloid

$PdCl_4^{2-}$

Pd/SiO_2

Scheme 1.

are mainly responsible for the induction period (Fig. 3) and the different rates of reaction as the O_2 and H_2 partial pressures are changed (Fig. 6). The induction period depicted in Fig. 3 is more pronounced for $Pd/SiO_2(03)$ than for $Pd/SiO_2(57)$ because the pore size of the former is much smaller. Consequently, the generation of $PdCl_4^{2-}$ and its transport to the bulk aqueous phase are inhibited. For the practical utilization of this process, one of the remaining challenges is to stabilize the colloidal palladium so that it is not transformed into Pd/frit. Attempts to increase the lifetime and/or the catalytic activity of the Pd system by adding reagents that are known to stabilize colloids were unsuccessful. These reagents included sodium citrate, poly(vinyl alcohol) and poly(ethylene glycol).

Although it is not explicitly indicated in Scheme 1, HCl plays an important role in the formation of $PdCl_4^{2-}$ from the reduced forms of Pd. The previous study demonstrated that > 0.01 M HCl was needed to form the colloid from a $Pd/SiO_2(57)$ catalyst. The importance of protons in inhibiting the decomposition of H_2O_2 has long been known [11], and the results of Fig. 5B confirm this observation. In this case, $PdCl_4^{2-}$ was used to produce the active phase; therefore, HCl was not required to generate $PdCl_4^{2-}$ as an intermediate in the formation of colloidal Pd.

4.2. Decomposition of H_2O_2

At the largest acid concentrations used in this study (1 M), the decomposition of H_2O_2 probably does not become significant at H_2O_2 concentrations less than about 0.5 wt%, but at larger concentrations the decomposition reaction, as well as the loss of colloid, may cause the nonlinear behavior shown in Fig. 2. At considerably larger concentrations, the decomposition reaction, which is first order [11], becomes a limiting factor, especially with $Pd/SiO_2(57)$ as the catalyst (Table 1). Thus, the ultimate H_2O_2 concentration that can be achieved depends on several factors including the source of Pd, the concentration and stability of the colloid, and the HCl concentration. Selectivities > 60% were obtained after 1 h for the conditions of Fig. 2; hence, the H_2O_2 concentration was about 0.1 wt% and the decomposition

of H_2O_2 would not have been significant. At longer times with larger concentrations of H_2O_2, the selectivities would be less.

Choudhary and co-workers [13] have recently shown that the support strongly influences both the rate of formation and the rate of decomposition of H_2O_2, with PdO/fluorinated-Al_2O_3 being among the best of the catalysts that they studied. Fluorination of the alumina significantly decreased the rate of H_2O_2 decomposition.

Clearly, the "support" material can play an important role in the steady state concentration of H_2O_2, which makes $PdCl_2$ an attractive source of palladium for colloid formation. The data of Fig. 2 show that after 15 h the largest concentration of H_2O_2 was attained when the palladium was introduced as $PdCl_2$, and the results of Table 1 confirm that the system derived from $PdCl_2$ was the only one for which there was a net *increase* in the amount of H_2O_2 when the original solution contained 2 wt% H_2O_2. Most supports are considered to be inert with respect to H_2O_2 formation; however, Park et al. [14] reported that an H-beta zeolite had a small amount of activity, but poor selectivity, for generating H_2O_2.

4.3. Effect of pressure

Reactions were not carried out in this study at total pressures greater than 760 Torr; although, Izumi et al. [2] have reported in a patent the weight percent of H_2O_2 and the selectivity at the end of 20 h for pressure up to 15.2×10^3 Torr. Their catalyst was Pd/hydrous silicic acid and the solution was 0.03 N in HCl and 1 N in H_2SO_4. The O_2/H_2 ratio was 2.5. At 760 Torr they observed 0.78 wt% H_2O_2, which is comparable to the amount shown in Fig. 2, but the selectivity was only 30%. The amount of H_2O_2 increases almost linearly with pressure up to 7.6×10^3 Torr, while the selectivity increased to a value of 79%. At 15.2×10^3 Torr the wt% H_2O_2 and selectivity were 12.45 and 88%, respectively. These results demonstrate that a significant advantage in both H_2O_2 formation and selectivity can be gained by operating at higher pressures

4.4. Insight into the reaction mechanism

Although important mechanistic questions remain unresolved, the Raman results shown in Fig. 8 provide strong evidence that oxygen remains in a diatomic form during hydrogenation. This is consistent with the mechanism suggested by Pospelova and Kobozev [11,15], who proposed that O_2 is adsorbed in the molecular form on Pd and reacts with adsorbed H to yield HO_2 as a surface intermediate. By contrast, on Pt, which is a catalyst for H_2O production, O_2 is believed to adsorb in a dissociative form. The behavior of O_2 on Pd dispersed in an aqueous phase is different from O_2 on a Pd (111) surface under UHV conditions for which

Yates and co-workers [16] observed dissociative adsorption at about 200 K. As expected, dissociative adsorption was accompanied by extensive isotopic mixing when $^{16}O_2$ and $^{18}O_2$ were employed, but no $^{16}O\,^{18}O$ cross-products were detected when only molecular adsorption occurred. The absence of isotopic mixing is therefore a valid test for exclusively molecular adsorption.

5. Conclusions

1. Under the conditions of these experiments, colloidal Pd is the principal catalytic component for the direct conversion of H_2 and O_2 to H_2O_2.

2. In the presence of H_2, O_2, and HCl, the palladium is present in the colloidal form, as $PdCl_4^{2-}$, as the metal supported on the frit, and as Pd/SiO_2 if silica is present. The amount in each form varies with the time on stream and the O_2/H_2 ratio.

3. Hydrochloric acid, together with O_2, promotes the dissolution of palladium metal, and protons inhibit the decomposition of H_2O_2.

4. Oxygen remains in the diatomic form during the production of H_2O_2 on palladium.

Acknowledgments

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