of foreign metal atoms on electrode surfaces.[30] Adatom layers only a few monolayers deep begin to take on the bulk electrocatalytic properties of the underpotentially deposited pure metal. Further, adatoms can be removed through oxidation and dissolution.[31] In contrast, the alloys studied in this work are subjected to the opposite process, which creates a surface with an electrocatalytic activity very similar to the metal making up the major fraction of bulk material.

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Registry No. Pt, 7440-06-4; $ZrPt_3$ alloy, 104675-03-8; $HfPt_3$ alloy, 137917-27-2; H_2SO_4, 7664-93-9; H_2, 1333-74-0; CO, 630-08-0.

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(30) Adzic, R. R. In *Advances in Electrochemistry and Electrochemical Engineering 13*; Gerischer, H., Ed.; John Wiley and Sons: New York, 1985.

(31) Rodriguez, R. R.; Tornquist, W. J.; Guillame, F.; Griffin, G. G. In *ACS Symposium Series No. 378*; Soriaga, M. P., Ed.; American Chemical Society: Washington, D.C., 1988; Chapter 25.

Mechanism of the Reduction of Water by Reduced Methyl Viologen Mediated by Platinized Alumina: H/D Isotope Effects

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The rate of oxidation of reduced methyl viologen ($MV^{\bullet+}$) by water, catalyzed by colloidal Pt/Al_2O_3, is reduced by a factor of $\simeq 5$ when D_2O is used as a solvent rather than H_2O in the presence of a pH 4.40 acetate buffer. In contrast, the rate measured in the presence of a pH 3.05 buffer is reduced only slightly when D_2O replaces H_2O. H/D isotope separation factors for the methyl viologen mediated reduction of water to hydrogen catalyzed by Pt/Al_2O_3 are 4.22 (±0.15) at pH 4.40 and 5.99 (±0.11) at pH 3.05, at 25 °C. These data are interpreted in terms of the electrochemical model for metal-catalyzed redox reactions with a pH-dependent mechanism for the hydrogen-evolving reaction. It is proposed that hydrogen atom combination on the catalyst surface is the rate-limiting step at pH 4.40, whereas at pH 3.05 diffusion of $MV^{\bullet+}$ is rate limiting and hydrogen evolution proceeds via the electrochemical reaction between a surface-adsorbed hydrogen atom and a solution-phase proton.

Introduction

The kinetics and mechanism of the reduction of water by reduced methyl viologen mediated by a platinum catalyst, i.e.

$$2MV^{\bullet+} + 2H^+ \xrightarrow{Pt_{cat}} 2MV^{2+} + H_2 \qquad (1)$$

has been the subject of numerous studies.[1-12] Much of the data collected to date support an electrochemical model for the catalysis, such as that described by Spiro and co-workers in their studies of metal-catalyzed redox reactions.[13-15] In this model the role of the catalyst is simply to conduct electrons from one redox couple to another, and the mechanisms for electron transfer from each redox couple to the colloidal particle are the same as those observed at a macroscopic electrode of the catalytic material.

Isotope effects and particularly isotope separation factors have been widely used in studies of hydrogen evolution at metal electrodes.[16-31] Theoretical isotope separation factors for the possible hydrogen-evolving mechanisms have been calculated,[32-38] and comparison between calculated and experimental isotope separation factors has proven useful in delineating possible mechanisms, especially when taken into consideration with other electrochemical measurements such as Tafel slopes and the dependence of the rate on proton concentration.[21] If as the electrochemical model suggests, the colloidal Pt catalysts act in a similar way to a macroscopic electrode, then isotope effects may also be useful in mechanistic studies of colloidal redox catalysis. Kopple et al. used isotope effects to probe the mechanism of hydrogen evolution from water using Cr^{2+} and $(CH_3)_2COH^{\bullet}$ radicals with gold sols as catalysts and concluded that similar mechanisms operate at both macroscopic gold cathodes and the catalyst particles.[39]

In a previous paper we described the results of a kinetic study of reaction 1 using a platinized alumina catalyst.[12] This choice of catalyst was made because it is highly reproducible, is active with a high hydrogen generating efficiency, and when dispersed

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(1) Meisel, D.; Mulac, W. A.; Matheson, M. S. *J. Phys. Chem.* **1981**, *85*, 179.

(2) Miller, D. S.; Bard, A. J.; McLendon, G.; Ferguson, J. *J. Am. Chem. Soc.* **1981**, *103*, 5336.

(3) Miller, D. S.; McLendon, G. *J. Am. Chem. Soc.* **1981**, *103*, 6791.

(4) Nenadovic, M. T.; Micic, O. I.; Adzic, R. R. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 1065.

(5) Albery, W. J.; Bartlett, P. N., McMahon, A. J. *Photogeneration of Hydrogen*; Harriman, A., West, M., Eds.; Academic Press: London, 1982; p 85.

(6) Delcourt, M. O.; Keghouche, N.; Belloni, J. *Nouv. J. Chim.* **1983**, *7*, 131.

(7) Matheson, M. S.; Lee, P. C.; Meisel, D.; Pellizzetti, E. *J. Phys. Chem.* **1983**, *87*, 394.

(8) Venturi, M.; Mulazzani, Q. G.; Hoffman, M. Z. *J. Phys. Chem.* **1984**, *88*, 912.

(9) Brandeis, M.; Nahor, G. H.; Rabini, J. *J. Phys. Chem.* **1984**, *88*, 1615.

(10) Douglas, P. Ph.D. Thesis, University of London, 1985, pp 293–348.

(11) Albery, W. J.; Bartlett, P. N.; McMahon, A. J. *J. Electroanal. Chem.* **1985**, *182*, 7.

(12) Mills, A.; Douglas, P.; Russell, T. *J. Chem. Soc., Faraday Trans. 1* **1990**, *86*, 1417.

(13) Spiro, M.; Ravno, A. B. *J. Chem. Soc.* **1965**, 78.

(14) Spiro, M. *Chem. Soc. Rev.* **1986**, *15*, 141 and references therein.

(15) Spiro, M.; Freund, P. L. *J. Chem. Soc., Faraday Trans. 1* **1983**, *79*, 1649.

(16) Walton, H. F.; Wolfenden, J. H. *Trans. Faraday Soc.* **1983**, *34*, 436.

(17) Horiuti, J.; Okamoto, G. *Sci. Pap. Inst. Phys. Chem. Res. Tokyo* **1936**, *28*, 231.

(18) Rome, M.; Hiskey, C. F. *J. Am. Chem. Soc.* **1954**, *76*, 5207.

(19) Fukada, M.; Horiuti, J. *J. Res. Inst. Cat.* **1962**, 43.

(20) Enyo, M.; Hoshi, M.; Kita, H. *J. Res. Inst. Cat.* **1962**, 153.

(21) Bockris, J. O.'M.; Srinivasan, S. *Electrochim. Acta* **1964**, *9*, 31.

(22) Enyo, M.; Matsushima, T. *J. Res. Inst. Cat., Hokkaido* Univ. **1966**, *14*, 248.

(23) Enyo, M.; Yokoyama, T.; Hoshi, M. *J. Res. Inst. Cat., Hokkaido Univ.* **1966**, *13*, 222.

(24) Yokotama, T. *J. Res. Inst. Cat.* **1967**, *15*, 84.

(25) Enyo, M. *J. Res. Inst. Cat.* **1967**, *15*, 1.

0022-3654/92/2096-816$03.00/0

does not coagulate upon saturation with H_2, unlike many other colloidal platinum catalysts. The pH-dependent kinetic data were interpreted in terms of an electrochemical model, with diffusion of $MV^{\bullet+}$ as the rate-limiting step at pH ≤ 3.1 and with hydrogen atom combination on the catalyst surface (the Volmer–Tafel mechanism, eqs 2 and 3), rate limiting at pH ≥ 4.4.[12]

$$H_3O^+ + e^- + M \rightarrow M\text{-}H + H_2O \text{ (fast discharge)} \quad (2)$$

$$2M\text{-}H \rightarrow 2M + H_2 \text{ (slow combination)} \quad (3)$$

In this work we report results from further studies with this catalytic system in which we have determined H/D isotope separation factors for hydrogen evolution and examined isotope effects on the rate of the reaction.

Experimental Section

Materials. Methyl viologen was purchased as the hydrated chloride salt from the Aldrich Chemical Co. The acetic acid and sodium acetate used as buffers were obtained from BDH and made up to give a final buffer concentration of 0.05 mol dm^{-3}. The zinc rod (99.9%) used to reduce methyl viologen was purchased from Aldrich, as was the D_2O (99.9%). Details of the preparation and characteristics of the Pt/Al_2O_3 catalyst have been given elsewhere.[12] For some of our studies the catalyst was made using 99.9% D_2O as solvent, rather than H_2O, in each of the preparative steps. Prior to its use, the catalyst was dispersed in buffered H_2O or D_2O and subjected to ultrasound for 1 min to provide a good dispersion. The catalyst dispersion was then saturated with H_2 for 20 min before being purged with N_2 for at least 20 min. After this process the catalyst dispersion was ready for injection into the reaction vessel containing $MV^{\bullet+}$ and the zinc rod in the buffered H_2O/D_2O mixture. All gases were supplied by BOC and the N_2 was white-spot, O_2-free grade. The water used was doubly distilled and deionized.

Methods. Kinetic Measurements. Rates for the loss of $MV^{\bullet+}$ were determined using the spectrophotometric method and apparatus described previously.[12] All experiments were carried out using $[MV^{2+}] = 0.01$ mol dm^{-3}, $[MV^{\bullet+}]_i \simeq 3 \times 10^{-5}$ mol dm^{-3}, and 0.05 mol dm^{-3} acetate buffer, at 25 °C. Initial rate measurements are accurate to ±5%.

The difference in dissociation constants between CH_3COOH ($pK_a = 4.76$ in pure water)[40] and CH_3COOD ($pK_a = 5.31$ in pure D_2O)[40] results in the value of pD ($-\log [D^+]$) in pure D_2O being 0.55 greater than the value of pH in pure H_2O for the same buffer composition. Because we have kept the buffer composition constant when changing from H_2O to D_2O, rather than trying to compensate for this effect, pH and pD values for the kinetic studies in pure H_2O and D_2O are not the same. For convenience, in the text the experimental conditions will be specified by the pH maintained by the buffer composition in pure H_2O.

Isotope Separation Measurements. The reaction vessel contained 50 cm^3 of a buffered solution of MV^{2+} (0.01 mol dm^{-3}) in an H_2O/D_2O mixture which was stirred continuously at 25 °C. The reaction solution was purged with N_2 for 20 min prior to the reduction of some of the MV^{2+} to $MV^{\bullet+}$ by introducing a zinc rod into the solution, via a rubber septum. During this time the head space of the vessel was continuously swept out with N_2 to maintain a low O_2 concentration. The reduction of the H_2O/D_2O mixture to $H_2/HD/D_2$ by $MV^{\bullet+}$, via reaction 1, was initiated by injecting 0.05 cm^3 of an N_2-purged buffered dispersion of the catalyst (0.01 g cm^{-3}) into the reaction vessel once an adequate concentration of $MV^{\bullet+}$ had been generated, which was usually $\simeq$2 min after initial insertion of the zinc rod.

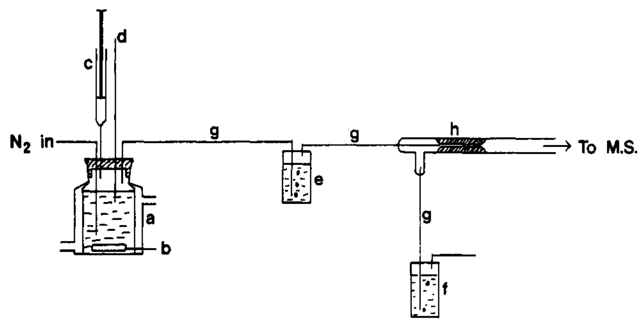

Figure 1. Schematic diagram of the instrumental arrangement: (a) water-jacketed reaction vessel, (b) stirrer bar, (c) 0.05-mL syringe, (d) zinc rod, (e, f) H_2SO_4 traps, (g) glass capillary, (h) capillary inlet to MS ion source.

TABLE I: Isotope Effects on Initial Rates of $MV^{\bullet+}$ Oxidation[a]

solvent	[catalyst][b]/ µg cm^{-3}	pH[c]	$-d[MV^{\bullet+}]_i/dt$/ 10^{-7} mol dm^{-3} s^{-1}
H_2O	5	3.05	4.6
D_2O	5	3.05	4.0
H_2O	14	4.40	3.3
D_2O	14	4.40	0.63

[a] All experiments with $[MV^{2+}] = 0.01$ mol dm^{-3}, $[MV^{\bullet+}]_i \simeq 3 \times 10^{-5}$ mol dm^{-3}, and 0.05 mol dm^{-3} acetate buffer at 25 °C. [b] Final concentration in solution. [c] This is the pH of the buffer solution in pure H_2O. The pD values in D_2O are 0.55 higher than the pH values in pure H_2O.

N_2 was then bubbled through the reaction solution at a rate of $\simeq$0.5 mL s^{-1} as a carrier gas for the $H_2/HD/D_2$ produced in the reaction. This gas stream was carried by a short length of quartz capillary (a 0.3-mm-diameter untreated gas chromatography capillary, supplied by Phase Separation Ltd.), through a concentrated sulfuric acid trap to remove H_2O/D_2O, then onto the bleed inlet of a quadrupole mass spectrometer, and finally through a second sulfuric acid trap to prevent interference by back-diffusion of atmospheric water vapor. Some experiments were carried out in which the zinc rod was removed immediately prior to injection of the catalyst, while for others the rod was left in solution for the duration of the experiment. We could detect no difference in isotope separation factors for these two methods, but the latter gave a better signal to noise ratio and was the generally adopted procedure. Figure 1 shows the experimental arrangement.

The mass spectrometer was set to repetitively scan the mass range 1–4 at a frequency of 2 s/scan and the output passed to a Gould 4072 digital oscilloscope where signal averaging of 16–32 traces was carried out to give an adequate signal to noise ratio. The Micromass Q50 quadrupole mass spectrometer was suitably adapted to analyze the gas sample via a fine capillary inlet leading directly into a conventional electron impact ion source, operated at 70 eV. Electron impact cross-sections for H_2, HD, and D_2 were assumed to be identical.[41] Mass discrimination factors over m/z 2–4 were determined using accurately made up H_2/He gas mixtures with appropriate correction for variations in their respective electron impact cross-sections,[42] and the discrimination at m/z 3 was assumed to be midway between that of m/z 4 and m/z 2. Although the mass discrimination factor between m/z 4 and 2 varied between $\simeq$7/1 and $\simeq$2/1, depending upon in-

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(26) Hammerli, M.; Mislan, J. P.; Olmstead, W. J. *J. Electrochem. Soc.* **1969**, *116*, 779.

(27) Hammerli, M.; Mislan, J. P.; Olmstead, W. J. *J. Electrochem. Soc.* **1970**, *117*, 751.

(28) Enyo, M. *Electrochim. Acta* **1973**, *18*, 155.

(29) Matsushima, T.; Enyo, M. *Electrochim. Acta* **1974**, *19*, 117.

(30) Matsushima, T.; Enyo, M. *Electrochim. Acta* **1974**, *19*, 125.

(31) Matsushima, T.; Enyo, M. *Electrochim. Acta* **1974**, *19*, 131.

(32) Horiuti, J.; Nakamura, T. *J. Res. Inst. Cat.* **1951**, *2*, 73.

(33) Horiuti, J.; Fukada, M. *J. Res. Inst. Cat.* **1962**, 43.

(34) Bockris, J. O.'M.; Srinivasan, S. *J. Electrochem. Soc.* **1964**, *111*, 844.

(35) Bockris, J. O.'M.; Srinivasan, S. *J. Electrochem. Soc.* **1964**, *111*, 853.

(36) Bockris, J. O.'M.; Srinivasan, S. *J. Electrochem. Soc.* **1964**, *111*, 858.

(37) Enyo, M. *Electrochim. Acta* **1976**, *21*, 15.

(38) Tsionsky, V. M.; Krishtalik, L. I. *J. Res. Inst. Cat, Hokkaido Univ.* **1980**, *28*, 371.

(39) Kopple, K.; Meyerstein, D.; Meisel, D. *J. Phys. Chem.* **1980**, *84*, 870.

(40) Gary, R.; Bates, R. G.; Robinson, R. A. *J. Phys. Chem.* **1965**, *69*, 2750.

(41) Keiffer, L. J. *J. At. Data* **1969**, *1*, 19.

(42) Keiffer, L. J.; Dunn, G. H. *Rev. Mod. Phys.* **1966**, *38*, 1.

TABLE II: Control Experiments of Isotope Separation Factors

run no.	H_2O/D_2O ratio (v/v)	solvent used in catalyst prepn	pH[a]	$H_2/HD/D_2$ ratio	SF
1[b]	50/50	H_2O	3.05	none detected	
2[c]	0/100	D_2O	3.05	100/0/0	
3	0/100	D_2O	3.05	0/0/100	
4[d]	0/100	H_2O	3.05	0/1.5/98.5	≃6.8

[a] This is the pH of the buffer solution in pure H_2O. The pD values in pure D_2O are 0.55 higher than the pH values in pure H_2O. [b] No MV^{2+}, zinc rod immersed in buffer solution for 30 min. [c] No MV^{2+}, no zinc rod, H_2 passed through solution. [d] SF estimated using the H_2O/D_2O ratio calculated including contribution to H_2O from catalyst solution injected into the reaction mixture (0.05 mL).

strument settings, repeat measurements using widely different instrumental conditions gave identical isotope separation factors.

It should be noted that the concentration of $MV^{\bullet+}$ does not remain constant throughout the experiment, and isotope separation factors are averaged over a range of $MV^{\bullet+}$ concentrations as the reaction proceeds. Unfortunately, our experimental arrangement was not suitable for accurate time-resolved studies, but we could not identify any major changes in isotope separation factors for traces recorded at the beginning and end of any individual run.

Solvent mixtures were prepared on a volume to volume basis and mole fractions calculated using densities of 0.9970 and 1.1045 for H_2O and D_2O, respectively.[43] The isotopic contribution from the solvent injected with the catalyst dispersion and water of crystallization from reactants and buffer salts is negligible for all runs except control experiment run 4, where the solvent injected with the catalyst dispersion is the major source of H_2O in the reaction mixture.

Results and Discussion

Kinetic Studies. Table I shows initial rates for loss of $MV^{\bullet+}$ in pure H_2O and D_2O in the presence of pH 3.05 and 4.40 acetate buffers. The slight difference in rate at pH 3.05 is consistent with either a diffusion-controlled process (bearing in mind the ≃20% higher viscosity of D_2O as compared to H_2O)[43] or the difference between pD and pH in the different solvents.[12] However, the ≃5-fold decrease in rate when D_2O is used as solvent instead of H_2O, using pH 4.40 buffer, is much higher than expected even on the basis of the pH/pD shift,[12] and this observation prompted us to examine H/D isotope separation factors in more detail.

Isotope Separation Factors. The isotope separation factor (SF) is defined as the ratio of the atomic isotopic ratio in the gas phase to that in solution.

$$SF = \{[H]/[D]\}_{gas}/\{[H]/[D]\}_{aq} \tag{4}$$

Experimentally, this is given by

$$SF = [(Int.H_2 + Int.HD/2)/(Int.D_2 + Int.HD/2)]/[f_{H_2O}/f_{D_2O}] \tag{5}$$

where $Int.H_2$, $Int.HD$, and $Int.D_2$ are the corrected mass spectroscopic peak areas for H_2, HD, and D_2, respectively, and f_{H_2O}, and f_{D_2O} are the mole fractions of pure H_2O and D_2O used in preparing the reaction mixture.

In our experiments we have varied $[f_{H_2O}/f_{D_2O}]$ between 1 and 9. Low $[f_{H_2O}/f_{D_2O}]$ ratios maximize the accuracy of the experimental determination of SF and were used by Kopple et al. in studies of gold sols.[39] However, results obtained at higher $[f_{H_2O}/f_{D_2O}]$ ratios are easier to interpret theoretically,[32-39] and much experimental work with electrodes has been carried out with $[f_{H_2O}/f_{D_2O}] \geq 9$.[18-31]

Control Experiments. Table II shows results from four control experiments. Data from run 1 show that the zinc rod alone does not generate detectable amounts of hydrogen even at pH 3.05. The results from run 2 show that the catalyst is not effective in causing isotope exchange between solution and gas phase on the time scale of our experiments; hence, our data refer to kinetic isotope effects rather than the thermodynamic equilibrium composition between solution and gas phases. Results from run 3 show that the hydrogen pretreatment of the catalyst does not give a surface coverage of hydrogen which is accessible for evolution in these experiments. The results from run 4 show that H carried over from catalyst preparation, associated with either the citrate used in the catalyst preparation or H_2O adsorbed onto the Pt or alumina, is not preferentially evolved. The results from runs 3 and 4 confirm that we are correct in using the bulk H_2O/D_2O ratios in calculation of the separation factors. It is interesting to note that Kopple et al. found evidence of hydrogen abstraction from the citrate or poly(vinyl sulfate) stabilizers used in the preparation of their gold sols.[39]

TABLE III: Isotope Separation Factors at pH 4.40

run no.	H_2O/D_2O (v/v)	solvent used for catalyst prepn	H_2/HD ratio[a]	SF
5	50/50	H_2O	60.5/39.5	4.05
6	50/50	H_2O	63.4/36.6	4.45
7	50/50	H_2O	59.9/39.1	4.05
8	50/50	D_2O	61.3/38.7	4.16
9	75/25	H_2O	86.0/14.0	4.41
10	75/25	H_2O	85.6/14.4	4.28
11	90/10	H_2O	94.8/5.2	4.15
12	90/10	H_2O	94.9/5.1	4.23

[a] In some cases at 50/50 H_2O/D_2O a trace of D_2 (≤0.5%) could also be detected.

pH 4.40. Table III summarizes the results at this pH. The separation factor is independent of both the H_2O/D_2O ratio used and the solvent used for catalyst preparation and has an average value of 4.22 (±0.15). The electrochemical model predicts that in this pH region the separation factor should be the same as that observed on macroscopic electrodes at low overpotentials. In this regard, it is interesting to note that Fukada and Horiuti[19] and Hammerli et al.[26,27] obtained separation factors in the region of 3.8–4.4 at low overpotentials (≤≃50 mV) on Pt electrodes, which are comparable with the values reported here.

The mechanism for hydrogen evolution at low overpotentials on Pt macroelectrodes is generally considered to be one in which the catalytic combination of hydrogen atoms on the metal surface is rate limiting.[21,37] Theoretical calculations of the separation factor for this mechanism have been carried out[36,37] and give SF values in the range of 3.7–4.9. The lower value of 3.7, obtained by Enyo,[37] appears to agree best with the available experimental data. Of the possible mechanisms, only catalytic combination and slow molecular hydrogen diffusion would give rise to the Tafel slope of −27 (±1) mV/decade, previously measured for these Pt/Al_2O_3 catalysts.[12,21] Unfortunately, calculated H/D separation factors for these two mechanisms are close.[21] However, the diffusion model can probably be discounted because higher reaction rates can be obtained simply by reducing the pH.[12]

TABLE IV: Isotope Separation Factors at pH 3.05

run no.	H_2O/D_2O (v/v)	solvent used for catalyst prepn	$H_2/HD/D_2$ ratio	SF
13	50/50	H_2O	78.8/14.9/6.3	6.25
14a[a]	50/50	H_2O	77.7/16.2/6.2	6.00
14b[a]	50/50	H_2O	78.4/14.9/6.7	6.04
15	50/50	H_2O	80.3/10.9/9.1	5.93
16	50/50	D_2O	78.9/13.7/7.4	6.00
17	75/25	H_2O	91.5/6.3/2.2	5.88
18	75/25	H_2O	91.6/6.1/2.3	5.82
19	90/10	H_2O	96.3/3.7/tr[b]	5.88
20	90/10	H_2O	96.4/3.7/tr	6.04

[a] In this run SF was measured soon after catalyst injection as usual (14a) and also after the zinc rod had been left immersed in the N_2 purging solution in the presence of the catalyst for ≃2 h (14b). [b] tr = trace.

pH 3.05. Data for experiments at this pH are shown in Table IV. The separation factor is independent of both the H_2O/D_2O

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(43) MacKay, K. M.; Dove, M. F. A. In *Comprehensive Inorganic Chemistry*; Trotman-Dickenson, A. F., Ed.; Pergammon Press: New York; 1973; Vol. 1, Chapter 3, p 115.

ratio used and the solvent used for catalyst preparation and has an average value of 5.99 (±0.11). The results from run 14 show that the separation factor remains constant even after high catalyst turnovers. Although the separation factor remains constant for all H_2O/D_2O ratios, at this pH there is a significant fraction of D_2 produced at high D_2O concentrations and the ratio of HD/D_2 varies with the composition of the reaction solution. The separation factors are similar to those observed with gold sols (5–6.7),[39] but at 50/50 H_2O/D_2O we observed a HD/D_2 ratio of $\simeq 2/1$ compared to $\simeq 10/1$ for studies with gold sols.[39] In the absence of any suitable theoretical models for separation factors at high concentrations of deuterium, we offer no explanation for this difference in behavior. However, it is interesting to note that the ratio reported with gold sols approximates to that expected for the statistical scrambling of the $\simeq 6/1$ ratio of H to D liberated.

Isotope separation studies are particularly interesting at this pH because our kinetic studies can tell us nothing about the mechanism of the hydrogen-evolving reaction. Experimental work with Pt electrodes shows that the isotope separation factor increases from $\simeq 3.6$ at zero overpotential to $\simeq 6.5$ at an overpotential of $\geq \simeq 300$ mV.[19,26,27] Enyo has examined the effect of increasing overpotentials on SF theoretically in some detail and has had some success in matching theoretical predictions with experimental data.[37] The change in SF from $\simeq 3.6$ to $\simeq 6.5$ on increasing the overpotential has been interpreted in terms of a change in mechanism.[21,37] At low overpotential, catalytic combination is rate limiting (eqs 2 and 3), while at high overpotential the mechanism involves the electrochemical reaction (6) as the rate-limiting process.[37]

$$\begin{aligned} &\text{M–H} + H_3O^+ + e^- \rightarrow \\ &\qquad \text{M} + H_2 + H_2O \text{ (electrochemical reaction)} \quad (6) \end{aligned}$$

The pH dependence of the separation factor for colloidal Pt sols is very similar to that for macroelectrodes and presumably arises from the same change in mechanism. As the pH is reduced from 4.4 to 3.05, the difference in equilibrium potentials for $MV^{2+}/MV^{\bullet+}$ (−0.46 V vs NHE)[44] and $H^+/{}^1/{}_2H_2$ increases by $\simeq 80$ mV, which, by analogy to the behavior of Pt electrodes,[18,26,27,37] is enough to cause the observed increase in separation factor.

Conclusions

The rate of oxidation of $MV^{\bullet+}$ by water catalyzed by colloidal Pt/Al_2O_3 in the presence of a pH 4.4 buffer is reduced by a factor of $\simeq 5$ when D_2O is used as a solvent rather than H_2O. In contrast, the rate measured in the presence of a pH 3.05 buffer is reduced only slightly when D_2O replaces H_2O. This is consistent with the mechanism derived from kinetic studies, in which the reaction rate is controlled by diffusion of $MV^{\bullet+}$ to the catalyst surface at pH $\leqslant 3.1$ and by combination of hydrogen atoms on the catalyst surface at pH $\geqslant 4.4$.[12]

H/D isotope separation factors are strongly pH dependent and vary from 4.22 (±0.15) at pH 4.40 to 5.99 (±0.11) at pH 3.05. These separation factors are typical of those measured on Pt macroelectrodes at low and high overpotentials, respectively.[19,26,27] These results give substantial support to the electrochemical model used to describe this metal-catalyzed redox reaction[12] and add to the weight of evidence in favor of this model for metal-catalyzed redox reactions in general.[13–16] The data can be interpreted in terms of a changing mechanism for the hydrogen-evolving reaction. Catalytic hydrogen atom combination is the rate-limiting step at pH 4.40 (eqs 2 and 3), whereas at pH 3.05 the hydrogen-evolving reaction proceeds via the electrochemical reaction between a surface-adsorbed hydrogen atom and a solution-phase proton (eq 6).

Isotope separation studies have proved particularly useful in understanding the mechanism of hydrogen evolution at low pH, where diffusion of $MV^{\bullet+}$ to the catalyst is the overall rate-determining step. Under these conditions kinetic studies can give no insight into the processes subsequent to the diffusional encounter, but H/D isotope separation studies probe the hydrogen-evolving reaction directly.

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Registry No. $MV^{\bullet-}$, 15591-62-5; H_2O, 7732-18-5; Pt, 7440-06-4; D_2, 7782-39-0.

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(44) Summers, L. A. *The Bipyridinium Herbicides*; Academic Press: New York, 1980; Chapter 4.

Formation of Radical Ion Pairs in Aniline Adsorption on Zeolites

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The formation of the aniline radical cation was observed on H–mordenite and H–faujasite in which the distribution of aluminum among different framework and nonframework coordination sites has been characterized by high-resolution solid-state NMR. The configuration of the radical cation was defined by its hyperfine structure. Molecular oxygen adsorbed after (H–mordenite) or during (H–faujasite) the formation of these radical cations forms the superoxide ion O_2^- which interacts with one ^{27}Al ($I = {}^5/{}_2$) nucleus, as evidenced by the superhyperfine structure of simple six-line sets. Moreover, the value of the superhyperfine splitting of O_2^- seems to reflect the strength of the electron acceptor sites or of the Lewis acid sites, the strongest being on H–mordenite.

Introduction

The formation of organic radicals on appropriately treated zeolites is well documented. Radical cations were observed earlier on faujasite type zeolite, HY, from molecules having a low ionization potential like polynuclear aromatic hydrocarbons, arylamines, and phenylalkenes.[1,2] It was recently reported that, on some strongly acidic zeolites such as H–mordenite and H–ZSM-5, aromatics as simple as benzene and toluene, and olefins such as ethylene and propene which possess a relatively high ionization potential, can easily form radicals.[3–6] However, the unpaired

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(1) Stamires, D. N.; Turkevich, J. *J. Am. Chem. Soc.* **1964**, *86*, 749.
(2) Dollish, F. R.; Hall, W. K. *J. Phys. Chem.* **1967**, *71*, 1005.
(3) Shin, S. *J. Catal.* **1983**, *79*, 390.
(4) Lange, J.-P.; Gutsze, A.; Karge, H. G. *J. Catal.* **1988**, *114*, 136.

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