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Controlling factors in the direct formation of H_2O_2 from H_2 and O_2 over a Pd/SiO_2 catalyst in ethanol

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Abstract

The direct formation of H_2O_2 in ethanol over a Pd/SiO_2 catalyst has been studied under conditions that yield good selectivities for the peroxide, moderate rates of formation, and concentrations of H_2O_2 that approach 2 wt.%. Several factors, including the partial pressures of H_2 and O_2, the presence of protons along with chloride and/or bromide ions, and the reaction temperature significantly affect the rate of H_2O_2 formation, the selectivity of the reaction, and the loss of palladium from the support. Mass transport, which is a function of a particular system, may also limit the rate of peroxide formation. Halide ions (Cl^- or Br^-) and protons (derived from H_2SO_4 in this study) are essential for limiting the combustion reaction; i.e., in the absence of these ions almost no peroxide was formed. A selectivity for H_2O_2 approaching 80% was achieved using 2×10^{-5} M Br^- and 0.12 M H_2SO_4 with an O_2/H_2 ratio of 15. Bromide is particularly useful as the halide because it inhibits the loss of Pd from the support. The net formation rate for H_2O_2 was found to be first order with respect to H_2 and zero order with respect to O_2. The effects of changing the temperature from 5 to 15 °C were evaluated, and it was observed that the system was most stable at the lowest temperature. As might be expected, the initial rate of peroxide formation and the conversion of H_2 was the largest at 15 °C, but as the reaction proceeded the rate of peroxide formation and the selectivity decreased. These results further establish the complexity of this three-phase system that involves a network of reactions and the possibility that the catalyst undergoes change with time.

Keywords: Hydrogen peroxide; Hydrogen; Oxygen; Palladium/silica catalyst; Mass transport

1. Introduction

The direct formation of H_2O_2 from H_2 and O_2 is an attractive alternative to the current Riedl-Pfleiderer process, which involves the sequential hydrogenation and oxidation of an alkyl anthraquinone [1]. As a potentially commercial process, the direct formation route is currently being investigated in a demonstration facility by DegussaHeadwaters [2]. At a more fundamental level, the network of reactions that result in the formation of both H_2O_2 and H_2O have been extensively studied [3–8], and it is now evident that palladium is the best catalyst among the metals that have been investigated. But even with palladium as the catalyst, the system must contain protons and a suitable anion such as Cl^- or Br^-. In the absence of these components, water will be the dominant product.

A commercial catalyst will almost certainly involve palladium or a bimetallic involving palladium, on a support such as silica or carbon [9,10], and it will be important that the metal remain on the support. In our initial studies, which represent an extreme case, an aqueous 0.1–1.0 M HCl liquid phase was used, and the palladium was rather rapidly distributed between $PdCl_4^{2-}$ and a palladium colloid, which was believed to be the active state of the catalyst [11,12]. Although the colloid was of interest at a fundamental level, it would not be desirable in a practical system. As a result of operating the system at much smaller Cl^- concentrations (e.g., 10^{-4} M) the loss of Pd from the support is diminished [8], and with Br^- as the halide and water as the liquid phase, the loss of Pd is negligible [7].

Most of the studies have been carried out with water, methanol or ethanol as the liquid phase. As a substitute for chlorine in pulp/paper bleaching and in textile bleaching, water would be the desirable solvent; however, as a source of oxygen for epoxidation reactions in simple alcohols (methanol or ethanol) would be preferable [13]. Ethanol is potentially a

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better medium than water for carrying out the synthesis reaction because of a five-fold larger solubility of H_2 and an eight-fold greater solubility of O_2. A comparison of the two liquid phases has shown that the difference is primarily found in the instability of the aqueous system; the net formation rate for H_2O_2 decreased continuously during the first 4 h of reaction [14]. In this case, the reaction was carried out in 0.17 M HCl, and it is likely that an unstable Pd colloid was formed at this larger chloride concentration.

Another potential limitation in this three-phase reaction system is that of mass transport, which may either involve the rate of solubility of the gases into the liquid phase or the rate of diffusion across a boundary layer at the surface of the catalyst particle. For a particular reactor design, the rate of dissolution of the gases has been addressed by Thompson and co-workers [4], but the actual rate, of course, depends on the system (i.e., bubble size, stirring rate, etc.).

The purpose of the present study was to explore a number of different factors that may influence the net formation rate of H_2O_2, the selectivity for the conversion of H_2 to H_2O_2, and the stability of the system. Such factors include the presence of an acid, the effect of temperature and the influence of Cl^- and Br^-, both on the selectivity and the loss of palladium. Although the pressures employed are much less than those expected for a commercial process, the influence of the variables are qualitatively the same. Moreover, it is important to note that the maximum H_2O_2 concentration of about 2 wt.% attained in this study is larger than that achieved in the raw product using the Riedl-Pfleiderer process [15], and with the ethanol system, the concentration of H_2O_2 can be readily increased by partial evaporation of the alcohol.

2. Experimental

The catalyst used in this study was Pd/SiO_2 prepared by the incipient wetness method using aqueous $PdCl_4{}^{2-}$ and Cab-O-Sil M5 silica, which is a fumed silica with a surface area of about 200 m^2 g^{-1}. The loading of the Pd was 5 wt.% unless stated otherwise. The $PdCl_4{}^{2-}$ was formed by dissolving $PdCl_2$ in concentrated HCl followed by dilution with distilled water. After addition of the solution to the silica, the material was dried in air at 120 °C overnight, heated in flowing O_2/He (20/40 mL min^{-1}) at 400 °C for 3 h, cooled in flowing He to 300 °C, and finally reduced in flowing H_2/He (20/40 mL min^{-1}) for 2 h. Previous XPS results confirmed that the supported palladium was present as Pd(0), both after the reduction step and after the catalytic reaction in ethanol [14].

The reactions were typically carried out at atmospheric pressure and at 10 °C in the closed glass reactor described in Ref. [16]. The reactor had a vent that exited to a gas chromatograph (HP 5890 with a 5A molecular sieve column operating at 30 °C) so the composition of the gas could be analyzed for H_2 and O_2. In order to improve the accuracy of the analysis a mixture of H_2/N_2 containing 10% N_2 was used when the O_2/H_2 ratio was 4. When the O_2/H_2 ratio was 15:1, an H_2/N_2 mixture was used which contained 80% N_2; thus, the composition of the gases in the 15:1 mixture was 75% O_2, 5% H_2 and 20% N_2. All the oxygen used in these experiments was 99.99% in purity. Unless stated otherwise, the gases were introduced at a total flow rate of 50 mL min^{-1} via a glass frit (Ace, 4–8 μm) at the bottom of the reactor.

The liquid phase consisted of 60 mL of ethanol acidified with sulfuric acid to 0.12 M unless stated otherwise. The chloride concentration for each experiment was attained by adding appropriate amounts of aqueous HCl, or in one case KCl. The bromide was introduced as an aqueous solution of KBr. The addition of both acids/salts introduced small amounts (<1.0 mL) of water to the system.

The O_2/H_2 ratios in the range from 3:1 to 15:1 that were used in these experiments are in the explosive regime; therefore, appropriate precautions should be taken. In particular the dry catalyst *should not* be added to O_2/H_2 gas mixture. Hence, the protocol for adding the catalyst was the following: (a) the ethanol was first exposed to the O_2/H_2 gas mixture via the frit for 30 min, (b) then 5 mL of the liquid phase was taken out of the reactor and a slurry was made with catalyst, and (c) this slurry was added to the remaining solution in the reactor. Even with these precautions, explosions have occurred with the 4:1 ratio, resulting in the destruction of the reactor. We have ceased carrying out experiments at these smaller O_2/H_2 ratios. At a 15:1 ratio for the entering gas, the composition of the gas exiting the slurry was generally outside of the explosive regime.

At appropriate times after the reaction had been initiated by the addition of the catalyst, the gas phase was analyzed and the conversion of H_2 was determined. In addition, an aliquot of the liquid phase (ca. 0.2 g) was removed and analyzed for H_2O_2 using a colorimetric method with a $TiOSO_4/H_2SO_4$ reagent [17]. From the net rate of H_2O_2 formation and the rate of H_2 conversion, the selectivity for H_2O_2 could be determined using the equation

$$S_{H_2O_2} = \frac{\text{rate of } H_2O_2 \text{ formation (mol/min)}}{\text{rate of } H_2 \text{ conversion (mol/min)}} \times 100 \qquad (1)$$

3. Results and discussion

3.1. The effects of O_2/H_2 ratios and the orders of reaction with respect to H_2 and O_2

The net formation of H_2O_2, the conversion of H_2 and the selectivity for H_2O_2 as a function of reaction time at two different O_2/H_2 ratios are shown in Fig. 1. It is apparent from Fig. 1A that the net formation rate, which was constant for 5 h, was 3.2 times greater for the O_2/H_2 ratio of 4 than that observed for the O_2/H_2 ratio of 15. The respective specific rates were 34 $mmol_{H_2O_2}$ g_{Pd}^{-1} min^{-1} and10.6 $mmol_{H_2O_2}$ g_{Pd}^{-1} min^{-1}. In 5 h, the H_2O_2 concentrations reached levels of about 1.8 wt.% for the 4/1 ratio and about 0.6 wt.% for the 15/1 ratio. The change in O_2/H_2 ratio also affected the H_2 conversions in a complex manner. At $O_2/H_2 = 15$ the H_2 conversion remained nearly constant at 40%, but over the 5 h period at $O_2/H_2 = 4$ the conversion increased from ca. 38% to 46%. This increase in conversion may be attributed to an additional pathway for the