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Direct formation of H_2O_2 from H_2 and O_2 over a Pd/SiO_2 catalyst: the roles of the acid and the liquid phase

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Abstract

The direct formation of H_2O_2 from H_2 and O_2 was carried out over a Pd/SiO_2 catalyst in a medium of ethanol or water acidified with either H_2SO_4 or HCl. The H_2SO_4/ethanol system is the most favorable for peroxide formation. Both the proton and the anion, in the case of Cl^-, promote the net formation of the peroxide. Protons inhibit the reduction of H_2O_2 by H_2, and chloride ions limit the direct reduction of O_2 to water, presumably by blocking Pd ensembles. Sulfate ions, being noncoordinating ligands, do not serve this function; therefore the H_2SO_4/water system is a poor medium for producing the peroxide. By contrast, the H_2SO_4/ethanol system is believed to be effective because in the presence of O_2, acetate ions are formed from ethanol, and these ions block Pd ensembles in the same manner as chloride ions.
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1. Introduction

Since the early work of Pospelova and coworkers [1–3], there has been considerable effort dedicated to understanding the details of the direct reaction of H_2 and O_2 to form H_2O_2 [4–10]. The reaction is complicated because it involves a three-phase system that includes a solid catalyst (usually including Pd), a liquid phase, and the reagent gases. Research has focused on the state of the catalyst and the role of the liquid, which includes an acid. Other modifiers, such as Br^-, may be included to improve the selectivity for H_2O_2 formation. Work in our laboratory has shown that when the reaction is carried out in an aqueous HCl solution, Pd is lost from its support as $PdCl_4^{2-}$, which, in turn, may be reduced to colloidal Pd [4–7]. The latter form of Pd is believed to be the active component in this case. By contrast, in ethanol the Pd largely remains on the silica support during the reaction.

In this communication HCl and H_2SO_4, with either water or ethanol as the liquid phase, are compared. It is shown that with Pd/SiO_2, the H_2SO_4/ethanol system is the most favorable liquid phase for H_2O_2 formation, whereas in the H_2SO_4/water system almost no peroxide is formed. This surprising result has been reported previously by Thompson and coworkers [11], but the origin of the phenomenon was uncertain. In a comparison of the several systems, it is important to recognize that the solubility of H_2 is five-fold larger in ethanol than in water and the solubility of O_2 is eight-fold larger in ethanol than in water [11]. Moreover, because of surface tension and viscosity differences, the bubble size in ethanol is considerably smaller than that in water. These factors are important because at some level the reaction is transport limited.

2. Experimental

2.1. Preparation of the catalyst

A detailed description of the catalyst preparation, reactivity measurement, and analytical methods has been published

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elsewhere [6,7]. Briefly, the catalyst was 5 wt% Pd supported on Cab–O–Sil M5 silica, which has a surface area of ca. 200 $m^2\ g^{-1}$. The material was prepared by an incipient wetness method with an aqueous solution of $PdCl_4{}^{2-}$. The catalyst precursor was pretreated in flowing O_2 at 400 °C and reduced for 30 min under H_2 flowing at 20 $ml\ min^{-1}$. The average particle size was estimated by TEM to be 6 nm before reaction, and the particle size was distributed in a range of 5–40 nm after reaction in the H_2SO_4/ethanol system, and most of these particles were about 10 nm in diameter. As demonstrated by XPS, most of the supported Pd was in the metallic state.

2.2. Reactivity measurement

The reactions were carried out at atmospheric pressure and at 10 °C in glass reactors described in Ref. [6]. Hydrogen and oxygen were added via a glass frit to the stirred slurry containing the catalyst. The gases were introduced as a 4:1 O_2/H_2 mixture at a flow rate of 50 $ml\ min^{-1}$. At this ratio the O_2/H_2 gas mixture is explosive, and appropriate precautions should be taken. For example, the catalyst should be introduced as a slurry rather than in the dry state. The liquid phase consisted of 60 ml of ethanol or water acidified with HCl or H_2SO_4. Unless stated otherwise, the solutions were either 0.17 N in HCl or 0.24 N in H_2SO_4, and the amount of catalyst was 50 mg. The “ethanol solution” contained a small amount of water that was introduced with the acid.

3. Results and discussion

3.1. Synthesis of H_2O_2 in H_2SO_4-acidified solutions

The increase in the concentration of H_2O_2 as a function of time for the reaction carried out at two different normalities of H_2SO_4 in ethanol is shown in Fig. 1A. Over a period of 7 h in 0.24 N H_2SO_4, the concentration of H_2O_2 reached 2.4 wt%, which corresponds to a net rate of 32 $mmol_{H_2O_2}\ g_{Pd}^{-1}\ min^{-1}$. This is about 30% larger than the rate reported for the HCl/ethanol system [7] under the same reaction conditions (see below). At 0.12 N H_2SO_4 the rate was slightly smaller than that found in the 0.24 N H_2SO_4/ethanol solution. But when the liquid phase was water, acidified to 0.24 N in H_2SO_4, only a very small amount of H_2O_2 was formed during the first 2 h, and thereafter no additional peroxide was produced.

The hydrogen conversion levels and the selectivities are shown in panels B and C, respectively, for the H_2SO_4/ethanol system. Here the selectivity is defined as the percentage of H_2 that reacts to H_2O_2. With increasing acid strength in ethanol, the conversion of H_2 increases somewhat more than the rate of peroxide formation; hence, the selectivity decreases slightly. Surprisingly, in the aqueous phase the H_2 conversion remained constant at about 20%, even when no H_2O_2 was being formed, which means that all of the reacted H_2 was being converted to water.

The amount of Pd lost from the catalyst in the H_2SO_4/ethanol system was significantly less than that in the HCl/ethanol system. After 5 h of reaction the concentration of Pd in the liquid phase was 2.6×10^{-5} M in the former case and 6.5×10^{-5} M in the latter, as determined from inductively coupled plasma (ICP) analysis. Had all of the Pd entered the liquid phase, the concentration would have been 4.0×10^{-4} M.

3.2. Synthesis of H_2O_2 in HCl-acidified solutions

For purposes of comparison, previously reported results [7] obtained with the HCl/ethanol and HCl/water systems are shown in Fig. 2. Most notable is the fact that H_2O_2 formation continued over a 7-h period in the aqueous phase at a rate that was only about half of that found in ethanol.

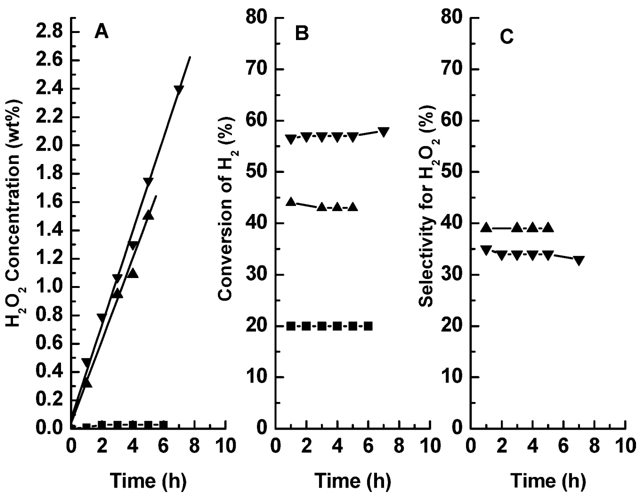

Fig. 1. Catalytic formation of H_2O_2 in the ethanol solution acidified to (▲) 0.12 N and (▼) 0.24 N in H_2SO_4, and (■) 0.24 N H_2SO_4/water: (A) concentration of H_2O_2, (B) conversion of H_2, and (C) selectivity for H_2O_2.

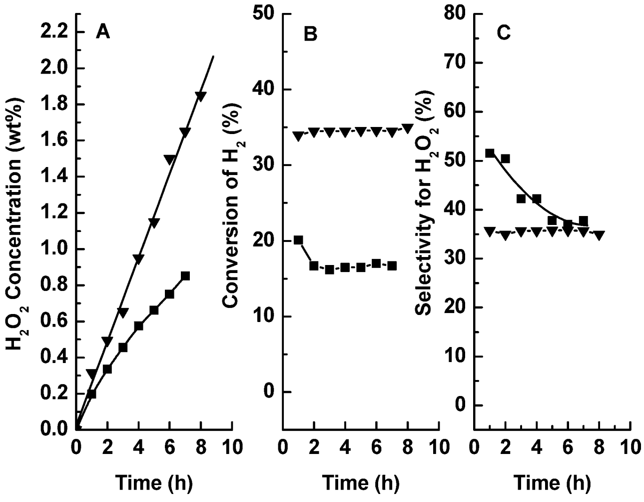

Fig. 2. Catalytic formation of H_2O_2 in (▼) 0.17 N HCl/ethanol and (■) 0.17 N HCl/water solutions: (A) concentration of H_2O_2, (B) conversion of H_2, and (C) selectivity for H_2O_2.

The selectivity decreased from 51 to 36% over 5 h. The latter selectivity is almost the same as that obtained with the HCl/ethanol system and is comparable to those obtained in the H_2SO_4/ethanol systems. The similarities between the ethanol and aqueous systems are somewhat fortuitous, however, since the state of the Pd varies between the two cases as noted above. The variation of rate with time, as observed for the aqueous system, is typical of the colloid, which is intrinsically unstable.

3.3. Combinations of HCl, H_2SO_4, water, and ethanol

In an effort to elucidate the roles of each component, several combinations of the two acids and the two liquids were studied; the results are presented in Fig. 3. In all cases 50 mg of Pd/SiO_2 was present. First, the reaction was carried out in an equal volume mixture of ethanol and water with H_2SO_4 as the acid. After 7 h, 0.8 wt% H_2O_2 was formed, which is about one-third of that produced in pure ethanol (Fig. 1A). The H_2 consumption was less than that in pure ethanol but more than that in pure water. Here water seems to have a dilution effect, but it does not completely inhibit the reactions when H_2SO_4 is the acid.

A second experiment involved the addition of HCl to the H_2SO_4/water system after the reaction had proceeded for 2 h. During the first 2 h the formation rate of H_2O_2 was very small, as expected, but when 0.17 N HCl was added the rate increased to about the level observed for the HCl/water system (Fig. 2A). From this result one can conclude that sulfate ions do not poison the catalyst when water is the liquid phase.

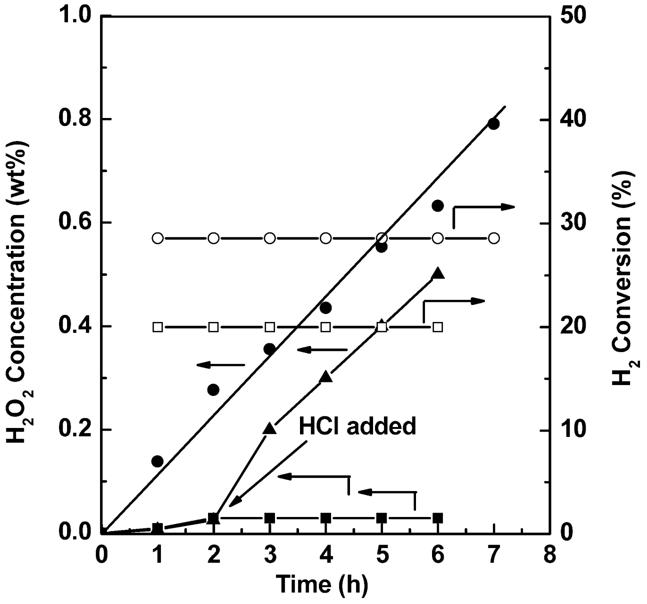

Fig. 3. Catalytic formation of H_2O_2 in 0.24 N H_2SO_4/water (30 ml)–ethanol (30 ml): (●) concentration of H_2O_2 and (○) conversion of H_2. Catalytic formation of H_2O_2 in 0.24 N H_2SO_4/water solution: (■) concentration of H_2O_2 and (□) H_2 conversion. After 2 h, 0.24 N H_2SO_4/water solution was made 0.17 N in HCl: (▲) concentration of H_2O_2.

In the previous study [7] it was found that in pure ethanol (no acid added) a small amount of H_2O_2 appeared during the first hour, but thereafter there was no *net* formation of the peroxide. Similar results were also reported for an aqueous system [5]. Meanwhile, in ethanol the H_2 conversion was 45%, and when H_2O_2 was added to the system, it decomposed over a period of 4 h, even in the presence of the reagents. These results confirm that one of the roles of the acid (protons) is to inhibit the subsequent reduction of H_2O_2 by hydrogen, as has been pointed out previously [6,7]. Other investigators have suggested that the role of the acid is to prevent the base-catalyzed *decomposition* of H_2O_2 [1,8,10]; however, with ethanol as the liquid phase, this seems unlikely. In a separate experiment H_2O_2 was added to nonacidified ethanol that contained the catalyst and O_2. Before the addition of H_2O_2, the system had been exposed to both reagents. The H_2O_2 concentration (0.8 wt%) decreased slightly at first and then remained constant for a period of 4 h; that is, in the absence of an acid the H_2O_2 did not decompose.

3.4. Secondary reactions in the H_2SO_4/ethanol system

Even in the presence of the acid, secondary reactions do occur, and these result in the loss of selectivity. This effect is illustrated by the results summarized in Table 1 and Fig. 4. The amount of catalyst was increased from 20 to 120 mg, and the concentration of H_2O_2, the conversion of H_2, and the selectivity were determined after 5 h on stream. Whereas the H_2 conversion continued to increase with catalyst loading, the concentration of H_2O_2 reached a maximum at a loading of 40 mg and decreased such that with 120 mg of catalyst almost no H_2O_2 was detected. The peroxide selectivity reached a maximum at a loading of 30 mg of catalyst.

The role of secondary reactions in these phenomena is confirmed by the results in Fig. 4. In these experiments the reaction was allowed to proceed for 2 h, and then ca. 0.8 wt% H_2O_2 was added to the system. When 30 mg of catalyst was present, the subsequent formation rate of H_2O_2 formation remained the same; however, when 90 mg of catalyst was added, the amount of H_2O_2 actually decreased with time.

These results may be understood in terms of consecutive reactions in which H_2O_2 is first formed and then is subse-

Table 1
Effect of catalyst amount on H_2O_2 concentration, H_2 conversion and selectivity for H_2O_2[a]

Amount of catalyst (mg)	H_2O_2 concentration (%)	H_2 conversion (%)	Selectivity for H_2O_2 (%)
20	1.3	35	32
30	1.5	37	45
40	1.9	49	40
50	1.7	55	34
70	0.5	65	10
90	0.1	68	1.9
120	Trace	75	Trace

[a] 5 wt% Pd/SiO_2, 0.24 N H_2SO_4/ethanol, after 5 h reaction.

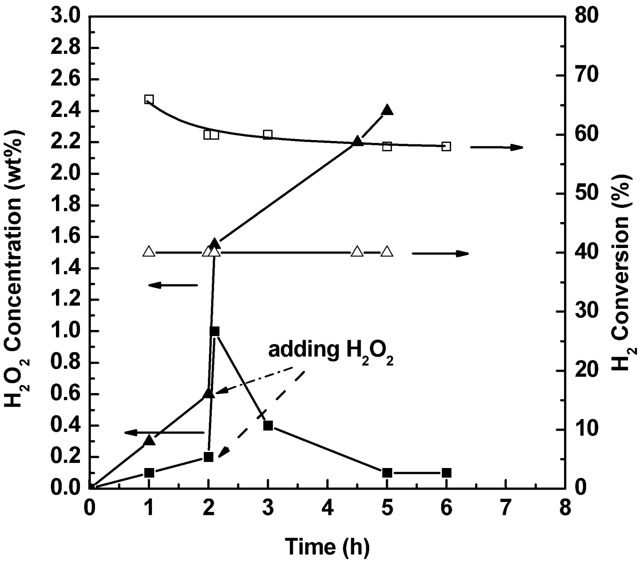

Fig. 4. Catalytic formation of H_2O_2 in 0.24 N H_2SO_4/ethanol solutions before and after the addition of H_2O_2: 30 mg catalyst, (▲) H_2O_2 concentration, (△) H_2 conversion; 90 mg catalyst, (■) H_2O_2 concentration, (☐) H_2 conversion.

quently reduced by H_2. But there is a question as to why the rates of the primary and secondary reactions do not both increase proportionally with catalyst loading. In the case of H_2 the conversion levels clearly exceed differential conditions; therefore, it is expected that the extent of conversion would not remain linear. The variation in the net rate of H_2O_2 formation may be related to diffusional effects; that is, the contact of H_2O_2 with Pd probably is not transport limited since the peroxide is completely dissolved in the ethanol, but the availability of both H_2 and O_2 at the catalyst is probably transport limited. One would expect the rate of H_2O_2 formation to remain constant, whereas the rate of H_2O_2 reduction would continue to increase with the addition of more catalyst. The fact that H_2O_2 is reduced more rapidly than it is formed is evident from the results of Fig. 4 when 90 mg of catalyst was present.

4. Conclusions

The results of this study further establish that the anion in an acid, as well as the proton, plays a role in the selective formation of H_2O_2. Moreover, the liquid phase also becomes involved in several ways. As noted above, with the HCl/water system, the strongly coordinating chloride ligands give rise $PdCl_4^{2-}$ complexes, which are intermediates in the formation of colloidal Pd when H_2 is present. Chloride ions in sufficiently high concentrations may also block Pd ensembles that promote the dissociation of O_2, which results in the direct formation of water. The positive role of bromide in improving the selectivity has been attributed to this effect, but much lower concentrations of bromide are need to achieve higher selectivities [10]. The sulfate ion is a noncoordinating ligand and would not be expected to block Pd ensembles. Finally, ethanol, but not water, may result in surface species that block the ensembles that are responsible for the direct formation of water. There is evidence from surface science that under mild conditions ethanol reacts with oxygen on the Pd(110) surface, forming surface acetate ions [12]. We have added acetic acid (0.01 N) to an almost inactive Pd/SiO_2–H_2SO_4/water system and have found that H_2O_2 is indeed formed at about the same rate as in the conventional HCl/water system (Fig. 2A). Taken together, these observations seem to provide a rational explanation for the behaviors of the several acid-liquid phase combinations that have been described here. One is able to understand, for example, why the H_2SO_4/ethanol phase is active and selective for the direct formation of H_2O_2, whereas the H_2SO_4/water phase results only in the formation of water. The secondary reduction of H_2O_2 may also play a role, but this does not appear to be a dominant reaction at the lower catalyst loadings.

Acknowledgments

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References

[1] T.A. Pospelova, N.I. Kobozev, E.N. Eremin, Rus. J. Phys. Chem. (Trans.) 35 (1961) 143.
[2] T.A. Pospelova, N.I. Kobozev, Rus. J. Phys. Chem. (Trans.) 35 (1961) 262.
[3] T.A. Pospelova, N.I. Kobozev, Rus. J. Phys. Chem. (Trans.) 35 (1961) 584.
[4] D.P. Dissanayake, J.H. Lunsford, J. Catal. 206 (2002) 173.
[5] D.P. Dissanayake, J.H. Lunsford, J. Catal. 214 (2003) 113.
[6] S. Chinta, J.H. Lunsford, J. Catal. 225 (2004) 249.
[7] Y.-F. Han, J.H. Lunsford, Catal. Lett., in press.
[8] P. Landon, P.J. Collier, A.F. Carley, D. Chadwick, A.J. Papworth, A. Burrows, C.J. Kiely, G.J. Hutchings, Phys. Chem. Chem. Phys. 5 (2003) 1917.
[9] A.G. Gaikwad, S.D. Sansare, V.R. Choudhary, J. Mol. Catal. A Chem. 181 (2002) 143.
[10] R. Burch, P.R. Ellis, Appl. Catal. B: Environ. 42 (2003) 203.
[11] V. Krishnan, A.G. Dokoutchaev, M.E. Thompson, J. Catal. 196 (2000) 366.
[12] R.P. Holroyd, R.A. Bennett, I.Z. Jones, M. Bowker, J. Chem. Phys. 110 (1999) 8703.