

ciation on the metal surface, (ii) surface diffusion across the metal/carbon interface, and (iii) reaction with active sites on the carbon to produce methane. Instead, Holstein and Boudart propose that, in the case of platinum-catalyzed hydrogenation of carbon, the rate-determining step is the breakage of carbon-carbon

(22) In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the numbering: e.g., III \rightarrow 3 and 13.)

bonds with the formation of a carbon-platinum bond. Subsequent removal of the carbide carbon takes place by interaction with hydrogen to form methane. It follows, therefore, that the rate of platinum-catalyzed hydrogenation of graphite should be enhanced by the addition of any species which facilitates the breaking of carbon-carbon bonds. The present surface chemical studies clearly demonstrate that TiO_2 species in intimate contact with Pt perform this function.

Qualitatively the catalytic hydrogenation of graphite may be regarded as a bifunctional process, with the titania activating the carbon and platinum serving to dissociate hydrogen.

Registry No. Pt, 7440-06-4; TiO_2 , 13463-67-7; graphite, 7782-42-5.

Separation Factor in the Photoassisted Catalytic Decomposition of Tritiated Water by Pt/ TiO_2

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(Received: August 12, 1985)

We measured first the hydrogen separation factor for the H_2O -HTO system in the photoassisted catalytic decomposition along with that for the H_2O - D_2O system. It was 15.4 ± 0.2 for H_2O -HTO at the initial stage of the reaction. For H_2O - D_2O , it was 5.1 ± 0.05 over a wide mixing ratio. These values are equivalent with those from electrolysis, indicating that the photoassisted decomposition proceeds with the same mechanism as the electrolysis. These results also confirmed that the catalytic process is the rate-determining step. The separation factors, however, decreased with reaction time to 6.2 ± 0.05 (H_2O -HTO), 3.6 ± 0.05 (H_2O -HDO), and 3.05 ± 0.05 (D_2O -HDO) due to the gas-liquid equilibration reaction.

Introduction

Extensive investigations have been carried out on photoassisted catalytic reactions,¹⁻³ among which great interest has been aroused in the photoassisted catalytic decomposition of water from the viewpoint of solar energy conversion.⁴ According to the postulated mechanism of this reaction,⁵ the hydrogen separation factor is considered comparable with that in electrolysis. Baba et al. have found that the separation factor for H_2O - D_2O (1:1) in the photoassisted decomposition is equivalent to that in the electrolysis.⁶ On account of this observation, the separation factor for H_2O - T_2O system is expected as large as 15-47, depending on the reaction mechanisms.⁷⁻¹⁰ However, no experimental observation has been reported in the photoassisted decomposition of H_2O - T_2O , in spite of its importance for mechanisms analysis. In addition, it is worthwhile to investigate the separation factor for the H_2O - T_2O system from the viewpoint of the enrichment and/or separation of tritium in/from tritiated water, which is one of the important problems in the tritium technology for heavy water moderated fission reactors and for the development of thermonuclear fusion reactors.

From these viewpoints, we measured the separation factors for the H_2O -HTO system in the photoassisted decomposition as well as for the H_2O - D_2O system. In this paper, we describe the first observation of the separation factor for H_2O -HTO. The implication of the observed values is discussed.

Experimental Section

Titanium dioxide (anatase) was prepared according to Kurosaki et al.:¹¹ hydrolysis of TiCl_4 solution (0.33 M) with 3 N ammonia solution at 273 K, drying of the precipitate at 397 K, and calcination at 873 K in air. Platinized TiO_2 (ca. 0.6 wt. %) was prepared in accordance with the modified procedures reported

by Courbon et al.:¹² impregnation of H_2PtCl_6 solution (1.7×10^{-2} M) over the TiO_2 powder, drying at 373 K, oxidation at 873 K in air, and reduction with H_2 at 40 kPa at 873 K. X-ray diffraction confirmed its anatase structure: the crystallite size was determined as 390 Å. The BET surface area was 30 m^2/g .

The reactant waters were mixtures of H_2O - D_2O and H_2O -HTO. The mixing molar ratio was in the range of 1/50 to 50/1 for H_2O - D_2O and $(1.8 \times 10^4)/1$ to $(3.6 \times 10^4)/1$ for H_2O -HTO. Ordinary water was used after distillation. Heavy water (NMR gradw, 99.95%) and tritiated water (HTO- H_2O , 1 Ci/ cm^3) were purchased from Merck and New England Nuclear, respectively. They were used without further purification.

The apparatus used for the measurement of separation factors consisted of a quartz reaction vessel, vacuum line, and a gas sampling device. The gas sampling device was connected to a radio-gas chromatograph (YANACO G2800-TCD/RD-4C). The Pt/ TiO_2 catalyst of 0.3 g was added to 5 mL of reactant water in the reaction vessel. The catalyst was dispersed with magnetic stirring and illuminated with 30-W deuterium lamp (Hamamatsu Photonics, L544) which was about 2 cm distant from the wall of

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[†] Faculty of Science.

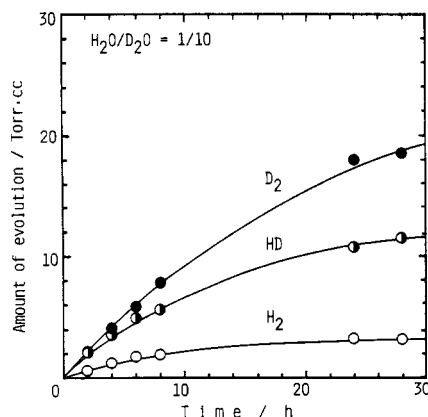


Figure 1. Time course of hydrogen isotope evolution from $\text{H}_2\text{O}-\text{D}_2\text{O}$ (1:10).

the reaction vessel. The reaction temperature was kept at 295 ± 3 K with water bath. The evolved gas was analyzed by the radio-gas chromatograph: a $\text{FeCl}_3/\text{active Al}_2\text{O}_3$ column of 1-mm diameter and 100-cm length was used at 77 K. It had been calibrated against hydrogen isotopes (H_2 , D_2 , HD, and HT).

Results and Discussion

The photocatalytic activity of the Pt/TiO_2 catalyst was 80 times larger than that of TiO_2 in the H_2O decomposition. The hydrogen evolution rate in H_2O decomposition over the Pt/TiO_2 catalyst was on the order of $1 \mu\text{mol}/\text{h}$. This is almost equivalent to the values reported by other investigators.^{6,13} However, oxygen evolution was not detected in the present study. This is considered due to the oxygen being adsorbed on TiO_2 surface till saturation, because the total amount of evolved hydrogen was on the order of several tens of micromoles, whereas the surface area of the catalyst was on the order of $1 \times 10^5 \text{ cm}^2$. The absence of oxygen evolution might arise from other processes as H_2O_2 formation in water,^{1,2} oxidation of surface impurities such as CO, or oxidation of organic impurities in water.

Figure 1 shows, as an example, the hydrogen evolution from $\text{H}_2\text{O}-\text{D}_2\text{O}$ (1:10). The evolution rate of a given hydrogen isotope gradually decreased with reaction time, reaching asymptotically a steady value. This was also true for all the experimental runs in the present study. Such time course was due to the reaction being measured in a closed system.

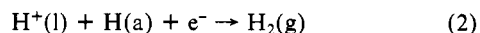
The time course of the hydrogen evolution could be described with the pseudo-first-order kinetics as

$$\ln [X_e/(X_e - X_t)] = k_{ap}t \quad (1)$$

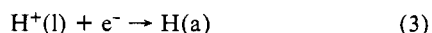
where X_e and X_t are the amounts of evolved hydrogen isotope, X , at steady state and at time t , respectively. k_{ap} is the apparent rate constant. X_e and k_{ap} were determined from the observed time course by means of least-squares curve fitting. The solid lines in Figure 1 are the calculated time course using X_e and k_{ap} determined as above. They agree well with the observed curves. It was found that k_{ap} was constant for a given hydrogen isotope irrespective of the mixing ratio of isotope waters. They were determined as 0.10 ± 0.006 (H_2), 0.07 ± 0.006 (HD), and 0.04 ± 0.006 (D_2 and HT) per hour.

In the hydrogen electrode reaction,^{7-10,14} three models have been presented as follows:

(I) charge-transfer overpotential model (slow electrochemical desorption)



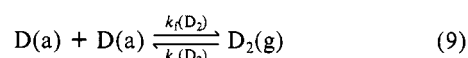
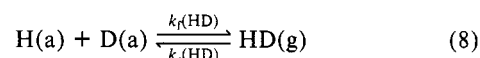
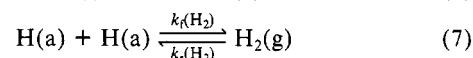
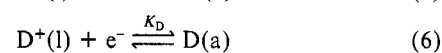
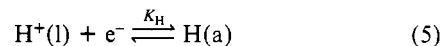
(II) chemical reaction overpotential model; (i) slow electrochemical discharge



(ii) slow association reaction/desorption



where (l), (a), and (g) indicate liquid, adsorbed, and gas phase, respectively. Assuming that the mechanism of the photoassisted decomposition is the same as electrolysis and reaction 4 is the rate-determining step, we describe the reaction process as follows, e.g., for $\text{H}_2\text{O}-\text{D}_2\text{O}$ system



where K , k_f , and k_r are equilibrium constant and rate constants for forward and reverse reactions, respectively. Rate equations for evolution of hydrogen isotopes are expressed as follows.

$$d[\text{H}_2]/dt = k_f(\text{H}_2)[\text{H}(\text{a})]^2 - k_r(\text{H}_2)[\text{H}_2] \quad (10)$$

$$d[\text{HD}]/dt = k_f(\text{HD})[\text{H}(\text{a})][\text{D}(\text{a})] - k_r(\text{HD})[\text{HD}] \quad (11)$$

$$d[\text{D}_2]/dt = k_f(\text{D}_2)[\text{D}(\text{a})]^2 - k_r(\text{D}_2)[\text{D}_2] \quad (12)$$

When the concentration of each hydrogen isotope molecule X , is $[X]_e$ at the steady state, the following equations are valid.

$$\ln \left(\frac{[\text{H}_2]_e}{[\text{H}_2]_e - [\text{H}_2]_t} \right) = \left(\frac{k_f(\text{H}_2)K_H^2[\text{H}^+]^2}{[\text{H}_2]_e} \right) t = k_r(\text{H}_2)t \quad (13)$$

$$\ln \left(\frac{[\text{HD}]_e}{[\text{HD}]_e - [\text{HD}]_t} \right) = \left(\frac{k_f(\text{HD})K_H K_D [\text{H}^+][\text{D}^+]}{[\text{HD}]_e} \right) t = k_r(\text{HD})t \quad (14)$$

$$\ln \left(\frac{[\text{D}_2]_e}{[\text{D}_2]_e - [\text{D}_2]_t} \right) = \left(\frac{k_f(\text{D}_2)K_D^2[\text{D}^+]^2}{[\text{D}_2]_e} \right) t = k_r(\text{D}_2)t \quad (15)$$

where $[\text{H}^+]$ and $[\text{D}^+]$ are constants in the present experimental conditions. These equations agree with the observed pseudo-first-order kinetics. In addition, they indicate that the apparent rate constant is independent of the mixing ratio of isotope waters, in agreement with the observations.

Consequently, the initial reaction rate, R , and the amount of hydrogen evolution at the steady state are described as, e.g., for H_2 evolution,

$$R(\text{H}_2) = \left(\frac{d[\text{H}_2]}{dt} \right)_{t=0} = k_f(\text{H}_2)K_H^2[\text{H}^+]^2 \quad (16)$$

$$[\text{H}_2]_e = k_f(\text{H}_2)K_H^2[\text{H}^+]^2/k_r(\text{H}_2) \quad (17)$$

In the present study, we define two distinct separation factors. One of them is that defined for the steady state. The separation factors for $\text{H}_2\text{O}-\text{D}_2\text{O}$ and $\text{H}_2\text{O}-\text{HTO}$ are

$$\alpha_{X_e} = (\text{H}_e/\text{D}_e)_g/(\text{H}/\text{D})_l \quad (18)$$

$$\beta_{X_e} = (\text{H}_e/\text{T}_e)_g/(\text{H}/\text{T})_l \quad (19)$$

The other one is that defined for the initial reaction rates:

$$\alpha_R = \{[2R(\text{H}_2) + R(\text{HD})]/[2R(\text{D}_2) + R(\text{HD})]\}_g/(\text{H}/\text{D})_l \quad (20)$$

$$\beta_R = \{[2R(\text{H}_2) + R(\text{HT})]/[2R(\text{T}_2) + R(\text{HT})]\}_g/(\text{H}/\text{T})_l \quad (21)$$

The initial reaction rate was determined from $k_{ap}X_e$.

Figure 2 shows concentration dependence of the separation factors. The observed value of α_R was independent of the mole

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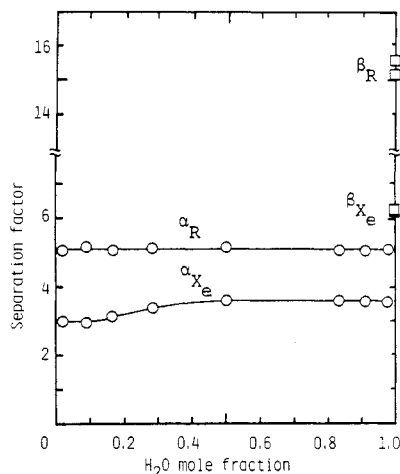


Figure 2. Concentration dependence of separation factors.

fraction of H_2O , being kept constant at 5.1 ± 0.05 . β_R was 15.4 ± 0.2 for H_2O -HTO of $1.8 \times 10^4/1$ and $3.6 \times 10^4/1$. On the other hand, α_{X_e} varied with the H_2O mole fraction. At the low H_2O fraction region, it was 3.05 ± 0.05 , whereas it was 3.6 ± 0.005 at the high fraction region. β_{X_e} was 6.2 ± 0.05 .

With regard to the H_2O - D_2O system, the separation factor in the photoassisted decomposition has been reported as 5.3 ± 0.1 for Pt/ TiO_2 catalyst.⁶ The present observations (α_R) agree quite

well with the above value. As for the H_2O -HTO system, the present results are the first observations in the photoassisted decomposition.

In electrolysis, the separation factors are reported as $\alpha = 5-7$ (smooth Pt surface)¹⁴ and $\beta = 14$.¹⁵ These values are quite close to the present observations, indicating that the photoassisted decomposition proceeds through the same mechanism as the electrolysis. In addition, the present results confirmed that the catalytic process (reaction 4) is the rate-determining step in the photoassisted decomposition, because the observed separation factors agree well with the theoretical prediction for this mechanism.⁷ The kinetic model also supports this conclusion.

On the other hand, the separation factors determined from the steady state were lower than the respective values of α_R and β_R . They agree quite well with those for the gas-liquid equilibration reaction: 3.6 for H_2O -HDO,¹⁶ 3.06 for D_2O -HDO,¹⁷ and 7 ± 2 for H_2O -HTO.¹⁸ It indicates that α_{X_e} and β_{X_e} observed in the present study were determined with the gas-liquid equilibration reaction.

Registry No. H_2O , 7732-18-5; D_2 , 7782-39-0; T_2 , 10028-17-8; Pt, 7440-06-4; TiO_2 , 13463-67-7.

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Polymer Films on Electrodes. 20. An ESR Study of Several Spin Probes Incorporated into Nafion

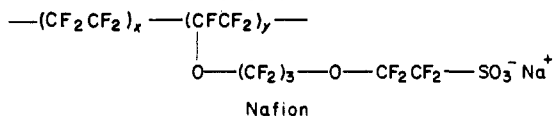
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The oxidative electrochemistry of protonated 2,2,6,6-tetramethylpiperidine-1-oxyl (Tempamine, TP) has been surveyed with Pt/Nafion modified electrodes. Protonated TP was shown to incorporate into Nafion films at pH lower than 9. Its oxidation is a reversible, one-electron process occurring at $E_{1/2} = 0.54$ V vs. SCE on Pt/Nafion electrodes (ca. 120 mV less positive than $E_{1/2}$ on bare Pt) and independent of the pH in the range 4-8. The ESR spectrum of Nafion-confined TP showed that the rotational correlation time was in the slow tumbling region and was estimated to be 1.2×10^{-8} s. This reveals an unusual anchoring effect by Nafion which had not been observed previously. The ESR spectra of some additional Nafion-confined spin probes such as vanadyl, manganese(II), and the cation radical of N,N,N',N' -tetramethyl-1,4-phenylenediamine (TMPD) were also surveyed. The results indicate that the motion of a given cation within Nafion is determined by the nature of the cation itself.

Introduction

Coating of electrodes with polyelectrolyte polymer films constitutes a versatile modification strategy, since ionic electroactive species can then be incorporated into these films from a contacting solution phase via ion-exchange reactions.¹ This approach was first introduced by Oyama and Anson² using poly(4-vinylpyridine) films to incorporate anionic electroactive compounds such as $\text{Fe}(\text{CN})_6^{3-}$ and IrCl_6^{3-} . Numerous reports³⁻⁵ have described the preparation and behavior of electrodes coated with films of the perfluorinated ion-exchange polymer, Nafion,⁶ which can elec-



trostatically bind cationic electroactive species through the sulfonic sites.

Our interest in this type of modified electrodes derives not only from the possibility of confining high concentrations of elec-

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