A mechanistic study of H_2O_2 and H_2O formation from H_2 and O_2 catalyzed by palladium in an aqueous medium

Sivadinarayana Chinta and Jack H. Lunsford [*]

Department of Chemistry, Texas A&M University, College Station, TX 77842-3012, USA

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Abstract

The simultaneous determination of H_2 conversion, selectivity for H_2O_2, and concentration of H_2O_2 has provided insight into the pathways for the reactions of H_2 and O_2 over colloidal palladium in an aqueous medium. Reactions typically were carried out at an O_2/H_2 ratio of 4 and at $10\,^\circ$C by introducing the gases at 1 atm into a solution that was 0.1 N in HCl and 0.01 M in Br^- ions. Palladium was added to the system as the metal supported on microspheroidal silica. Concentrations of H_2O_2 approaching 2 wt% have been achieved with selectivities, based on H_2 reacted, in excess of 90%. Water is formed both by a parallel reaction between H_2 and O_2 and by a secondary reduction of H_2O_2 by H_2. The parallel reaction is inhibited by the presence of bromine. Hydronium ions can serve as the source of hydrogen and may be involved in a catalytic cycle that includes their reaction with peroxide species to form H_2O_2.
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1. Introduction

The direct catalytic production of H_2O_2 from H_2 and O_2 has been explored as an alternative to the current commercial process that involves the use of alkylanthroquinone and hydroquinone intermediates [1]. The more fundamental aspects of the direct process have been reviewed recently, and it is evident that many issues concerning the reaction mechanism, as well as the active state of the catalyst, remain unresolved, in part because of the complexity of the three phase system [2]. In general, palladium is the most effective catalyst; however, Landon et al. [3,4] have reported that Au/Al_2O_3 was considerably more active than Pd/Al_2O_3 in a CH_3OH/H_2O liquid phase. But in this particular comparison, the latter catalyst was very nonselective for H_2O_2, which is an anomaly since the same authors [4] showed that Pd/sulfonated carbon exhibited favorable activity with selectivities in the range of 60–90%. Although the reaction has been carried out in several different liquids [5], emphasis here will be placed on the reaction in an aqueous phase that contains HCl and Br^- ions with palladium as the catalyst.

Typically, the palladium is introduced to the system as a supported material, but in the presence of O_2 and HCl at concentrations $\geqslant 0.1$ N, the metal is partially transformed to $PdCl_4{}^{2-}$ in the aqueous phase, and if H_2 is present, the reverse reaction of Pd(II) back to the metallic state also occurs [6,7]. Part of this reduced palladium is in the colloidal state, which is believed to be the most catalytically active form. A model has been proposed in which the H_2 and O_2 gas, present as small bubbles, is transported across a thin liquid film to the surface of the palladium where reaction occurs. During the course of the reaction the metastable colloid is continuously being transferred into palladium black, which is largely inactive. With respect to the reaction mechanism, Raman studies utilizing $^{16}O_2/^{18}O_2$ mixtures have shown that isotopic scrambling to produce $H_2{}^{16}O^{18}O$ does not occur [7]. This observation confirms that diatomic oxygen is a reactive intermediate. The diatomic oxygen is believed to exist as a peroxy species on the palladium.

Since water, rather than hydrogen peroxide, is the end product of the reduction of O_2 by H_2, the factors that affect the selectivity for H_2O_2 become important. It has long been recognized that inorganic acids stabilize H_2O_2 against further reaction [8]. The work of Choudhary and co-workers [9] has further demonstrated that the halides (Cl or F in this

* Corresponding author.
E-mail address: lunsford@mail.chem.tamu.edu (J.H. Lunsford).

case) may be added via the solid phase (e.g., as fluorinated γ-Al_2O_3). The mechanisms by which the halide influences the overall selectivity appear to be twofold: first, by directing the initial H_2/O_2 reaction to H_2O_2 rather than H_2O, and second, by inhibiting the secondary reactions of H_2O_2 to H_2O. With respect to the latter, there is a question as to whether the H_2O_2 is reduced by H_2 in the system

$$H_2 + H_2O_2 \rightarrow 2H_2O \qquad (1)$$

or whether H_2O_2 decomposes according to

$$H_2O_2 \rightarrow H_2O + \tfrac{1}{2}O_2. \qquad (2)$$

Landon et al. [4] present evidence that favors the role of reaction (1) in the loss of H_2O_2.

The present study was undertaken to address these and other mechanistic issues. Of particular interest was the possible role of H_3O^+ in a catalytic cycle as proposed by Stahl et al. [10] (see below). The effect of Br^- on the reaction was explored by simultaneously measuring the rate of H_2 consumption and the selectivity for H_2O_2 formation. As a practical matter, optimum conditions with respect to O_2/H_2 ratio, temperature, and acid concentration were determined.

2. Experimental

The two reactors depicted in Fig. 1 were constructed of Pyrex glass, which allows one to visually observe the state of the reacting system. Reactor A was open to the atmosphere at the top; whereas, reactor B was closed so that the gas exiting the slurry phase could be analyzed. Apart from this difference, the two reactors were essentially the same. They had an i.d. of 60 mm and were stirred by an impeller. The
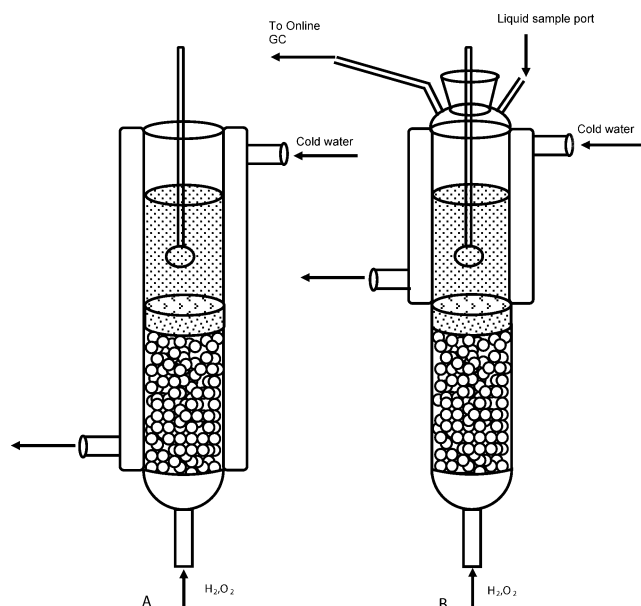
temperature was controlled to $\pm 0.1\,^\circ$C by passing a mixture of ethylene glycol and water through a jacketed region as shown in the figure. The gases were introduced through an Ace 4- to 8-µm fine glass frit. The volume below the frit was partially filled with 3-mm glass beads to reduce the dead volume. The total gas flow rate was 30 mL min^{-1}, unless otherwise noted, and the individual gas flow rates (O_2, H_2, He) were regulated using Scott mass-flow controllers. After a cursory study had been carried out, it was concluded that the best conditions for addressing the mechanistic questions were the following: an O_2/H_2 ratio of 4, 50 mL of an aqueous solution that was 0.1 N in HCl and 0.01 M in Br^- (introduced as NaBr), and a temperature of 10 $^\circ$C.

Palladium was introduced as Pd^0 supported on Cab-O-Sil M5 silica, which is a fumed silica having a BET surface area of ca. 200 m^2 g^{-1}. The material was prepared by the incipient wetness method using $PdCl_4{}^{2-}$ and was reduced in H_2 as described previously [11]. The Pd loading was 5 wt%. This is a very active catalyst for the *gas phase* reaction of H_2 and O_2 and can result in an *explosion* if added to a gas mixture that is within the explosive regime, as was the case in these experiments. Hence, the protocol for adding the palladium was the following: (a) the aqueous phase was first exposed to the desired O_2/H_2 gas mixture via the frit for 15–30 min, (b) then 10 mL of this solution was taken out of the reactor and a slurry was made with 40 mg of the Pd/SiO$_2$, and (c) this slurry was added to the remaining solution in the reactor. An additional hazard exists when a ring of palladium black, formed during the process, is deposited on the wall of the reactor above the aqueous phase. This occurs during long periods of reaction, and to avoid a potential explosion, the stirring of the reaction mixture was stopped, the reactor was lowered, and the slurry was swirled so as to remove the solid from the reactor wall.

At different times on stream, 0.2-mL aliquots of the liquid phase were removed from the reactor, and the amount of H_2O_2 formed was analyzed by colorimetry after complexation with a $TiOSO_4/H_2SO_4$ reagent. The amount of H_2 and O_2 in the entering and exiting gas streams was determined by gas chromatography using a HP 5890 chromatograph with a 5A molecular sieve column at 30 $^\circ$C. Argon was the carrier gas. For selectivity determinations, improved accuracy in the H_2 analysis was achieved by using a H_2/N_2 gas mixture that contained 10% N_2. The selectivity for H_2O_2, $S_{H_2O_2}$, is defined by

$$S_{H_2O_2} = \frac{\text{Rate of } H_2O_2 \text{ production (mol/min)}}{\text{Rate of } H_2 \text{ consumption (mol/min)}} \times 100.$$

Transmission electron microscope (TEM) images of the fresh and used silica material were obtained using a JEOL 2010 TEM instrument operating at 200 kV. The material was suspended in 100% ethanol by vigorous shaking. One drop of the slurry was deposited on a carbon-coated copper grid. The liquid phase was evaporated before the grid was loaded into the microscope. Both bright-field and dark-field images were recorded. The identity of the palladium particles was

Fig. 1. Schematic of (A) open and (B) closed reactors.

confirmed by electron diffraction. Optical microscopy images were obtained with a HIROX 3D microscope.

3. Results and discussion

3.1. The state of the catalyst

One of the surprising results from the previous study in this laboratory [6,7] was that in aqueous solutions $\geqslant 0.1$ N in HCl the palladium, originally supported on silica, left the support and was found in the slurry as $PdCl_4^{2-}$, colloidal palladium, and palladium black. The palladium black was deposited on the frit and was observed in the slurry as rather large, loosely bound conglomerates of smaller Pd particles. In the earlier work Davison grades 03 and 57 silica were used, both of which had significant internal pore structures that originally contained the Pd particles. An induction period in the formation of H_2O_2 was attributed to the slow transport of $PdCl_4^{2-}$ out of the pores, which is the initial step in the formation of the colloidal Pd.

The Cab-O-Sil material used in the present study is microspheroidal and as such has no internal pore structure. As shown in Fig. 2A, the Pd particles have a maximum in the particle size distribution of about 2.5 nm, which is smaller than the 6-nm average particle size that was found for the colloid derived from $Pd/SiO_2(57)$. Moreover, it is expected that the Pd^0 on the external surface of the microspheres would be more accessible for the formation of $PdCl_4^{2-}$. Consistent with this view, no induction period was observed when palladium supported on Cab-O-Sil was introduced to the system.

Nevertheless, with time in the presence of HCl and O_2 the dissolution of Pd occurs, and after ca. 2 min the yellow color of aqueous $PdCl_4^{2-}$ may be observed. Furthermore, after 2 h the active component, believed to be colloidal palladium, was largely suspended in the liquid as shown by the results of Fig. 3. That is, when the solid phases were removed by centrifugation and the liquid phase containing the colloid was returned to the reactor, the rate of H_2O_2 formation was unchanged. Observation of the solid phase by optical microscopy showed that the microspheroidal silica, present in the original sample, was transformed into relatively large particles of silica gel, approximately 200 μm in size, as shown in Fig. 4. The TEM results (not shown) revealed no supported Pd particles in the nanometer size range; although large agglomerates of palladium black may be seen on the silica gel particles as shown in Fig. 4B. The palladium black and the residual silica were introduced to a fresh acidified solution, and it was observed that over a period of 2.5 h, no H_2O_2 was produced. Upon standing overnight in air the slurry became yellow in color as a result of the slow oxidation of palladium black to $PdCl_4^{2-}$.
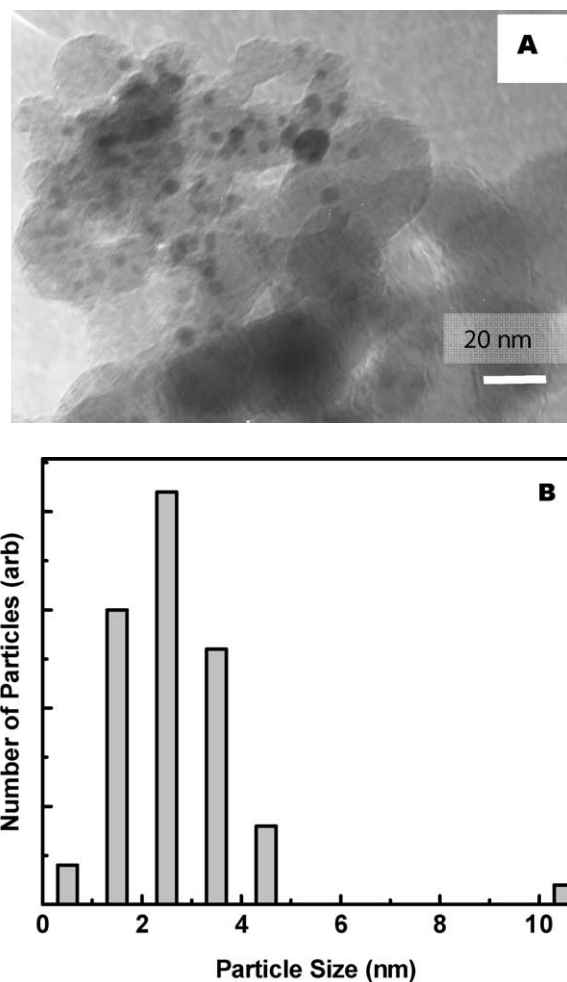

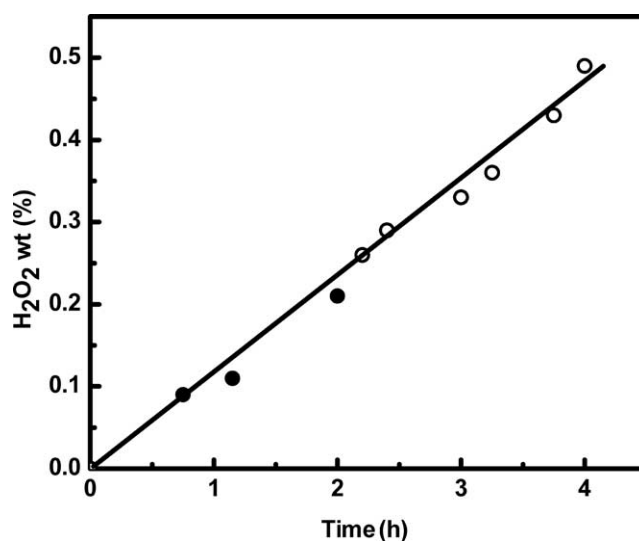Fig. 2. (A) Electron micrograph of fresh Pd/Cab-O-Sil catalyst; (B) particle size distribution of palladium.

Fig. 3. Catalytic formation of H_2O_2 (●) before and (○) after removal of the solid phases from an aqueous solution that was 0.1 M in HCl and 0.01 M in Br^-. The O_2/H_2 ratio was 4.
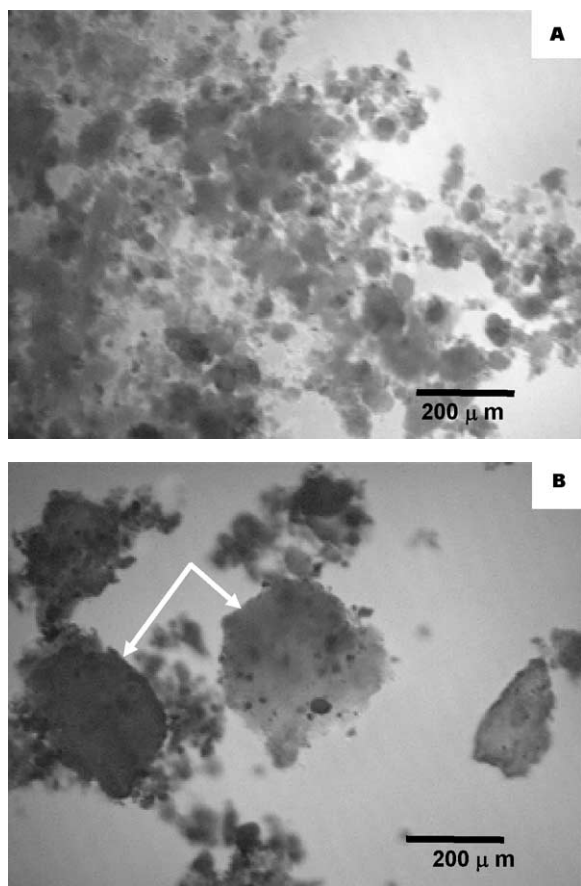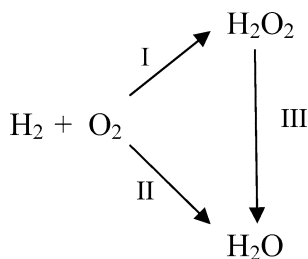
Fig. 4. Optical microscope images of (A) fresh Pd/Cab-O-Sil and (B) the solid phase after 2 h of reaction in 0.1 N HCl and 0.01 M Br⁻. The larger particles (ca. 200 μm) indicated by the arrows are silica gel.

Scheme 1.

3.2. The effects of Br⁻ ions and O_2/H_2 ratio on the formation of H_2O_2

As noted in the Introduction, halide ions have a signifi-cant effect on the yield of H_2O_2 over Pd. Bromide ions are especially effective as demonstrated by Gosser [12]; how-ever, it was not known whether these ions increased the rate of H_2O_2 formation from H_2, the selectivity for H_2O_2 formation in contrast to the direct H_2O formation, or the sta-bility of H_2O_2 with respect to decomposition or reduction by H_2 (Scheme 1). The results shown in Fig. 5 provide insight into some of these possibilities. A comparison of results ob-tained with and without bromide in the system reveals that the presence of Br⁻ increases the overall selectivity from
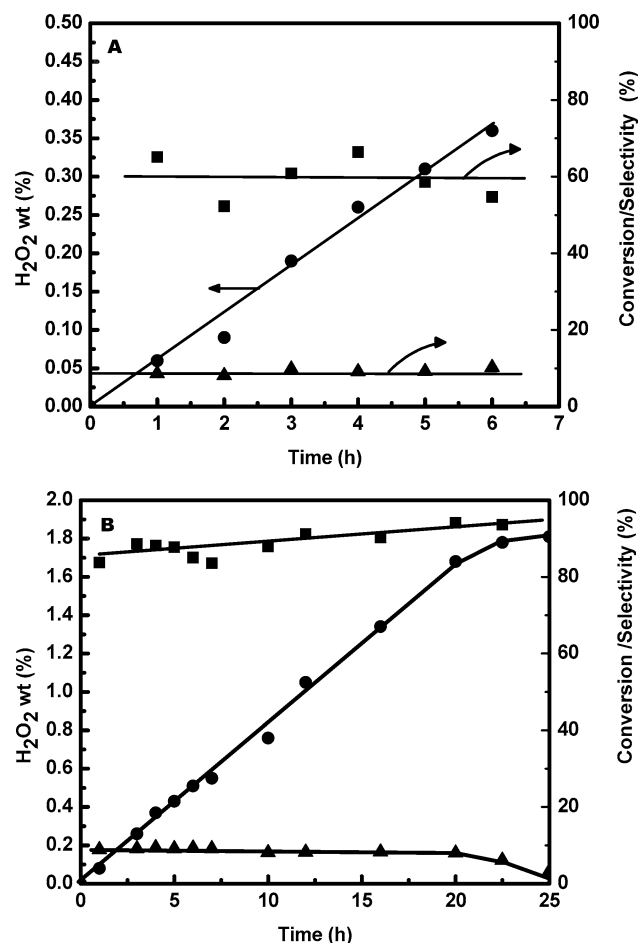

Fig. 5. Formation of H_2O_2 (A) in the absence of Br⁻ and (B) in the presence of Br⁻ (0.01 M); (●) wt% H_2O_2, (▲) H_2 conversion, and (■) selectivity for H_2O_2. The solution was 0.1 N in HCl and the O_2/H_2 gas ratio was 4:1.

about 60%, in agreement with results reported in our pre-vious study [7], to greater than 90%. By contrast the H_2 consumption rate, which corresponded to ca. 9% conversion, was not significantly affected by Br⁻ ions. The observation that the selectivity for H_2O_2 remained almost independent of the H_2O_2 concentration suggests that Br⁻ ions increase the selectivity for H_2O_2 formation (reaction I in Scheme 1), rather than inhibit the further reduction or decomposition of H_2O_2 (reaction III). For example, Br⁻ on the surface may block sites for the dissociation of O_2, as suggested by Burch and Ellis [13], thereby inhibiting the formation of H_2O. By contrast, we demonstrated previously that protons (or HCl) inhibit reaction III, which is a conclusion reached much ear-lier by Pospelova et al. [8].

These results at first appear to be in disagreement with those reported by Landon et al. [4], who found that the H_2O_2 selectivity decreased with time while the H_2O_2 concentra-tion first increased and then remained rather constant. The difference in results may be explained by the fact that Lan-don et al. used a closed system in which H_2 was continuously being depleted; whereas, in the present study, H_2 was con-tinuously being supplied to the liquid phase, which enabled
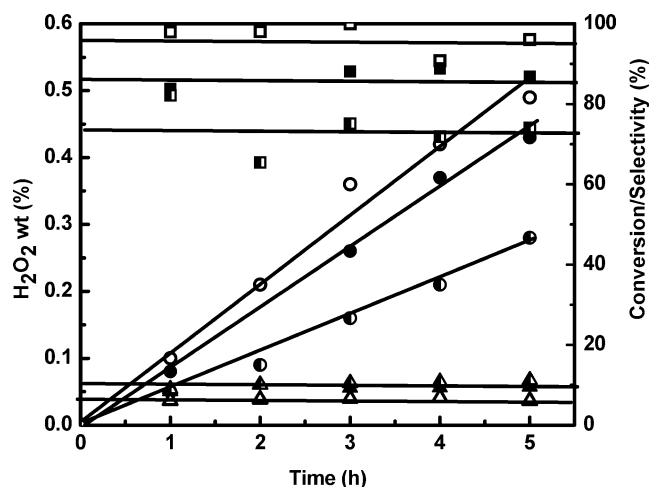
Fig. 6. Effect of $O_2:H_2$ ratio on the formation of H_2O_2: ($\bigcirc$) wt% H_2O_2, ($\triangle$) H_2 conversion, and ($\square$) selectivity at a 2:1 ratio; ($\bullet$) wt% H_2O_2, ($\blacktriangle$) H_2 conversion, and ($\blacksquare$) selectivity at a 4:1 ratio; ($\diamondsuit\!\!\!\bullet$) wt% H_2O_2, ($\blacktriangle$) H_2 conversion, and ($\blacksquare\!\!\square$) selectivity at a 6:1 ratio.

us to obtain a steady-state reaction for a long period. Landon et al. [4] also concluded that Br^- (or HBr) also suppresses the hydrogen combustion, but in their experiments HBr was found to decrease the conversion of H_2, indicating a nonselective poisoning of active sites.

As shown in Fig. 5B, the concentration of H_2O_2 reached after 20 h was 1.7 wt%. In a separate reaction carried out in reactor A, a concentration of 2.8 wt% was reached in 24 h. This is comparable to the concentration of H_2O_2 produced as the raw product in a commercial process and is considerably greater than the concentration of about 0.7 wt% reported previously [7]. The net rate of H_2O_2 formation, deduced from the slope of the concentration curve, was 10 mmol H_2O_2 g_{Pd}^{-1} min^{-1}, which corresponds to a turnover frequency (TOF) of about 1 min^{-1} based on the *total* amount of Pd present.

In the presence of Br^- ions the rate of H_2O_2 formation remained constant over a period of 20 h, but over an additional 5-h period the formation rate decreased to zero. As the formation rate decreased, the selectivity remained nearly constant. The decrease in activity is apparently a result of the net loss of colloidal palladium from the system.

The O_2/H_2 ratio had a significant effect on the selectivity, and consequently on the rate of H_2O_2 formation as shown by the results of Fig. 6. These experiments were carried out at a constant total flow rate. Larger O_2/H_2 ratios resulted in smaller selectivities for H_2O_2 formation, which indicates that reaction II has a higher order with respect to O_2 than reaction I; i.e., water is increasingly the product at larger O_2/H_2 ratios. Alternatively, the larger partial pressure of H_2 at the 2:1 O_2/H_2 ratio may favor reaction I. The percentage of H_2 converted increased as the O_2/H_2 ratio increased, but the moles of H_2 converted increased with decreasing O_2/H_2 ratio (increasing H_2 partial pressure), as might be expected from Scheme 1. The results obtained over a 5-h period show that the 2:1 ratio is favorable for achieving larger formation
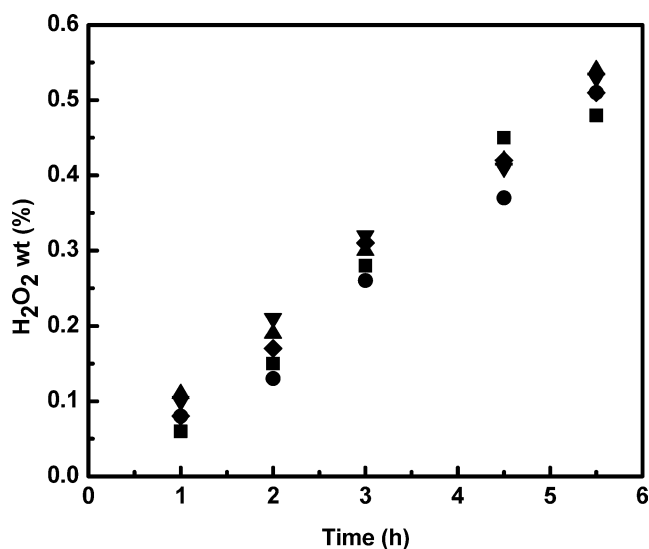

Fig. 7. Formation of hydrogen peroxide (H_2O_2, HDO_2 and D_2O_2) in different isotopic combinations: ($\bullet$) HCl, H_2O, $H_2 + O_2$; ($\blacksquare$) DCl, D_2O, $D_2 + O_2$; ($\blacklozenge$) HCl, D_2O, $D_2 + O_2$; ($\blacktriangle$) HCl, H_2O, $D_2 + O_2$; ($\blacktriangledown$) DCl, D_2O, $H_2 + O_2$.

rates for H_2O_2; however, for longer reaction times the rate at the 2:1 ratio decreased, and the frit became dark gray, indicating the deposition of palladium black. This is consistent with the larger partial pressures of H_2 at the interface between aqueous $PdCl_4^{2-}$ and the frit.

3.3. Absence of a kinetic isotope effect

In order to determine whether a kinetic isotope effect (KIE) existed, several combinations of H_2, D_2, HCl, DCl, H_2O, and D_2O were investigated, and the results are shown in Fig. 7. All of the net rates of H_2O_2, HDO_2, and D_2O_2 formation are the same, possibly with the exception of the HCl, H_2O, $H_2 + O_2$ combination which might have a slightly slower rate. This, however, would indicate an inverse KIE, which seems unlikely. The normal KIE for H_2 vs D_2 bond-breaking reactions at comparable temperatures is in the range of 2–5. For example, the reactions $OH + H_2 \rightarrow H_2O + H$ and $OH + D_2 \rightarrow DHO + D$ have a KIE of 5.4 at 250 K and 3.3 at 298 K [14]. Clearly, such a large KIE effect was not observed during the formation of hydrogen peroxide. The absence of a KIE is consistent with the reaction being transport limited, although other explanations may be valid. In particular, the formation of a palladium peroxy complex (see below) or the reaction of this complex with protons may be the rate-limiting steps in a catalytic cycle.

3.4. Transient studies

The present study, which utilized the continuous flow of gases, was suitable for transient studies that provide information on the factors affecting the subsequent reactions of H_2O_2 and, therefore, the net rate of H_2O_2 formation. The results obtained from the first set of transient experiments,
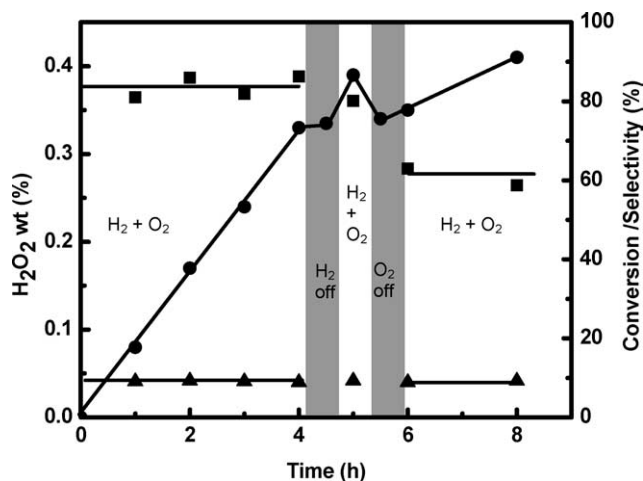
Fig. 8. Effect of gas compositions on (●) wt% H_2O_2, (▲) H_2 conversion, and (■) selectivity. The total gas flow rates were 30 mL min^{-1}. When present the flow rates of O_2 and H_2 were 24 and 6 mL min^{-1}, respectively. Helium was added, if needed, to maintain a constant total flow rate.

shown in Fig. 8, confirm that the H_2O_2 is stable in the presence of O_2 without H_2. During this period the solution became yellow, indicating that $PdCl_4^{2-}$ was being formed. When the H_2 was again mixed with O_2, the solution returned to being nearly colorless except for the gray cast that resulted from the palladium black, and the formation of H_2O_2 was renewed. The deletion of O_2 from the gas mixture resulted in an increase in the decomposition of H_2O_2, in agreement with the observations of other investigators [4,8] who have found that H_2 promotes the decomposition of or reacts with H_2O_2. Finally, exposure of the system to H_2 and O_2 for the third time again resulted in the formation of H_2O_2, albeit with a much smaller selectivity. Surface bromine may have been depleted in an irreversible manner. In these experiments He was used to replace H_2 or O_2 when either was deleted from the gas stream; thus, the total flow rate was kept constant.

The second transient experiment was designed to determine whether reaction (1) or reaction (2) was primarily responsible for the loss of H_2O_2 in the presence of only H_2. It is possible that H_2 removed O (or Br) from the Pd surface and caused it to be more active for reaction (2). If reaction (2) were dominant, one would expect to observe the continuous formation of O_2. In the transient experiment, O_2 was turned off and the evolution of O_2 from the system was followed as the reaction of H_2O_2 occurred. Prior to the time when O_2 was turned off, the experiment had proceeded for 4 h and the liquid phase contained 0.39 wt% H_2O_2. After 35 min with only H_2 flowing, the H_2O_2 concentration was 0.32 wt%, which corresponds to a H_2O_2 decomposition rate of 2.8×10^{-2} mmol/min or an anticipated O_2 production according to reaction (2) of 1.4×10^{-2} mmol/min. The rate of H_2O_2 loss was nearly constant. After 35 min the measured O_2 evolution from the system was 3×10^{-3} mmol/min, which is about 1/5 of that expected from the decomposition pathway. A blank experiment also was carried out in which O_2 and He were passed through an 0.1 N HCl solution, the

O_2 was turned off, and after 35 min the O_2 evolution rate was essentially the same as that determined during the loss of H_2O_2. These results indicate that reaction (2) is not significant and that most of the H_2O_2 is lost via reduction of by H_2 [reaction (1)]. With a different Pd catalyst and at much higher pressures of H_2, Landon et al. [4] likewise concluded that reaction (1) was dominant.

3.5. Insight into the reaction mechanism: The possible role of H_3O^+

Although the direct formation of H_2O_2 from H_2 and O_2 has traditionally been considered to be a heterogeneous catalytic process, Stahl and co-workers [10] have proposed a cycle based on mixed-ligand homogeneous complexes with (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) Pd^0 (η^2-dibenzylideneacetone) as the starting point. The addition of O_2 results in the displacement of the dibenzylideneacetone ligand and the formation of a peroxy complex that has been characterized by infrared spectroscopy and X-ray diffraction. Most importantly, from our perspective, this complex reacts with protons to produce H_2O_2 in 73% yield.

In the present study, the possible role of H_3O^+ was investigated by first preparing a Pd/SiO$_2$ material that contained no palladium hydride. A 100-mg sample was reduced in a 35% H_2 in He gas mixture for 3 h at 400 °C and then exposed to pure He for 2 h at 350 °C to decompose any hydride that may have been present. Under the flow of He, the sample was transferred to the aqueous phase that had been presaturated with O_2. The solution was 0.1 N in HCl. Apart from the water itself, the only source of hydrogen in the system was the H_3O^+. The solution was subsequently tested for H_2O_2, and it was found that 2.7×10^{-2} mmol of H_2O_2 was present, which may be compared with 4.7×10^{-2} mmol Pd in the system. The H_3O^+, of course, was in large excess. During the process $PdCl_4^{2-}$ was formed as indicated by the orange color of the solution. These results suggest that a palladium peroxy species may react with H_3O^+ in the aqueous phase to form H_2O_2.

By analogy with the catalytic cycle proposed by Stahl et al. [10], one may construct the cycle shown in Scheme 2 for the system described here. In this cycle Pd^0 in the form of a colloid reacts with O_2 in the presence of chloride ions to form a dichloroperoxopalladium(II) complex which subsequently reacts with H_3O^+ to yield H_2O_2 and $PtCl_4^{2-}$. The $PdCl_4^{2-}$ is then reduced back to the colloidal state by H_2, with the formation of HCl. In our system visual observation confirms that the reduction of $PdCl_4^{2-}$ in the presence of H_2 is a rapid process that occurs on the time scale of seconds. The reaction back to $PdCl_4^{2-}$ occurs on the time scale of several minutes, which is consistent with the observed TOF of about 1 min. Raman studies to detect the peroxo complex are underway; however, this may be difficult if its rate of reaction with protons is faster than its rate of formation. The possible involvement of this homogeneous-heterogeneous mechanism is an interesting alternative to a
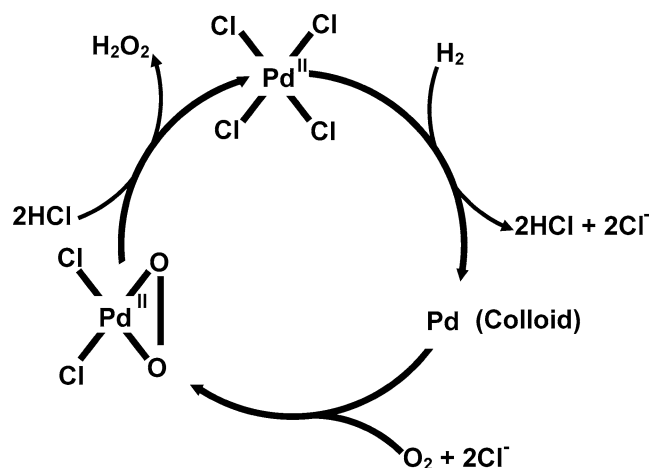
Scheme 2.

purely homogeneous process in which surface H reacts with a peroxo complex on Pd.

As a variation on this scheme, the peroxy species may form on the surface of colloidal Pd^0, in a manner similar to that which occurs on Pd(111) surfaces at low temperatures under UHV conditions [15]. Hydronium and chloride ions then react corrosively with the surface palladium peroxide to form H_2O_2 and $PdCl_4^{2-}$. This variation is attractive because it provides a plausible explanation for the role of bromine in inhibiting the dissociation of diatomic oxygen on Pd^0.

4. Conclusions

1. Palladium supported on microspheroidal silica is an effective source of colloidal palladium that is active and selective as a catalyst for the direct conversion of H_2 and O_2 to H_2O_2.
2. The presence of Br^- ions increases the selectivity for H_2O_2, possibly by blocking sites for O_2 dissociation with the subsequent formation of H_2O.
3. No KIE was observed when various combinations of H_2, D_2, HCl, DCl, H_2O, and D_2O were used. This observation is consistent with a transport-limited reaction.
4. Hydrogen peroxide is stable in the presence of O_2 but is reduced by H_2 to H_2O.
5. Hydronium ions, rather than adsorbed hydrogen, may react with a peroxo species to form H_2O_2. The H_3O^+ is reformed during the reduction of $PdCl_4^{2-}$ by H_2.

Acknowledgments

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