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A comparison of ethanol and water as the liquid phase in the direct formation of H_2O_2 from H_2 and O_2 over a palladium catalyst

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Ethanol and water have been compared as the media in which hydrogen peroxide is produced from the reaction of H_2 and O_2 over a palladium catalyst. There are significant differences between the reaction in the two media with respect to the net rate of H_2O_2 formation, the state of the active Pd and the mechanism of the reaction. The reactions were carried out at atmospheric pressure and at 10 °C, with O_2 and H_2 being introduced in a 4:1 ratio through a glass frit. In ethanol, using 50 mg of 5 wt% Pd/SiO_2, 1.8 wt% H_2O_2 was attained in 7 h; whereas, about half this amount was attained in water. In addition, the net formation rate did not remain constant in water. Both systems were 0.17 N in HCl, which facilitated the formation of colloidal Pd in water but not in ethanol. The loss of activity in water is attributed to the instability of the colloid, which has been shown previously to be the active state of Pd. By contrast, these results show that supported Pd is the active state of the metal in the ethanol system. The mechanism for the formation of the nonselective product, water, also is affected by the media in which the reaction is carried out. In ethanol, water is formed by the direct reaction of H_2 and O_2, while in the aqueous phase, water appears to be formed both by the direct pathway and by the reduction of H_2O_2.

KEY WORDS: hydrogen peroxide; hydrogen; oxygen; palladium; ethanol; water.

1. Introduction

Hydrogen peroxide is commercially produced by a circuitous process involving alkylanthroquinone and hydroquinone intermediates [1]. For environmental and economic reasons there is renewed interest in replacing this process with one in which H_2 and O_2 are reacted together over a suitable catalyst. Although the direct process has been known to occur for many years [1], systematic studies have only recently shown that commercially acceptable yields of H_2O_2 may be achieved, even at moderate pressures [2]. The mechanism of the reaction has been addressed, although the system involves three phases (solid catalyst, gaseous reagents and liquid medium) and transport limitations make fundamental studies difficult [2–6].

A primary focus of this investigation was to compare water and ethanol as the liquid phases. Hydrogen peroxide in both of these media has practical applications. Water, for example, would be the solvent of choice in H_2O_2 solutions used for the bleaching of paper; whereas, ethanol (or another alcohol) would be better for epoxidation reactions in which H_2O_2 is used as the source of oxygen [7]. Ethanol is potentially a better medium than water for carrying out the synthesis reaction because of a fivefold larger solubility of H_2 and an eightfold greater solubility of O_2 [2]. In addition, the surface tension of ethanol is considerably greater than that of water and the viscosity is somewhat less. Both of these factors contribute to a smaller bubble size when the reagent gases are dispersed through a frit [8], as was the case in these experiments.

Thompson and coworkers [2] carried out a study in which several different organics (methanol, ethanol, isopropanol, dioxane and acetone), as well as water, were used as the liquid phase, and palladium supported on a hafnium phosphate viologen phosphonate material was the catalyst. Even though their system was limited by mass transfer at the liquid–gas interface, differences in the rate of H_2O_2 formation were observed among the organics, with methanol being the most favorable for achieving the largest rate. In ethanol, the rates were somewhat less. The results obtained with water depended very strongly on the acid that was used. (An acid is always required in the direct formation of H_2O_2.) Curiously, Thompson and coworkers found that with H_2SO_4 as the acid no H_2O_2 was produced, but with HCl as the acid the H_2O_2 formation rate in water, at least initially, was comparable to that observed with the organics. Possible reasons for these differences in acid/liquid phase will be discussed in this note.

Another, but related, issue is the state of the active palladium. Previously we have presented evidence that in the HCl/aqueous system colloidal palladium is formed under reaction conditions, even when the metal is introduced as Pd/SiO_2 [4–6]. This colloidal Pd is believed to be involved in a catalytic cycle that may be, in part, homogeneous. Although such a system is very interesting at a fundamental level, the management of a

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colloid would be difficult in a commercial process. In such a process one would prefer a traditional supported catalyst, which would allow convenient separation of the catalyst from the product. We will present evidence that with the HCl/ethanol system, supported Pd is the primary form of the active catalyst, rather than the colloid.

2. Experimental

2.1. Preparation of catalyst and reactivity measurement

Palladium was introduced to the system as Pd (5 wt%) 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 an aqueous solution of $PdCl_4^{2-}$ and was reduced in H_2 as described previously [9]. Briefly, the material was pretreated in O_2 at 400 °C and reduced at 300 °C under 20 mL min^{-1} of flowing H_2 for 30 min.

The reactions were carried out at atmospheric pressure and at 10 °C in one of the two reactors described in Ref. [6]. The reagent gases were introduced into the reactors via a fine glass frit and the slurry containing the catalyst was stirred so as to minimize diffusion limitations. One of the reactors was open to the atmosphere at the top, and the other was connected to a gas chromatograph so that the concentration of H_2 exiting the reactor could be periodically determined. Improved accuracy in the H_2 analysis was achieved by using a H_2/N_2 mixture that contained 10% N_2. The H_2O_2 formed during reaction was analyzed colorimetrically after complexation with a $TiOSO_4/H_2SO_4$ reagent. The selectivity for H_2O_2, $S_{H_2O_2}$, was determined from the rate of H_2O_2 formation and the rate of H_2 conversion using the equation

$$S_{H_2O_2} = \frac{\text{Rate of } H_2O_2 \text{ formation (mole/ min)}}{\text{Rate of } H_2 \text{ conversion (mole/ min)}} \times 100 \tag{1}$$

Most experiments were carried out using a 4:1 O_2/H_2 gas mixture at a total flow rate of 50 mL min^{-1}. The liquid phase consisted of 50 mL of ethanol or water that had been acidified with 10 mL of aqueous HCl solution to give 60 mL of liquid having the desired acid normality. Thus, the "ethanol solution" contained 10 mL of water in addition to the small amount of water that was formed during reaction. The solutions were 0.17 N in HCl unless stated otherwise. Following each experiment residual Pd that had deposited in the frit was removed by filling the reactor with a 1 N HCl solution and passing pure O_2 through it. In most cases a yellow–orange color solution, resulting from $PdCl_4^{2-}$, was observed.

Since the 4:1 O_2/H_2 gas mixture is in the explosive regime, care was taken to avoid contact of the gas mixture with a dry catalyst. This was achieved by first mixing 50 mg of the catalyst with 10 mL of the solution and returning this slurry to the solution that remained in the reactor. It should be noted that with ethanol as the liquid phase the catalyst remained wet, even in the upper regions of the reactor, but when experiments were carried out with methanol, which has a larger vapor pressure, explosions occurred as particles of the catalyst became dry! Experiments utilizing methanol were discontinued.

2.2. Characterization of the catalysts

X-ray diffraction (XRD). The X-ray powder diffraction patterns were measured with a Bruker D8 diffractometer using Cu K(α) radiation.

Transmission electron microscopy (TEM). TEM measurements were performed on a 200 keV microscope (JOEL 2010). The catalyst was suspended in ethanol, and one drop of this slurry was deposited on a carbon-coated copper grid. The liquid phase was evaporated before the grid was loaded into the microscope. Larger particles of Pd (> 5 nm) were identified by energy dispersive X-ray (EDX) analysis.

X-ray photoelectron spectroscopy (XPS). A Perkin–Elmer (PHI) Model 5500 spectrometer with Mg-K(α) radiation was used to obtain Pd and Si binding energies and relative amounts of Pd in the samples. The binding energy (BE) of Pd was referenced to the Si(2p) peak at 103.1 eV.

3. Results

3.1. Characterization of the solid phase

As determined from TEM images, palladium in the original reduced material had an average particle size of 6 nm with particles being mainly in the range of 4–8 nm. This is approximately the size of the colloidal particles derived from Pd/SiO_2 under reaction conditions [4,5]. After 5 h of reaction in ethanol the Pd particles grew somewhat as indicated by the results shown in figure 1a, from which the maximum in the particle size distribution was determined to be at about 8 nm; however, there were a few particles in this material that had a particle size greater than 20 nm. From the results of figure 1b, which was obtained after 5 h of reaction in water, it is evident that much larger particles were present, some of which exceeded 250 nm in size. These larger particles may have been present in the aqueous phase as Pd black, rather than as supported Pd. The maximum in the particle size distribution in this sample was at about 10 nm.

From X-ray diffraction line broadening a particle size of 4 nm for the fresh sample and the sample after reaction in ethanol was determined using the Scherrer equation. The calculated particle size was 6 nm after reaction in water. Obviously the line broadening analysis did not reflect the presence of the considerably larger

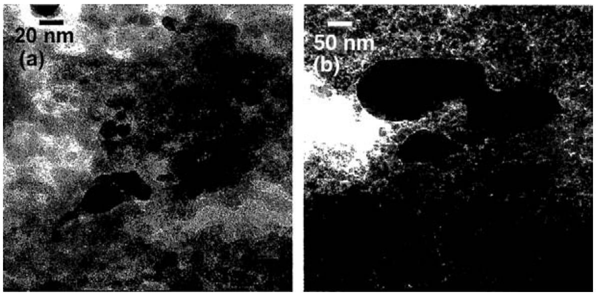


Figure 1. TEM images of the solid phases after the catalytic formation of H_2O_2 had occurred for 5 h in (a) ethanol and (b) water.

particles. A sample of Pd powder (Johnson Matthey Puratronic grade) had a particle size of 34 nm as determined by XRD line broadening. The XRD patterns also confirmed that Pd was present in the metallic state; no evidence was found for crystalline PdO.

Analysis of the fresh Pd/SiO_2 catalyst by XPS revealed lines at 335.1 and 340.4 eV, which are characteristic of Pd(0) in the $3d_{5/2}$ and $3d_{3/2}$ states, respectively. The sample after reaction in ethanol exhibited lines at 335.3 and 340.6 eV. Within experimental error these values are the same as those observed for the fresh catalyst. Following reaction in water the binding energies were shifted to 335.8 and 341.1 eV, and the full width at half maximum was increased from 2.7 eV in the fresh sample to 3.4 eV. The increase in both the binding energies and the line widths suggest that some Pd(II) may have been present on the sample, perhaps as $PdCl_2$. The binding energies for Pd(II) are at 336.5 and 341.6 eV [10].

3.2. H_2O_2 formation conversion of H_2 and selectivity in ethanol and water

The increase in the concentration of H_2O_2 as a function of time for the two liquid phases is shown in figure 2a. Clearly, there are significant differences in the results obtained with the two media. In ethanol, the formation of H_2O_2 remained almost constant over a period of 8 h, which is important from a practical viewpoint, and the concentration of H_2O_2 approached 2 wt%. The specific rate in ethanol was 22 mmole H_2O_2 g_{Pd}^{-1} min^{-1}. In H_2O the concentration of H_2O_2 reached only about 1 wt% during the same period, and the initial H_2O_2 formation rate (taken as the slope of the H_2O_2 concentration versus time curve) was ca. 80% of the rate in ethanol. Contrary to the results of Choudhary and coworkers [11], supported PdO was found to be an inactive catalyst under our experimental conditions.

In addition to the increased rate of H_2O_2 accumulation, the rate of H_2 consumption also increased in ethanol as shown in figure 2b. Thus, the activity for all hydrogenation reactions (see below) generally increases. The rate of H_2 consumption remained nearly constant over the 8 h period. By contrast, in water the rate of H_2 consumption decreased initially and was less over the entire period than that observed with ethanol as the liquid phase.

The results of figure 2c depict the changes in selectivity that occurred in both media. The selectivity in ethanol remained constant at 35%, while the selectivity in water decreased from about 50% to 36% over 6 h and thereafter remained constant. The nearly equivalent steady state selectivities are probably fortuitous considering the complexity of the two systems.

Results obtained with a medium composed of 30 mL of ethanol and 30 mL of water, with other components being the same, showed H_2O_2 formation rates and H_2 consumption rates that were intermediate between those obtained with nominally pure ethanol and with water. After 7 h the concentration of H_2O_2 was 1.3 wt%, and the H_2 conversion was 20%. The steady state H_2O_2 selectivity, however, was 51%, which is larger than that

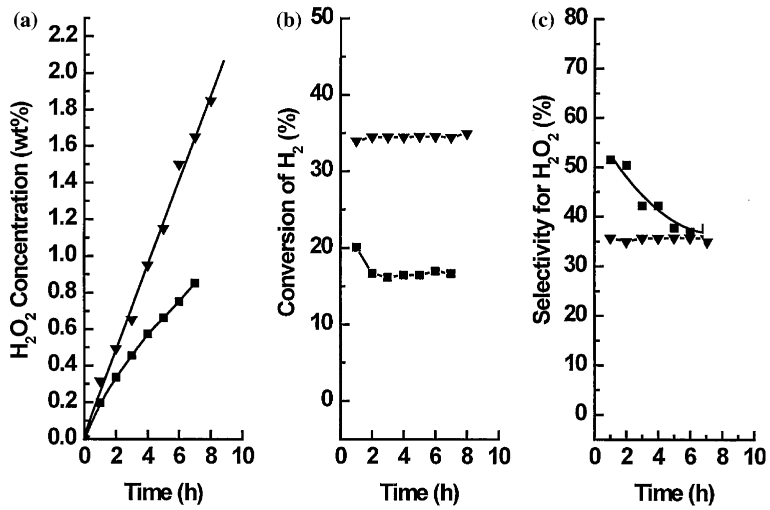


Figure 2. Catalytic formation of H_2O_2 in ethanol (▼) and water (■) as a function of time: (a) H_2O_2 concentration, (b) conversion of H_2 and (c) selectivity for H_2O_2.

reported for either nominally pure ethanol or water. These results confirm that, except for moderate changes in selectivity, the small amount of water present in the nominally pure ethanol would not significantly affect the behavior of this system.

The differences observed with ethanol and water as the liquid phases may result from secondary reactions involving the reduction of H_2O_2 by H_2. This secondary reduction of H_2O_2 is negligible in ethanol as shown by an experiment in which H_2O_2 was added after 2 h of reaction. As a result of this addition, the H_2O_2 concentration was increased from 0.7 to 1.7 wt%. The formation of H_2O_2 then continued at *the same net rate* for an additional 4 h. By contrast, with water as the liquid phase the concentration of H_2O_2 reached 0.3 wt% after 2 h and was increased to 0.8 wt% by the addition of H_2O_2. Thereafter, in contrast to the results obtained in ethanol, the concentration of H_2O_2 slightly decreased over the next 3 h to a level of 0.7 wt%. From figure 2a the expected concentration of H_2O_2 after 5 h would have been about 0.6 wt%. The results in water can be understood in terms of H_2O_2 reduction that occurs at a rate comparable to the rate of H_2O_2 formation. The rate of H_2O_2 reduction will depend on the concentration of H_2O_2; thus, at longer reaction times there is a decrease in the net rate of H_2O_2 formation as is evident from figure 2a for the water system.

3.3. The state of the active palladium

Experiments were carried out to determine whether the active form of palladium was mainly colloidal Pd, as determined previously for aqueous systems [4–6], or whether supported Pd might be active with ethanol as the liquid phase. Evidence for the role of colloidal Pd was based to a large extent on the observation that the H_2O_2 formation continued even after the remaining solids, including the silica and palladium black, had been removed from the system by centrifugation [4–6]. This type of experiment was repeated with 10 mg of catalyst, and the results are shown in figure 3. In water, as reported previously, the H_2O_2 formation reaction continued at the same rate after the solids had been removed and the liquid was returned to the reactor. It is important that the procedure be carried out within a couple of minutes to prevent the oxidation of colloidal Pd and that the glassware be free of detergent. When ethanol was the liquid phase, no H_2O_2 formation was observed after the solids had been removed, but after the solids were returned to the reactor the formation continued, albeit at a slower rate. Some of the Pd may have been lost during the transfer of materials. The results obtained with the ethanol system show that H_2O_2 is formed on supported palladium.

The results of figure 3 also provide insight into the effect of catalyst amount. With the ethanol system the rate of H_2O_2 formation was linearly proportional to the amount of catalyst; i.e., with 1/5 the amount of catalyst the amount of H_2O_2 formed after 1 h was reduced by a factor of 5. This was not the case with the water system, for which the amount of H_2O_2 formed decreased more than a factor of 5. The latter result is not surprising since only a fraction of the Pd that leaves the surface forms the colloid. The remaining material is present mainly as Pd black, although some may deposit on the walls of the reactor or on the frit, particularly when the O_2/ H_2 ratio is less than 4 [4,5].

The state of Pd is also evident from the results depicted in figure 4, which show the concentration of Pd^{2+} and the concentration of H_2O_2 formed as a

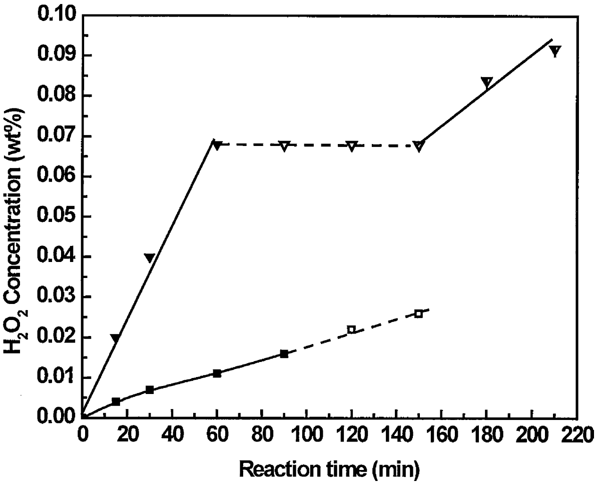


Figure 3. Catalytic formation of H_2O_2 in ethanol and aqueous phases before and after the removal of 10 mg catalyst: in ethanol (▼) before and (▽) after, and in water (■) before and (□) after removal of the catalyst; (⧨) after addition of the solid phase back to the ethanol system.

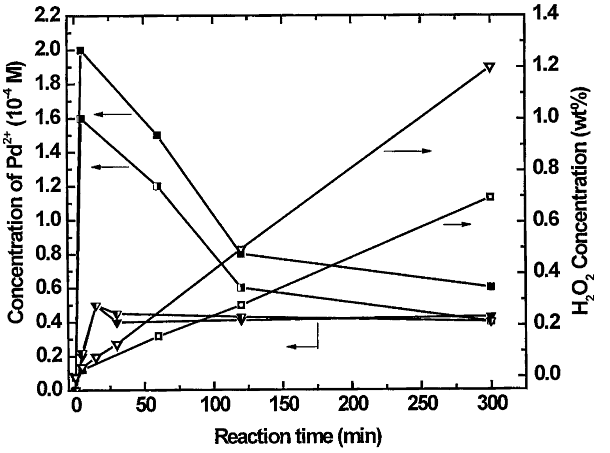


Figure 4. Time dependent Pd^{2+} and H_2O_2 concentrations. Concentration of Pd^{2+} in the aqueous phase: (■) original and (◧) after standing in air for 12 h. Concentration of Pd^{2+} in the ethanol phase: (▼) original and (⧨) after standing in air for 12 h. Concentrations of H_2O_2 formed in (□) water and in (▽) ethanol.

function of reaction time with 50 mg of catalyst, which is equivalent to 4.0×10^{-4} M if all of the Pd formed Pd^{2+}. The amount of Pd^{2+} was determined by a spectrophotometric technique [12] and was confirmed by inductively coupled plasma (ICP) analysis. A 3 mL aliquot was removed from the reactor after particular reaction times. After centrifuging out the solids, part of the sample was analyzed for H_2O_2 and part was analyzed immediately for Pd^{2+}. The remainder was allowed to stand overnight in air and was analyzed for Pd^{2+}. The difference is taken to be the amount of colloidal Pd present in the sample. Even though a significant amount of the slurry was removed from the system over the course of the reaction, the H_2O_2 formation rates were essentially the same as those shown in figure 2. During the early stages of the reaction, the distribution of Pd in the system was quite different for the two liquids. With water 40% of the Pd had entered the solution as Pd^{2+} and another 10% was present as colloidal Pd. These amounts decrease to 10% and 5%, respectively. The Pd^{2+} and colloidal Pd lost during the 5 h of reaction in water is converted to Pd black, as confirmed by an experiment in which the Pd was introduced as $PdCl_2$. With ethanol as the liquid phase, approximately 10% of the Pd was lost from the catalyst as Pd^{2+} during the first 5 min, but thereafter the concentration of Pd^{2+} in solution remained nearly constant. Moreover, none of the Pd was present in the colloidal form, within experimental error. These results support the view that H_2O_2 is formed over supported Pd in the ethanol system and over colloidal Pd in the aqueous system; however, since only a relatively small fraction of the Pd is present as the colloid, the specific activity of the colloid is greater than that of the supported Pd. This observation must be understood in light of transport phenomena. That is, transport of the reagents to the colloidal Pd may be more efficient than transport to the supported Pd.

For comparison with supported Pd, it was of interest to determine the catalytic properties of pure Pd black powder. With 50 mg of Pd powder (20 times the amount introduced as the Pd/SiO_2 catalyst), the rate of H_2O_2 formation was about 1/6 of that shown in figure 2 for the HCl/ethanol system. Meanwhile, the selectivity was only 12%. The much lower selectivity for the Pd black powder suggests a particle size effect (i.e., lower selectivity with larger particles). In the aqueous phase only very small amounts of H_2O_2 were formed, and the extent of H_2 consumption was below the detection limits. This may reflect the lower solubility of the gases and the larger bubble size in water, but it also may result from the inability of the system to form significant amounts of colloidal Pd from the Pd black. Colloidal Pd is a metastable state, with bulk Pd being the end product; thus, the reverse reaction from Pd black to colloidal Pd is limited. When O_2 was passed through an aqueous HCl slurry of Pd powder, the formation of Pd^{2+} was much slower than with a supported Pd material.

3.4. Optimization of the ethanol system

Because of the advantages of carrying out the reaction in ethanol, experiments were carried out to optimize the system (a) by employing different HCl concentrations and (b) by the addition of Br^-. The results obtained with 0.04 and 0.09 N HCl are compared in figure 5 with those obtained in the usual 0.17 N HCl solution. To complete the series, a reaction was carried out in ethanol without any HCl. At times up to 5 h the rates of H_2O_2 formation in 0.04 and 0.09 N HCl were larger then those for the 0.17 N HCl solution. More-

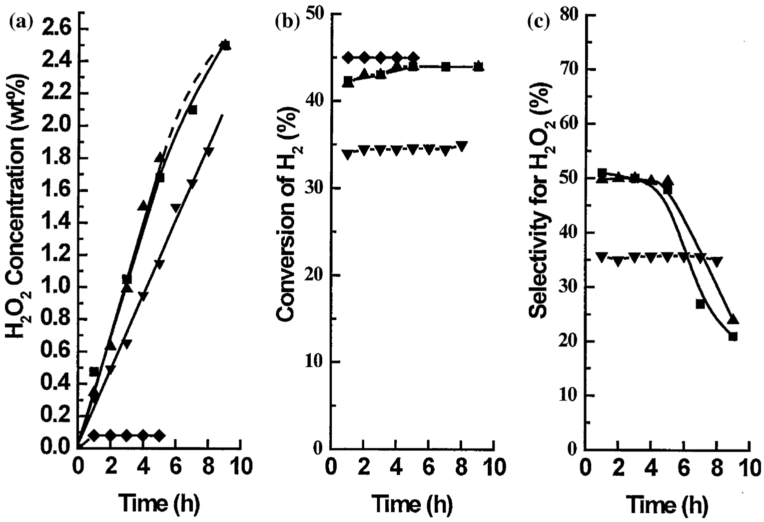


Figure 5. Catalytic formation of H_2O_2 in the ethanol solution acidified with different concentrations of HCl: (a) concentration of H_2O_2, (b) conversion of H_2 and (c) selectivity for H_2O_2 with (◆) no HCl, (▲) 0.04 N HCl, (■) 0.09 N HCl and (▼) 0.17 N HCl.

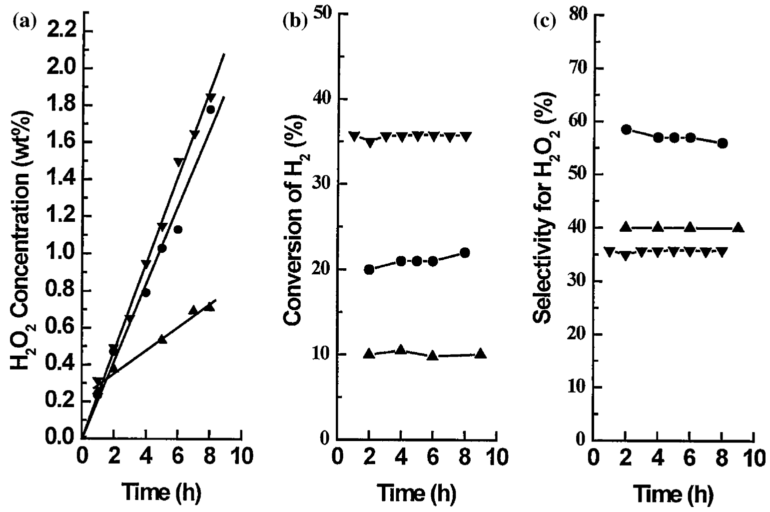


Figure 6. Effects of Br^- on the formation of H_2O_2 in the ethanol system: (a) reactivity, (b) conversion of H_2 and (c) selectivity for H_2O_2 in (▼) Br-free, (●) 20 ppm Br^- and (▲) 1000 ppm Br^- solutionts.

over, an H_2O_2 concentration in excess of 2.4 wt% was achieved in 9 h with the less acidic solution. The latter solutions also had a selectivity of ca. 50% for 5 h, but this decreased to about 20% by 9 h. The pH of the less acidic system was measured during reaction and was found to remain constant; therefore, HCl was not lost as the reaction proceeded. The decrease in net H_2O_2 formation rate and the consequent decrease in selectivity may result from an increase in the rate of H_2O_2 reduction at the larger H_2O_2 concentrations.

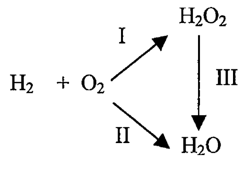
With nominally pure ethanol as the liquid phase a small amount of H_2O_2 appeared during the first hour, but thereafter there was no *net* formation of H_2O_2. These results are similar to those reported previously for an aqueous system [5]. Meanwhile, the H_2 conversion was constant at 45%. In a separate experiment, H_2O_2 was added to the liquid phase to a level of 0.9 wt%, and the H_2O_2 concentration was subsequently measured for several hours with H_2 and O_2 being introduced. Within a period of 4 h the H_2O_2 concentration returned to the original level of 0.08 wt%. The rate of H_2O_2 loss is about the same as the rate of H_2O_2 formation with 0.17 N HCl in the system. In still another experiment with nominally pure ethanol and no HCl, H_2O_2 was added to a level of 0.8 wt% after 2 h, and H_2 was deleted from the gas stream. After a small decline, the H_2O_2 concentration remained constant at a level of 0.76 wt%. Thus, it appears that in the absence of HCl the reduction of H_2O_2 to H_2O occurs at a rate that is comparable to its rate of formation, but the rate of decomposition of H_2O_2 is a relatively slow process.

As noted by several investigators [6,12–14], the presence of Br in the aqueous system resulted in larger selectivities for H_2O_2 formation. In this study, Br^- was added as KBr, usually after the reaction had proceeded for 1 h, and the effects on the net H_2O_2 formation, H_2 conversion and selectivity are depicted in figure 6. With the addition of Br^- to a level of only 0.02 mM the H_2O_2 formation rate was almost unchanged while the H_2 conversion decreased to 20%. As a consequence, the selectivity increased to 59% and then decreased slightly to 56% after 7 h. The addition of Br^- to a level of 1 mM further decreased the H_2 conversion to only 10%, but the H_2O_2 formation rated declined markedly so that the selectivity increased only slightly with respect to the case without any Br^-. In a separate experiment, the Br^- was added before the catalyst was introduced, and the effect was nearly the same.

4. Discussion

These results may be interpreted by considering the mechanism described in scheme 1.

The objective, of course, is to produce hydrogen peroxide and not water, which may be formed both by a direct pathway (reaction II) and by an indirect one (reactions I and III). The results described above indicate that in ethanol acidified to 0.17 N with HCl the subsequent reduction of H_2O_2 was not significant. This is supported by the constant formation rate of H_2O_2, even at larger concentrations, (figure 2a) and the fact that addition of H_2O_2 to the system did not alter this rate. Thus, water must be formed mainly by



Scheme 1.

reaction II. This reaction must be significant with respect to reaction I since the $S_{H_2O_2}$ was a rather modest 35%. At 0.09 N and smaller acid concentrations, however, the net rate of H_2O_2 formation decreased significantly at larger concentrations (figure 5a), and in the nominally pure ethanol the H_2 reduction of H_2O_2 was quite evident. Thus, the reduction of H_2O_2, rather than its simple decomposition, is primarily responsible for reaction III.

With water as the liquid phase, even at 0.17 N HCl, the net rate of H_2O_2 formation did not remain constant (figure 2a), primarily as a results of a change in the state of the Pd from supported Pd(0) to a mixture of Pd^{2+}, colloidal Pd and Pd black. Concomitantly, the selectivity for H_2O_2 decreased (figure 2c). These results, together with the observation that no additional H_2O_2 was formed after H_2O_2 was added to the system, indicate that reaction III becomes dominant as transformations in the state of the Pd occur. In summary, at sufficiently high acidity (e.g., 0.17 N HCl) the formation of water is mainly via the direct reaction (reaction II) in ethanol and probably by a combination of the direct reaction and the indirect reaction (reactions I and II) in water.

It has been previously shown using Raman spectroscopy that O_2 does not dissociate during the formation of H_2O_2 [5], and it has been suggested that when O_2 does dissociate, water is the product. Furthermore, the dissociation of O_2 is believed to require an ensemble of Pd atoms, and Br^- adsorbed on the surface limits the concentration of such ensembles. The results of figure 6 support this hypothesis. Statistically, with small additions of Br^-, the ensembles would be more strongly affected than single Pd atoms. (If one assumes 20% metal dispersion, for a solution that is 0.02 mM in Br^- there is sufficient halide in solution to cover ca. 30% of the Pd). Hence, the selectivity for H_2O_2 was significantly enhanced for the 0.02 mM Br^- solution, primarily because of a large decrease in the H_2 conversion (figure 6). But at the much larger Br^- concentration of 1 mM, both the ensembles and the single Pd atom sites would be extensively blocked, resulting in the large decrease in the rate of H_2O_2 formation and the H_2 conversion.

Perhaps the most significant difference between the ethanol and the water systems is the active state of the Pd. The new evidence presented here indicates that formation of H_2O_2 occurs on the supported Pd when ethanol is the liquid phase; in contrast, formation of H_2O_2 occurs on colloidal Pd when water is the liquid phase [4–6]. The dissolution of supported Pd into the liquid phase as $PdCl_4^{2-}$ is initially much more extensive in water than in ethanol, and this favors the formation of the colloid. The colloid is intrinsically unstable, which results in the formation of Pd black. The H_2O_2 formation rate, therefore, decreases more rapidly in the aqueous system. Even in ethanol, Pd is slowly lost from the catalyst, which would be a consideration in the commercial application of this technology.

5. Conclusions

Ethanol is superior to water as the liquid phase for the direct formation of H_2O_2 from H_2 and O_2 over a palladium catalyst. After 8 h of reaction up to twice as much H_2O_2 may be attained in ethanol as in water, primarily as a result of the stability of the active phase. In ethanol, the active Pd component remains on the SiO_2 surface but in water it first becomes colloidal and then is converted to relatively large particles of palladium black. The rather modest selectivity of 35% for the conversion of H_2 to H_2O_2 in ethanol may be improved to ca. 58% by the addition of Br^- in small concentrations. For achieving maximum H_2O_2 yields, the stability of the desired product in the presence of H_2 is an important factor. At moderate H_2O_2 levels (e.g., up to 3 wt%) and with 0.17 N HCl, the catalytic reduction of H_2O_2 by H_2 is not an important reaction in the ethanol system, which is in contrast to the behavior in the water system.

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