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Catalysis of the Hydrogen Evolution Reaction by Colloidal Ag Anchored in Perfluorosulfonate Resin[1]

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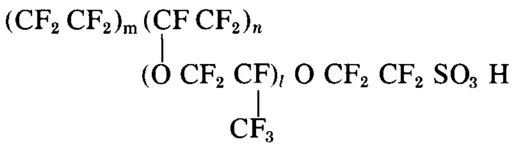
Colloidal silver particles were produced and characterized in the perfluorosulfonate membrane, Nafion 120. The size of the particles thus produced exceeds the size of the water clusters in the membrane. The hydrogen evolution reaction in the Cr^{2+}/H^+ system could be catalyzed by these membrane-anchored catalysts. The rate of this reaction was found to be first order in $[Cr^{2+}]$ and the reaction was found to be mass transport limited. Analysis of the rate of this reaction indicates that only a small fraction of the particles' surface is accessible to the reactants.

INTRODUCTION

Catalysis of water decomposition to hydrogen and oxygen has become of increasing interest recently in view of its relevance to the prospects of solar energy storage. Thus, many reports in the literature have shown that reactive intermediates can be efficiently diverted into the hydrogen or oxygen evolution reactions in the presence of the appropriate redox catalysts (*1–7*). The use of ion exchange resins to anchor such catalysts may, in addition to the conventional advantages of such supports, provide some advantages in photochemically induced electron transfer reactions. Studies on the effects of such materials on photochemical charge transfer reactions have recently been reported (*8–10*). In this context, it seemed of interest to study the thermal hydrogen evolution reaction catalyzed by metal clusters anchored in the cluster network of such an ion exchange membrane. Nafion[2] membrane of the general form:



$$\begin{array}{l}(\mathrm{CF_2\,CF_2})_m(\mathrm{CF\,CF_2})_n\\ \qquad\quad\;|\\ \qquad\quad(\mathrm{O\,CF_2\,CF})_l\,\mathrm{O\,CF_2\,CF_2\,SO_3\,H}\\ \qquad\qquad\quad\;|\\ \qquad\qquad\;\mathrm{CF_3}\end{array}$$

was chosen as the supporting matrix since its chemical, thermal and mechanical stability ensures no interference of the matrix itself in any side reactions. Small angle X-ray scattering studies established the cluster network model for the morphology of this material (*11*). The network according to this model consists of hydrated SO_3^- head groups and counter ions clusters (of ~40 Å in diameter) interconnected by short channels (of ~10 Å in diameter) all immersed in the fluorocarbon backbone. The similarity of this structure to inverted micelles has been pointed out (*12*) and was also found to affect the kinetics of luminescence quenching in the cluster network (*10*).

The detailed studies of Henglein have demonstrated that colloidal metallic silver can serve as a redox catalyst for the hydrogen evolution reaction (*13*). Among

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[2] Nafion is a registered trademark of DuPont Corporation.

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the reactive intermediates effective in this reaction were some metal ions at their lower oxidation state (*14*). Moradpour *et al.* observed that the reaction of Cr^{2+} to produce hydrogen can be efficiently catalyzed by colloidal platinum and gold. Although we find that both metals could be deposited in the Nafion membrane, silver was used in this study due to the higher degree of reproducibility in the preparation of the latter catalyst.

EXPERIMENTAL

Catalyst Preparation

Pieces of the Nafion membrane at constant weight of 0.185 g (~$1.91 \times 1.91 \times 0.025$ cm^3) in the H form was exchanged with the desired amount of aqueous Ag_2SO_4 solution. In determining the amount of Ag^+ to be exchanged, it is instructive to use the recently determined (*15*) value for the selectivity coefficient, $K_{H^+}^{Ag^+} = 1.07$, of Ag^+. This selectivity coefficient is defined as $K_{H^+}^{Ag^+} = (\chi_{Ag^+}[H^+]_w)/(\chi_{H^+}[Ag^+]_w)$, where χ is the ionic fraction of ions in the membrane and the subscript w represents concentration of the ion in the aqueous phase. Its value was carefully determined at constant ionic strength (*15*) of 0.01 *M* and we find it to vary only slightly with ionic strength down to 10^{-3} *M*. In accordance with Yeager and Steck's results, it is also only slightly dependent on χ_{Ag^+}. However, we find that reduction of Ag^+ by the method described below is never complete and reliance on this value therefore cannot be carried over to the reduced metal.

The exchanged membrane was transferred to plain water, bubbled with H_2 at elevated temperature (~60°C). The membrane, which at this stage acquired a yellow tint, was then stirred in Ar bubbled 1 *N* H_2SO_4 to wash out any unreacted Ag^+ left in the membrane. From this stage on, the membrane was kept in Ar-saturated solutions since it was found that Ag tends to oxidize upon standing in air-saturated solutions. The amount of Ag deposited in the membrane was calculated from the total amount of Ag_2SO_4 in the exchanged solution before and after equilibration with the membrane and the amount washed out by the acid solution after reduction. All concentrations of the dopants in the membrane are calculated assuming that the volume available is the total volume of the water-swollen membrane.

Materials

Stock solutions of Cr^{2+} were prepared by oxidation of metallic chromium in 0.02 *N* H_2SO_4. These were diluted with the various solutions under Ar using the syringe technique. Total chromium concentrations were determined spectrophotometrically as chromate after oxidation with H_2O_2 in basic solutions. All other materials were used as received. Water used throughout this study was triply distilled.

H_2 Production

The membrane-supported catalyst was equilibrated with the vigorously stirred Ar-saturated solution in the syringe. A predetermined amount of Cr^{2+} solution was injected into the syringe and the amount of H_2 produced was extracted on a Van Slyke manometer directly connected to a gas chromatograph (Infotronics 153C, dual 13X molecular sieve columns, Ar carrier). This procedure was repeated at various intervals after injection of the Cr^{2+} solutions on a fresh sample of the Nafion membrane.

RESULTS AND DISCUSSION

A. Characterization of the Catalyst

The absorption spectra of the membrane-anchored Ag clusters was monitored immediately after reduction of the Ag^+ ions by H_2 and following equilibration with 1 *N* H_2SO_4. As can be seen in Fig. 1, the initial spectrum peaking at 375

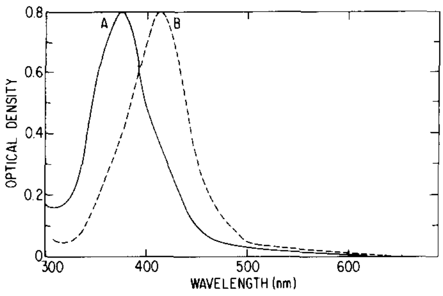

FIG. 1. Absorption spectra of the Nafion-anchored Ag catalyst. (A) immediately after reduction with H_2, (B) following equilibration with 1 N H_2SO_4. $[Ag]_m$ in the membrane is ca. 2×10^{-3} g-atom liter^{-1}.

nm is shifted to 412 nm following the treatment with sulfuric acid. Similar spectra were observed for colloidal silver produced in aqueous solutions (*13*). The absorption spectra of these colloids shifts to the red with the increased size of the particles. It was noticed that the spectrum of the Nafion-anchored catalysts changes at a much slower rate when equilibration with the acid was avoided. It seems therefore that the high acidity promotes the rate of aggregation of smaller-sized clusters in the membrane. The size of the Ag aggregates in the acid-treated membrane was indeed found by the electron microscopy experiments described below to be in the range expected to absorb light at this wavelength.

Electron microscopy of the membrane-anchored silver particles reveals particles of sizes somewhat bigger than the cluster size determined by small-angle X-ray scattering (*11*). In Fig. 2, a typical electron micrograph of these catalysts is shown. The average radius of these particles was determined from the measurement of some 200 particles to be 70 ± 20 Å. The size distribution is quite large and is dependent on the exact experimental procedure for the preparation of the catalyst. Similar measurements for the size of the particles indicate that at lower initial concentrations of Ag^+ particles of larger size and wider size distribution range are obtained. We were unable to observe at the highest magnification (×150,000) available to us any substructure in the silver particles. This, however, does not allow any conclusion on whether the growth of the particles ruptures the membrane morphology or whether the cluster network is maintained. It is clear, however, from the results discussed above that the large particles result from the aging procedure. Estimates of the amount of silver obtained from the concentration of particles observed in the electron micrographs agree with those calculated from the amount of Ag^+ reduced to within ±50%.

B. Diffusion in and out of the Membrane

Due to the high sensitivity of Cr^{2+} to oxygen, its rate of diffusion into the Nafion membrane was mimicked by Cu^{2+}. When the amount of Cu^{2+} was below the ion exchange capacity of the membrane, the rate of intake of Cu^{2+} was found to be first order in $[Cu^{2+}]$ in the aqueous phase. The rate of adsorption thus follows the rate law $d[M^{2+}]_m/dt = k[M^{2+}]_w$ where the subscript m and w represent concentrations in the membrane and water, respectively. This can be integrated to give $\ln(1 - S([M^{2+}]_m/[M^{2+}]_{w,0})) = -Skt$, where the subscript 0 signifies the initial concentration of the cation in the aqueous phase and S is the ratio of volume of the membrane after water swelling and the volume of aqueous phase in equilibrium with the membrane (under our experimental conditions $S = 1.62 \times 10^{-3}$). The above semilogarithmic dependence was obeyed under a variety of experimental conditions. The "lifetime" of M^{2+} in the aqueous phase ($1/Sk$) was, however, dependent on the rate of stirring of the aqueous phase. At a high enough rate of stirring, the adsorption rate became independent of the stirring rate. Under these conditions, the rate of diffusion in the aqueous phase does not affect the rate of adsorption into the membrane. The rate of diffusion within

Fig. 2. Electronmicrograph of the silver particles anchored in Nafion.

the resin has been shown to be the rate-determining step in the exchange of divalent cations. We then obtain $k = 0.48$ sec^{-1} for the adsorption rate constant (lifetime of ca. 20 min under the experimental conditions used). A diffusion coefficient of $\sim 10^{-7}$ cm^2/sec for Cu^{2+} in Nafion can be roughly approximated.

For the present study, the point of interest is the possibility that the rate of adsorption of M^{2+} from the aqueous phase may become the rate-determining step in the silver-catalyzed reaction. This is clearly not the case since, as is shown below, the hydrogen evolution reaction is much slower than the rate of adsorption. Furthermore, it was also found that the anchored Ag clusters up to total [Ag] of 0.01 g-atom $liter^{-1}$ in the membrane had no observable effect the rate of adsorption of Cu^{2+} into the membrane. The total concentration of silver in the following experiments was kept below this level. Diffusion of gases in and out of the membrane was checked by monitoring the lifetime of $Ru(bpy)_3^{2+*}$ in the membrane equilibrated with oxygenated or Ar saturated solution as previously described (*10*). It was found that in well-stirred solutions, most of the oxygen would diffuse out of the membrane in less than 10 min. Furthermore, when H_2-saturated samples of Nafion were transferred to an Ar-saturated solution, practically all of the H_2 could be extracted in less than 15 min. This is again fast compared to the H_2 production rate to be discussed below and cannot therefore play a significant role in the measurements of the kinetics of this reaction.

C. Hydrogen Production by the Nafion-Anchored Catalyst

In Fig. 3 we show characteristic time profiles for the H_2 production from Cr^{2+} catalyzed by the Ag catalyst anchored in Nafion.

$$Cr^{2+} + H^+ \rightarrow Cr^{3+} + \tfrac{1}{2}H_2. \qquad (1)$$

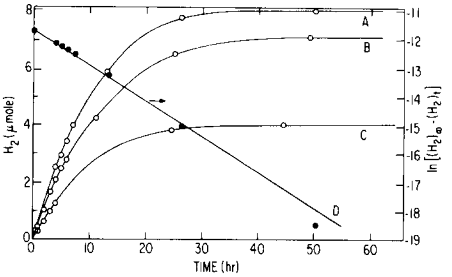

FIG. 3. Rate of H_2 production by Cr^{2+} on Ag anchored in Nafion membrane at constant $[Ag]_m = 3.5 \times 10^{-3}$ g-atom $liter^{-1}$ and varying initial $[Cr^{2+}]$. (A) $[Cr^{2+}]_0 = 4.4 \times 10^{-2}$ *M*; (B) $[Cr^{2+}]_0 = 3.9 \times 10^{-2}$ *M*; (C) $[Cr^{2+}]_0 = 2.2 \times 10^{-2}$ *M*; (D) Semilogarithmic plot for (A).

Close-to-stoichiometric conversion of Cr^{2+} to H_2 was observed in all experiments. No production of H_2 was obtained in the absence of the catalyst. The turnover numbers for the silver catalyst in the particular experiment of Fig. 3 were higher than 20 and the same piece of Nafion could be used for further H_2 production upon injection of fresh Cr^{2+} solution, as long as the ion exchange capacity of the membrane was not exceeded.

Plots of $\ln\{[H_2]_\infty - [H_2]_t\}$ vs t, where $[H_2]_t$ and $[H_2]_\infty$ are the amounts of H_2 produced at time t and at the end of the reaction, respectively, yield straight lines (Fig. 3D), indicating that the reaction is first order in $[Cr^{2+}]_m$.

The rate of H_2 production was measured at various concentrations of Cr^{2+}, while the amount of catalyst and the acidity of the solution were kept constant. As can be seen in Fig. 3, the kinetics still follows the same rate law and the rate constant obtained is indeed independent of $[Cr^{2+}]$. This was found to be the case also in all other experiments to be described below. The same rate constant was also obtained when the product, Cr^{3+}, was added to the membrane up to $[Cr^{3+}]_m = 0.11$ *M* (ca. 20% of the maximum ion exchange capacity of the membrane). Since this concentration is approximately 3 times higher than the highest Cr^{2+} concentration used, we may conclude that inhibition or poisoning of the catalyst by Cr^{3+} does not occur to any appreciable extent.

The effect of acid concentration in the solution which is equilibrated with the membrane was measured at constant concentration of silver particles and constant $[Cr^{2+}]_0$. Changing $[H_2SO_4]$ in the aqueous solution from 10^{-4} to 10^{-2} N had only little effect on the rate of H_2 production (Fig. 4). The high acidity of sulfonated ion exchange resins has been demonstrated by ^1H NMR studies (*17*). Furthermore, the perfluorosulfonated resins were used as super acids in catalysis of many organic reactions (*18*). From the ion exchange capacity of the membrane (0.83 meq/g), the density of the dry membrane (1.98 g/cm^3), and volume of the interior water of the swollen membrane (ΔV = 34% of the dry polymer), one calculates an acidity of 4.8 N in the interior aqueous phase of the membrane. It is therefore not surprising that changes of the acidity in the exterior aqueous phase in the range described above have a rather small effect on the catalysis. On the other hand, when the external acidity was increased to 1 N H_2SO_4, a pronounced increase in the rate constant is observed (Fig. 4). We attribute this increase in the rate constant to the increased mobility of Cr^{2+} in the membrane. Supporting electrolytes have been shown to increase cations diffusion in ion exchange resins (*19*). Surprisingly, it was noted that the rate constant for H_2 production is also somewhat increased when the external solution is at neutral pH. We offer no explanation for this increase in rate.

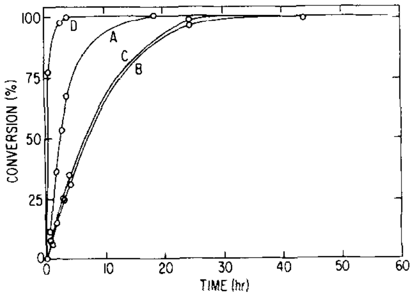

FIG. 4. Rate of H_2 production by Cr^{2+} catalyzed by Ag anchored in Nafion membrane at various acidities of the solution. $[Ag]_m$ = 3.5 × 10^{-3} g-atom liter^{-1}; $[Cr^{2+}]_0$ = 4.4 × 10^{-2} M. (A) H_2O; (B) 10^{-4} N H_2SO_4; (C) 10^{-2} N H_2SO_4; (D) 1 N H_2SO_4.

The rate constant for the H_2 production can be calculated from the slopes of the logarithmic plots in Fig. 3 to yield k_{obs} = 3.0 × 10^{-5} sec^{-1} or in terms of Ag gram-atoms, k = 8.6 × 10^{-3} M^{-1} sec^{-1}. A better presentation of k is probably in units of surface area. This can be calculated from the total $[Ag]_m$ and taking the average radius observed in the electron microscopy experiments r = 70 Å. Assuming the density of the silver particles to be the same as that of the bulk metal (ρ = 10.5 g/cm^3), the concentration of the silver particles can be calculated from C_p = $3[Ag]_m M/4\pi r^3 \rho N_0$ (in units of moles of particles per liter, M = 108 g-atom^{-1}). The total surface area of the particles in such a sample would then be A = $3[Ag]_m M/r\rho \times 10^3$ cm^{-1} (cm^2/cm^3). Under the experimental conditions of Fig. 3, the rate constant would therefore be k = 1.9 × 10^{-7} cm sec^{-1}.

Spiro has analyzed the general mechanism of heterogeneous catalysis by metals in solutions and has provided ample evidence that in a multitude of redox reactions the metal catalyst acts simply as a conductor of electrons (*20*). This point of view was also applied by Henglein to explain the catalysis of redox reactions of reactive intermediates by colloidal silver (*13*, *14*). The detailed electrochemical treatment of Spiro (*21*) for such catalytic reactions may therefore be adopted for the present system as well. The lack of any effect of the product Cr^{3+} concentration on the rate of H_2 evolution indicates that the reverse reaction -1 is slow enough to be neglected. If the reaction now occurs at the Tafel region on the silver particle, the catalytic rate would depend on the reductant concentration in a fractional order (*21*). For the reaction to be first order in [Cr^{2+}] the mass transfer limit has be to reached. Under such conditions the catalytic rate is given by $V = (D/r\rho)$ [Cr^{2+}], where D is the diffusion coefficient, r the stoichiometric number, and ρ the thickness of the diffusion layer (*21*). A typical value for the mass transfer coefficient ($D/r\rho$) in the presence of high concentrations of supporting electrolytes is $\sim 10^{-3}$ cm/sec. Since D for divalent cations in the ion exchange resin is reduced by some two orders of magnitude as compared to that in water, we would expect the observed rate constant to be $\sim 10^{-5}$ cm sec^{-1}. This value is still much bigger than the observed rate constant. A possible explanation for this small value may lie in an overestimate of the surface area available for the reaction. In fact, one would indeed expect the polymeric backbone to screen some fraction of the surface area from the diffusing reactants. It seems therefore that, although rather small particles could be produced in the matrix of the membrane, a large amount of the catalyst surface is lost through this screening effect.

CONCLUSION

Metallic catalysts can easily be produced in the network of ion exchange membranes. The size of these catalysts, however, is not predetermined by the morphology of the membrane itself. Sizes of metal particles much bigger than the size of a single water cluster of the membrane were observed in this study. This may occur either as a result of rupturing of the cluster network during the particle growth process or through growth of particles along the cluster network intercombining several clusters together. The high acidity of interior water phase of the membrane ensures fast proton discharge on the particle when the latter is charged cathodically. The diffusion rate on the other hand is somewhat reduced and the total rate becomes mass transfer limited. The catalyst surface in the membrane although nominally very large is effectively reduced by the polymeric backbone.

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