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

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Received 9 July 2002; accepted 24 September 2002

Abstract

The direct formation of H_2O_2 from H_2 and O_2 is an attractive alternative to the current technology that involves the hydrogenation of an alkylanthroquinone to the corresponding hydroquinone, followed by the reaction of the hydroquinone with oxygen to yield H_2O_2. The direct reaction is generally catalyzed by palladium, although there is evidence that the addition of small amounts of platinum may enhance the yield of peroxide. The palladium may be in a supported form or it may be present as a colloid derived from $PdCl_4^{2-}$ ions in solution. The reaction takes place in a three-phase system that includes the reagent gases, the palladium catalyst, and a solvent, which is usually water. Other solvents, including methanol, are also effective. The solutions contain an inorganic acid and often halide ions (Cl^- or Br^-) to inhibit the decomposition of H_2O_2 and perhaps the nonselective oxidation of H_2 to H_2O. At sufficiently high concentrations of an acid, the dissolution of supported palladium occurs. Because of the three-phase system, the rates may be transport-limited. The solubility of H_2 in H_2O is small; therefore, high reagent pressures are used to enhance formation rates and the ultimate yields of H_2O_2. Safety issues that result from having the reagents at high pressures are significant, and to avoid contact of H_2 and O_2 in the gas phase, the introduction of H_2 through a membrane has been demonstrated. A number of fundamental issues remain unresolved including the active state of the palladium and the reaction mechanism, although it has been shown that the oxygen remains in a diatomic form during the production of H_2O_2.
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Keywords: Hydrogen peroxide; Palladium catalyst; Palladium colloids; Support effects

1. Introduction

Hydrogen peroxide is a commodity chemical that is being used on an increasing scale as a bleach in the pulp and paper industry and in the treatment of waste waters [1]. As a replacement for chlorine (including hypochlorite and chlorine dioxide), it is an environmentally friendly oxidant that plays an important role in "green chemistry." Moreover, hydrogen peroxide has been shown to be effective in the removal of residual aromatic sulfur compounds from fuels [2]. If this became a commercial process, there would be an additional increase in the demand for hydrogen peroxide.

The discovery of the TS-1 molecular sieve and its ability to promote the selective epoxidation of olefins using hydrogen peroxide as the source of oxygen has provided yet another large-scale potential application for this oxidant [3]. There are numerous examples in which hydrogen peroxide is used to generate epoxides for use as fine chemicals [4].

The history of hydrogen peroxide formation and the current technology for its production have been reviewed by Hess [1]. The commercial production of H_2O_2 is a circuitous process that involves the catalytic hydrogenation of an alkylanthroquinone to the corresponding hydroquinone, followed by its treatment with O_2 to produce H_2O_2 and the original anthroquinone [1]. This process, known as the Riedl–Pfleiderer process, was developed in Germany during World War II. One advantage is that H_2 and O_2 are added separately in the cycle; hence, potentially explosive mixtures of the two gases are avoided. The process involves a number of steps, including purification from a raw product that contains about 2 wt% H_2O_2. In addition, there is slow degradation of anthraquinone, which is a relatively expensive chemical.

As a potentially less expensive route to H_2O_2, its *direct formation* from H_2 and O_2 has been actively investigated, particularly in industrial research laboratories, and numerous patents on this subject have appeared over the past two decades [5–10]. Until recently, however, very little has been published in scientific journals. Early work on the direct formation of H_2O_2 has been noted by Pospelova et al.

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[11–13], who published a series of three papers in 1961 that even today form the basis for our understanding of this process.

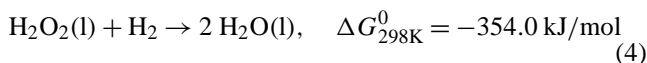The free energy change for the formation of H_2O_2 via the reaction

$$H_2 + O_2 \rightarrow H_2O_2(l), \quad \Delta G^0_{298K} = -120.4 \, \text{kJ/mol} \quad (1)$$
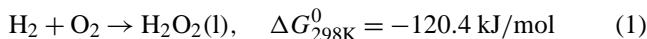
is quite favorable and the reverse reaction under normal reaction conditions is negligible; but the competing reaction

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O(l), \quad \Delta G^0_{298K} = -237.2 \, \text{kJ/mol} \quad (2)$$
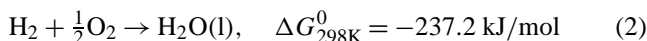
has an even larger negative ΔG^0 value. In addition, the decomposition of H_2O_2 via the reaction

$$H_2O_2(l) \rightarrow H_2O(l) + \tfrac{1}{2}O_2, \quad \Delta G^0_{298K} = -116.8 \, \text{kJ/mol} \quad (3)$$
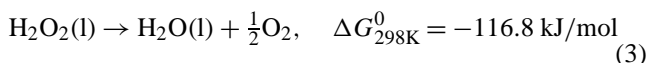
also has a negative free energy. The reaction

$$H_2O_2(l) + H_2 \rightarrow 2\,H_2O(l), \quad \Delta G^0_{298K} = -354.0 \, \text{kJ/mol} \quad (4)$$

is sometimes written separately, but from a stoichiometric viewpoint, it may be considered to be the sum of reactions (2) and (3). For the purpose of this review, reaction (4) will not be considered further.

The ultimate yield of H_2O_2 depends, of course, on the relative rates of the first three reactions, which in turn will depend on a number of factors, including the partial pressures of the reagents. The catalysts for these three reactions need not be the same, and, in general, many more materials are effective for reactions (2) and (3) than for reaction (1). Among the noble metals, palladium appears to be unique in its ability to catalyze reaction (1), although one patent indicates that gold in the form of particles 50 nm in diameter on a hydrophobic support is active [14]. Based on a low-level theoretical approach, Sellers and co-workers [15] concluded that gold and silver should be favorable catalysts for the production of H_2O_2, but we have shown that gold in the form of a foil is also effective in the decomposition of H_2O_2 [16]. Although platinum itself is predominantly a catalyst for reaction (2), as a promoter it can substantially enhance the yield of H_2O_2 [8]. The origin of this promotional effect is not currently known.

Pospelova et al. [11], as well as other investigators [17,18], have observed that inorganic acids play a critical role in inhibiting reaction (3). Protons play a dominant role, although when HCl or HBr is employed, the halide ions also are important [9,11], and the halide ions may be added separately as a salt such as NaBr. Pospelova et al. [11] found that HCN slows down both the synthesis and decomposition of H_2O_2.

2. The liquid phase

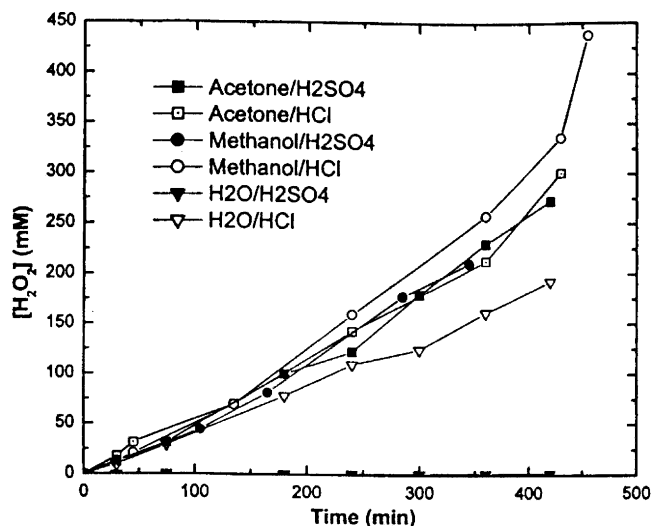The reaction normally is carried out in a three-phase system that includes supported or unsupported palladium,

Fig. 1. Direct formation of H_2O_2 in acetone, methanol, or water that contains different acids at 0.03 M concentration. The catalyst contained 11.4 wt% Pd on hafnium phosphate viologen phosphonate (Ref. [19]).

water, and the gaseous mixture. In most cases reaction (1) is probably transport-limited (see below). The solubility of H_2 in water is small (0.81 mM at 25 °C); therefore, Anderson and co-workers [19] carried out experiments in methanol and other organic phases. The solubility of H_2 in methanol at 25 °C is 3.96 mM. As shown in Fig. 1, at reaction times up to ca. 200 min the rate of H_2O_2 formation was similar for all liquid phases provided HCl was present, but this is not surprising because, according to the authors' calculations, the reaction was limited by the rate of H_2 mass transfer into the liquid phase. As an aside, the authors noted that halide ions were not required when an organic phase was used; i.e., the reaction occurred with only the addition of H_2SO_4. In order to overcome the H_2 solubility limitation in H_2O, most results reported in patents were obtained at pressures up to 100 bar or greater.

3. Catalyst supports

Many different supports have been used; however, the most common are silica and charcoal. As noted recently by Choudhary and co-workers [17], the state of the support has a marked influence on reaction (1), as well as on reactions (2) and (3). The results shown in Fig. 2 demonstrate that a catalyst initially composed of PdO/fluorinated γ-Al_2O_3 was much more selective for H_2O_2 formation than the comparable unfluorinated material, even though the rates of H_2 conversion and the low rates of H_2O_2 decomposition were comparable. Chlorination was as effective as fluorination. These results imply that halided alumina inhibits reaction (2), but not reaction (3). The reactions were carried out in 0.02 M aqueous H_2SO_4, with no halide added to the system. A comparison with the results of Fig. 1 suggests that the role of the added halide may be to modify the
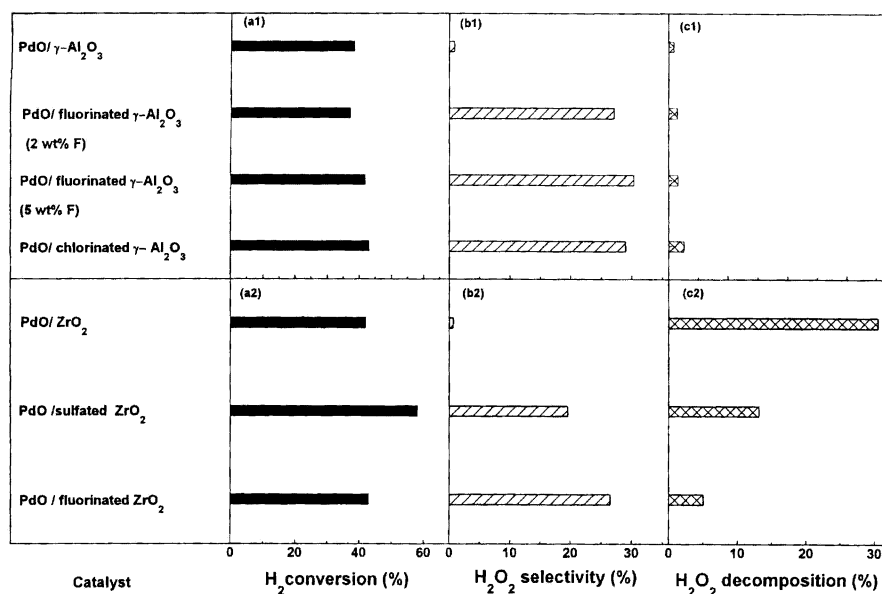
Fig. 2. Performance of alumina- and zirconia-supported (with or without modification) PdO catalysts in the direct oxidation of H_2 and in the decomposition of H_2O_2, both at 22 °C (Ref. [17]).

support or the palladium in such a way as to minimize reaction (2). When the reaction was carried out on PdO/ZrO_2, reaction (3) dominated the net amount of H_2O_2, and in this case fluorination inhibited the decomposition reaction. Thus, depending on the support, fluorination may inhibit either reaction (2) or reaction (3). Sulfate ions were less effective than fluoride ions in this respect. Supports themselves are generally considered to be inactive with respect to H_2O_2 formation; however, Park et al. [20] have reported that an H-beta zeolite had small activity, but poor selectivity, for generating H_2O_2.

4. The role of colloids

Research in our laboratory has focused on the role of colloidal palladium in the direct formation of H_2O_2 [18,21]. The colloidal palladium may be derived either from Pd/SiO_2 or from $PdCl_2$ via reduction of $PdCl_4^{2-}$ ions in acidic aqueous solutions. Evidence for the significant role of colloidal palladium as the dominant catalytically active form of the material, at least under certain conditions, comes from a number of experimental results. First, when the catalyst was introduced to the system as Pd supported on a porous silica, as shown in Fig. 3, the rate of H_2O_2 formation *remained the same* upon removal of the solid phase when the solution was either 1 N or 0.1 N in HCl. Therefore, some form of palladium in the liquid phase was responsible for the H_2O_2 production. When the solution was 0.01 N in HCl, the rate, which was much less, decreased further after removal of the solid phase. Second, when the Pd was added as $PdCl_2$ (i.e., no support), the specific rate was even greater than when Pd/SiO_2 was used, even though the total amount of palladium was the same. Third, although the colloidal

palladium is in a dynamic state, as illustrated in Scheme 1, and its concentration changes during the course of the reaction, the rate of H_2O_2 formation remains proportional to the amount of colloid rather than the total amount of Pd in the system. Fourth, electron microscopy has confirmed the presence of a colloid in the aqueous phase when either $PdCl_2$ or Pd/SiO_2 is the source of Pd. In evaluating these results, one should note that they were obtained mainly at a 2 : 1 O_2/H_2 ratio, which is within the explosive regime, whereas
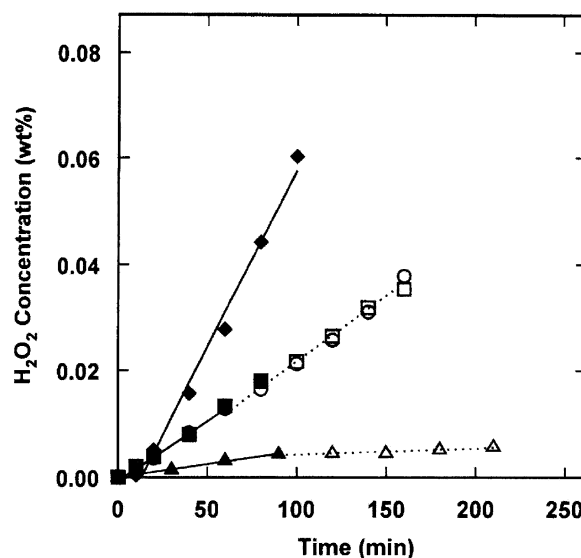

Fig. 3. Catalytic formation of H_2O_2 in an aqueous phase before and after the removal of 2.2 mg of 5 wt% Pd/SiO_2: (■) before and (□) after the removal of the solid phase from a 1 M HCl solution; (●) before and (○) after the removal of the solid phase from an 0.1 M HCl solution; (▲) before and (△) after the removal of the solid phase from an 0.01 M HCl solution. Peroxide formation in a nominally 1.0×10^{-4} M $PdCl_4^{2-}$ solution containing 1 M HCl is depicted by (◆) (Ref. [21]).

Pd/frit ◄——— Pd colloid

PdCl$_4^{2-}$

Pd/SiO$_2$
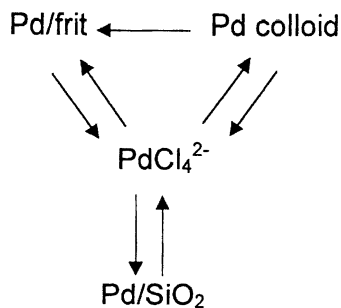
Scheme 1.

most fundamental studies have been carried out at ca. 25 : 1 O_2/H_2 in order to avoid the explosive regime. The much larger $O_2 : H_2$ ratio would favor aqueous $PdCl_4^{2-}$ rather than the colloid.

The state of Pd on the support has usually been assumed to be Pd^0; however, Choudhary and co-workers [17] have concluded that PdO is the more active and selective form of palladium. Since Pd^{2+} is reduced by H_2 at a typical reaction temperature of 25 °C, it seems that a steady state distribution of Pd^0/Pd^{2+} would exist during the reaction and that the reduction step may result in the formation of water.

5. Reagent transport models

The relative inactivity of the Pd/SiO$_2$ catalyst in 0.01 N HCl (Fig. 3) has suggested that transport limitations may be involved. Stated another way, why is the palladium inside the pores of the silica so inactive? Clearly, the H^+ and Cl^- concentrations were large enough to inhibit H_2O_2 decomposition. In these experiments the gases were introduced through a frit and were dispersed in the liquid phase as small bubbles. It has been proposed that the rate limiting transport occurs at the interface between a bubble and colloidal palladium as illustrated in Fig. 4 [21]. One should note that the concentration of H_2 in the bubble is about 50 times that in the aqueous phase. Diffusion of the bubbles inside the pores of the silica is unlikely, and in this case the transport of *dissolved* H_2 into the pores is the dominant factor controlling the rate. The calculation
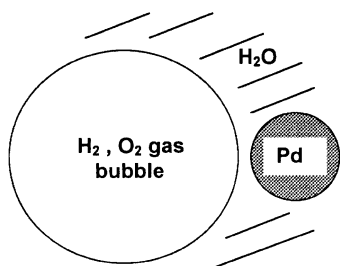
of a diffusion rate based on the model of Fig. 4 would be useful; however, several important unknowns cannot be approximated with any degree of confidence. These include the film thickness, the time that a colloidal particle spends in contact with the bubble, and the interfacial area. Preliminary experiments indicate that the bubble size is important. Moreover, as noted above, the reaction rate is proportional to the colloid concentration. Thompson and co-workers [19] addressed the issue of mass transfer of H_2 from the bubbles into the liquid phase and concluded that this was the rate limiting factor in their experiments, during which gases were introduced via a 2-mm tube rather than via a fine frit.

6. Reaction mechanism

Transport limitations in this 3-phase system make it difficult to obtain kinetic data that can be used to elucidate mechanisms. But the question of oxygen dissociation during H_2O_2 formation has been investigated using a mixture of $^{16}O_2$ and $^{18}O_2$ [18]. If a dissociated form of oxygen were involved, one would expect to find $H_2^{16}O^{18}O$ as a major product. From the Raman spectra shown in Fig. 5, it is evident that only $H_2^{16}O_2$ with a peak at 879 cm^{-1} and $H_2^{18}O_2$ with a peak at 830 cm^{-1} were present as products. 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. This result is consistent with the mechanism suggested by Pospelova and Kobozev [12], who proposed that HO_2 is formed as a surface intermediate. The addition of a second hydrogen atom results in H_2O_2. By contrast, on Pt, which is a catalyst for H_2O production, O_2 is believed to adsorb in a dissociative form.

Fig. 4. Model depicting the transfer of reagents across a gas–liquid interface between a bubble and a Pd particle (Ref. [18]).
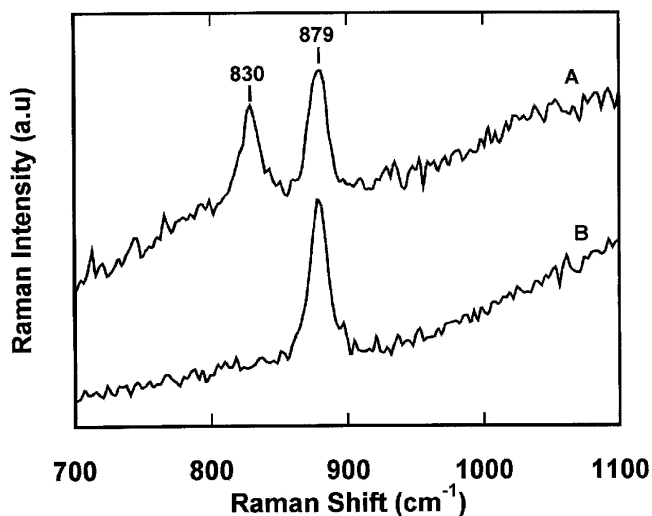
Fig. 5. Raman spectra of H_2O_2 after reaction of H_2 with (A) an $^{16}O_2/^{18}O_2$ mixture and with (B) $^{16}O_2$ (Ref. [18]).

Table 1
Production of H_2O_2 at different pressures[a,b]

Total pressure (bar)	H_2O_2 concentration (wt%)	Selectivity (%)
1.0	0.78	30
3.0	3.49	55
5.1	5.70	60
10.1	9.20	79
20.3	12.45	88

[a] Ref. [5].
[b] Results obtained at 30 °C by reacting H_2 and O_2 ($O_2 : H_2 = 2.5$) over 10 mg of 5 wt% Pd/hydrous silicic acid for 20 h. The acid concentration was 0.03 N in HCl and 1 N in H_2SO_4. The gases were continuously added to the aqueous phase at the pressure indicated.

7. Effect of pressure

Most of the results described to this point were carried out at 1 bar and the maximum concentration of H_2O_2 has generally been less than 1 wt%. A notable exception is found in the work of Thompson and co-workers [19], who investigated the reaction over a catalyst containing hafnium phosphate and viologen phosphate with supported Pd and reported that 13 wt% H_2O_2 could be attained in anhydrous methanol, albeit for a reaction time of 20 h. At the much higher pressures reported in the patent literature, H_2O_2 concentrations in excess of 24% with 79% selectivity based on H_2 conversion was attained in 3 h [22]. This should be compared with the 2 wt% H_2O_2 produced by the anthraquinone process.

Whereas the effect of increasing pressure has been described in several patents, the results of Izumi et al. [5] are of particular interest because of the systematic increase in pressure, beginning at 1 bar. The data of Table 1 show that the amount of H_2O_2 increased almost linearly up to about 10 bar, but increase in the selectivity for H_2O_2 formation was not the linear with respect to pressure. The larger yields of H_2O_2 and the somewhat larger selectivities may be understood, at least qualitatively, from reactions (1)–(3). Namely, reaction (1) probably is first order with respect to either H_2 or O_2, while reaction (2) is less than first order with respect to H_2 and O_2. Reaction (3) is expected to be zero order with respect to both gases, and it may be effectively inhibited by chloride ions except at the largest H_2O_2 concentration.

8. Reactor designs and safety issues

Recent patents describe continuous liquid flow reactors that operate at high pressures. These include slurry reactors and trickle bed reactors [22,23]. In the latter, the catalyst bed is fixed and the liquid phase moves over the solid particles as a thin film. This method potentially has the advantage of reducing transport limitations. In one scaled-up system it is widely known that a damaging explosion occurred; however, the explosion was not a result of a reaction between hydrogen and oxygen, but, rather, the reaction of high-pressure oxygen with a Teflon-lined steel container that was in contact with a catalyst. Although no economic studies on the direct process have been published in the open literature, the higher concentrations of H_2O_2 that can be achieved and the absence of separation steps suggest advantages over the current technology. On the other hand, safety issues associated with the use of high pressure H_2 and O_2 are a consideration. Mixtures of H_2 and O_2 in the gas phase can be avoided by employing a membrane reactor, as recently reported by Choudhary et al. [24]. In such a reactor, hydrogen is transported through a cylindrical Pd–Ag alloy/alumina membrane. Higher selectivities were obtained when the alloy was coated with a Pd/PdO film. Oxygen was bubbled into the aqueous phase that was in contact with the Pd–Ag alloy. Complete hydrogen conversion was achieved at selectivities of ca. 40%. The H_2 pressure on the gas side of the membrane was 2.4 bar and the O_2 pressure was 1 bar. Presumably, both pressures could be increased to improve the rate of H_2O_2 formation, which was rather small for the conditions employed.

9. Challenges for future research

At the fundamental level, our understanding of the catalytic formation of H_2O_2 and the accompanying formation of water through side reactions is far from being complete. Such basic questions as the active state of palladium have not been adequately answered. Pospelova et al. [12] concluded that Pd_2^0 centers were responsible for the formation of H_2O_2, whereas Choudhary and co-workers [18] presented evidence supporting the role of PdO. Interpretation of experimental results is complicated by the fact that, at least to some degree, there is continuous oxidation and reduction of Pd as described in Scheme 1. The oxidation occurs because of the dissolved O_2 and is facilitated by the presence of protons and halide anions, all of which are necessary to achieve a selective reaction. Thus, even if one began with pure Pd^0 or PdO, the system would not remain in such a state. The catalysts used by Thompson and co-workers [19,25] contained viologen (N,N'-dialkyl-4,4'-bipyridinium), and they concluded that hydrogen is split into protons and electrons by the noble metal, with the electrons being transferred to the viologen groups. The reduced viologen then reacts with O_2 to give the H_2O_2 product.

An even more difficult issue is that of obtaining intrinsic rates for reaction (1), i.e., rates that reflect the true activity of the catalyst and not transport limitation or side reactions. Transport limitations appear to be endemic to three phase catalytic systems, and in our experience almost everything that is done to improve the dispersion of the gases increases the rate of H_2O_2 formation. Transport limitations may be alleviated at high pressure because of the increased solubility of H_2, but at pressures near 1 bar they make it very difficult to obtain reliable kinetic data. Partial poisoning of the ac-

tive Pd may provide a solution, although the selectivity may significantly decrease, since the sites responsible for reactions (2) and particularly (3) may remain active. Decreasing the loading of the catalyst would not be sufficient since this may only limit the contact between the palladium particles and the gas bubbles (Fig. 4).

With respect to the reaction mechanism, the state of the active form of hydrogen has not been determined. Is the unique selectivity of Pd for H_2O_2 formation related to its ability to form palladium hydrides or is only surface hydrogen involved? Furthermore, do H_3O^+ ions play any role in producing the active form of hydrogen? Transient experiments may provide answers for some of these questions.

In order to fully understand the overall reaction scheme, it is important to determine simultaneously the extent of reactions (2) and (3), along with reaction (1). Since halide ions play such an important role in selectivity, their effect on the three possible reactions should be evaluated independently in the manner described by Choudhary and co-workers [17]. But even these experiments are deficient since the coexistence of H_2, O_2, and H_2O_2 will determine the states of palladium.

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