

Oxidation and Reduction of Substances in Aqueous Solution in Presence of Water-Repellent Catalyst

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INTRODUCTION

The surface of a conventional solid catalyst composed mainly of metal oxides such as Al_2O_3 , SiO_2 , TiO_2 , and Fe_2O_3 is hydrophilic. When such a catalyst is used in an aqueous solution, the surface is completely covered by water. It has been understood, therefore, that a conventional solid catalyst has little effect on the reaction of a substance in an aqueous solution with an insoluble gas, for example, oxidation of SH^- ion by O_2 and reduction of NO_3^- ion by H_2 . Since the surface of a hydrophilic catalyst is covered with a layer of water, O_2 or H_2 gas is not brought into contact with active sites of the catalyst surface. Under such circumstances the reaction rate may be controlled by the dissolution of O_2 or H_2 gas into the aqueous solution.

In order to overcome the drawbacks of a hydrophilic catalyst an attempt has been made in the present study to prepare and utilize a water-repellent or hydrophobic catalyst for a reaction in an aqueous solution involving O_2 and H_2 gas. It has been discovered that several reactions are greatly accelerated in the presence of a water-repellent catalyst. The term "water-repellent catalyst" instead of "hydrophobic catalyst" is used in the present paper, since it better represents the nature and function of the catalyst. A water-repellent catalyst is defined as a catalyst whose surface is at least partly water repellent and forms a gas-solid interface when it is in contact with a gas in an aqueous solution.

Consequently a function of a water-repellent catalyst is to form a three-phase, i.e., gas-liquid-solid interface, which provides reaction sites for the gas and liquid components.

A water-repellent catalyst has been used in the H_2 - O_2 recombiner for a lead-acid battery (1, 2) and in the isotopic exchange between HDO (liquid) and H_2 (gas) for the deuterium concentration (3-5). In these applications the catalyst is not used to cause a chemical reaction of a substance in the aqueous solution, but the water repellency is utilized merely to avoid surface wetting. Recently it has been reported in patents that a water-repellent catalyst with an electroconductive support (carbon) has been applied to various chemical reactions in aqueous solutions (6, 7). An electrode catalyst which is used in the H_2 - O_2 fuel cells with KOH or H_3PO_4 electrolyte can be said to be a water-repellent catalyst with electroconductivity (8, 9).

We have prepared a number of water-repellent catalysts from various support materials (electroconductive and nonconductive) and applied the catalysts to several reactions. The fundamental nature of the water-repellent catalyst is investigated and the preliminary experimental results are reported in this paper.

EXPERIMENTAL

Preparation of Catalyst

As a support of the water-repellent catalyst, titania, alumina, active carbon, and PTFE (polytetrafluoroethylene) are used

TABLE I
 Catalyst Supports

Support	Shape	Density (g/cm ³)	Surface area ^a (m ² /g)	Pore volume ^b (ml/g)	Supplier (Brand name)
TiO ₂	Sphere, 5 mm	1.0	40.	0.27	Sakai Chemicals (CS-246)
Al ₂ O ₃	Sphere, 5 mm	0.9	200.	0.37	Mizusawa Chemicals (Neobead C)
C	Sphere, 0.35 mm	0.6	1000.	0.55	Kureha Chemicals (BAC-M)
PTFE ^c	Cylinder, 6 mm o.d.-4 mm i.d.	0.8	<1.	0.25	Junkosha (TA-008)

^a Measured by BET method.

^b Measured by mercury porosity.

^c Porous PTFE.

and listed in Table 1. When a hydrophilic support is used to prepare a water-repellent catalyst, a PTFE dispersion solution (Daikin Industry, D-1) is used to give the water repellency to the catalyst. In Fig. 1 the standard method for the preparation of a water-repellent catalyst is shown in the case of Pt-TiO₂-PTFE. The TiO₂ support is impregnated with the PTFE dispersion solution (PTFE 1.5 wt%) and calcined at

320°C for 0.5 h. The support is then impregnated with a H₂PtCl₆-C₂H₅OH solution and reduced at 250°C for 1 h in a H₂ stream. The content of PTFE was adjusted to about 0.6 wt%. In case the porous PTFE is used for a catalyst support, the support is directly impregnated with an acetone solution of H₂PtCl₆. The loading of noble metal (Pt or Pd) is about 0.5 wt% in all catalysts. The surface area and pore volume of the cata-

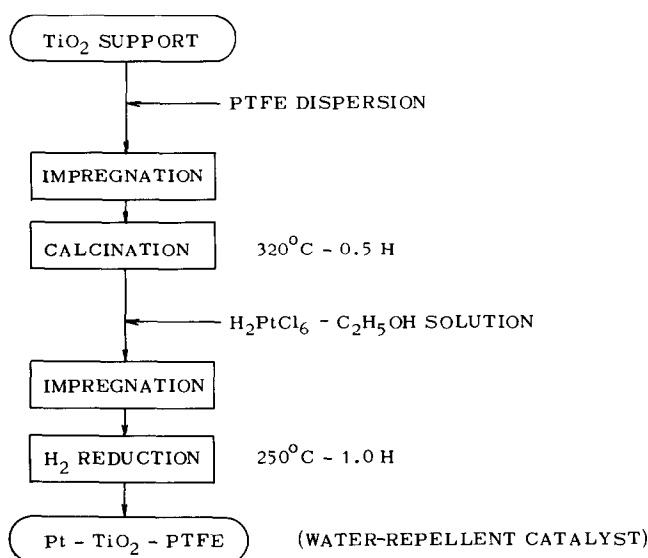


FIG. 1. Preparation of water-repellent catalyst (Pt-TiO₂-PTFE).

TABLE 2
 List of Catalysts Tested

No.	Name	Support	PTFE dispersion	Remarks
1	Pt-PTFE ^a	PTFE ^a	Not treated	
2	TiO ₂ -PTFE	TiO ₂		
3	Pd-TiO ₂ -PTFE			
4	Pt-Al ₂ O ₃ -PTFE	Al ₂ O ₃	Treated	Water-repellent catalyst
5	Pd-Al ₂ O ₃ -PTFE			
6	C-PTFE	C		
7	Pt-C-PTFE			
8	Pd-C-PTFE			
9	Pd-TiO ₂	TiO ₂		
10	Pd-Al ₂ O ₃	Al ₂ O ₃	Not treated	Hydrophilic catalyst
11	C	C		

^a Porous PTFE.

lysts impregnated with the PTFE dispersion were found to decrease by about 10% those of the supports. For the purpose of a comparison a catalyst without the water-repellent treatment and a catalyst without the loading of a noble metal are also prepared. All the catalysts used in the present study are listed in Table 2.

Experimental Apparatus

An experimental apparatus to investigate effects of the water-repellent catalyst is shown in Fig. 2. A reaction vessel made of glass with a volume of 500 ml was placed in a water bath. About 200 ml of a reactant solution with 10 g of catalyst was brought into the reaction vessel through which O₂ or H₂ gas was bubbled at a flow rate of 1 N liter/h (normal liter per hour). During the course of the reaction the pH of the solution was usually changed and monitored by a pH meter.

In the present study the reduction of

CuSO₄ and KNO₃ solution by H₂ gas, and the oxidation of NaSH solution by O₂ gas were investigated. The activity of a water-repellent catalyst was determined by analyzing the reactant and product concentrations. The concentration of NH₄⁺ was measured by the Nessler method, and those of NO₃⁻ and NO₂⁻ by absorbance at 520 nm after colorination by naphthylamine reagent. The iodine titration method was employed to analyze SH⁻, S₂O₃²⁻, and SO₃²⁻ using formaldehyde and ZnSO₄ as a masking reagent.

RESULT AND DISCUSSION

Reduction of Cu²⁺ by Hydrogen

Hydrogen gas was bubbled through a solution containing 0.5 mole/liter CuSO₄ in the presence of Pt-PTFE catalyst at 50°C. It was observed that a metallic material which was identified to be copper by an X-ray diffraction analysis was formed on the catalyst surface. Figure 3 shows a photo-

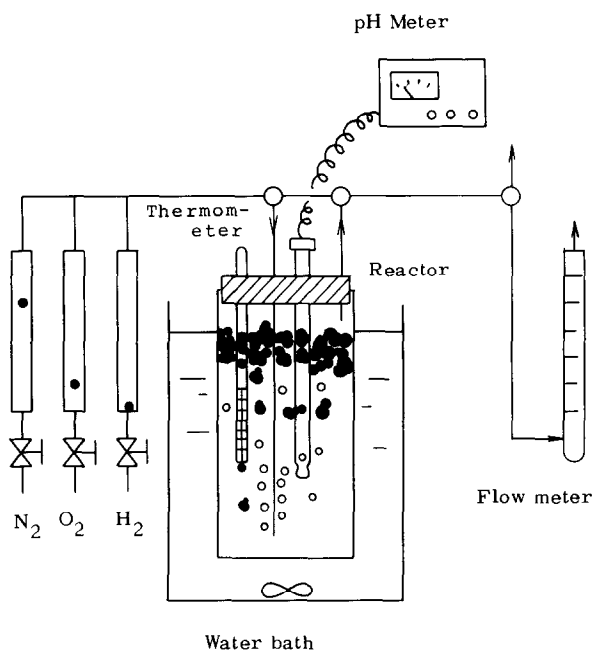


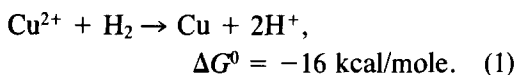
FIG. 2. Experimental apparatus.

graph of the copper foil with a thickness of about $50\ \mu\text{m}$. An experiment was performed using Pt-C-PTFE catalyst, and the formation of metallic copper on the catalyst surface was observed. For the purpose of comparison several experiments were per-

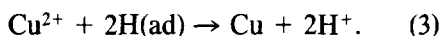
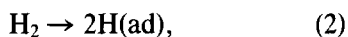
formed in the presence of a hydrophilic catalyst, and in the absence of a catalyst. It was found that the reduction of Cu^{2+} by H_2 gas, if any, was very slow under these circumstances. The overall reaction of the reduction of Cu^{2+} by H_2 is given by



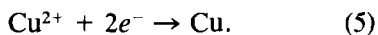
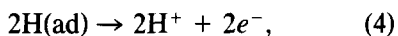
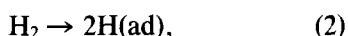
FIG. 3. A photograph of copper foil formed on Pt-PTFE catalyst.



Since reaction (1) is greatly enhanced in the presence of a water-repellent catalyst, and Cu foil is formed on the catalyst surface, it is supposed that the reaction proceeds via adsorbed hydrogen,



The reaction process could be described by using a microscopic electrochemical reaction (local cell),



The electrochemical potential of reaction (5) is 0.34 V with respect to the standard hydrogen electrode.

It has long been known that copper ions are reduced to copper metal by hydrogen gas under high pressures, which is known as "wet smelting." The rate-determining step of the process is the dissolution of hydrogen gas into the solution. The metal ions which can be reduced by hydrogen gas thermodynamically could be predicted by the ionization tendency (10). The ions of metal elements which are noble to hydrogen, i.e., Cu, Ag, Hg, Pt, Au, can be reduced by hydrogen gas and those which are base to hydrogen, i.e., Al, Co, Ni, Sn, Fe, etc., cannot be reduced. We have also performed the reduction of AgNO_3 and H_2PtCl_6 solution and found that metallic Ag and Pt are formed on the surface of the water-repellent catalysts. The reduction of Ni^{2+} and Fe^{3+} to the metal was not possible in the presence of the water-repellent catalyst.

Reduction of NO_3^- Ion by Hydrogen

Hydrogen gas was bubbled through a solution containing 0.01 mole/liter KNO_3 at a flow rate of 1 N liter/min and at a temperature of 50°C for 2 h. The decrease of NO_3^-

TABLE 3

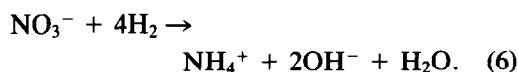
Reduction of NO_3^- Ion by H_2 Gas in Presence of Water-Repellent Catalyst

Catalyst	NO_3^- decrease (%)	NH_4^+ formation (%)
Pd-TiO ₂ -PTFE	36.1	32.9
Pd-TiO ₂	7.0	6.1
TiO ₂ -PTFE	0.3	Trace
Pd-Al ₂ O ₃ -PTFE	72.2	11.5
Pt-Al ₂ O ₃ -PTFE	32.0	14.8
Pd-C-PTFE	40.5	33.5
Pt-C-PTFE	12.2	12.4

and formation of NH_4^+ in the presence of various catalysts are summarized in Table 3. A water-repellent catalyst without noble metal loading (TiO₂-PTFE) has little effect on the reaction. A hydrophilic catalyst (Pd-TiO₂) showed slight catalytic activity, but the reaction rate was much lower than that of the water-repellent catalysts.

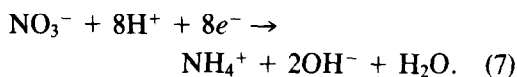
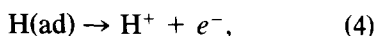
On the other hand the water-repellent catalysts (Pd-TiO₂-PTFE, Pd-C-PTFE) showed high activity, the amount of NH_4^+ formed being approximately equal to that of NO_3^- consumed. In the case of Pt, Pd-Al₂O₃-PTFE catalysts the amount of NH_4^+ formed was appreciably less than that of NO_3^- consumed. The formation of NO_2^- was found to be negligibly small. The formation of N_2 was not examined in the present study. There was a possibility that a part of NO_3^- was adsorbed on the catalyst and was not detected by the present analytical procedure. Comparing the activities of Pt and Pd in the water-repellent catalysts, Pd was more active than Pt on the reduction of NO_3^- by hydrogen.

The overall reaction for the reduction of NO_3^- to NH_4^+ by H_2 will be given as follows:



The valence state of nitrogen atom changes from +5 to -3. Though details of the reaction path are not known at present,

it seems that NO_3^- is reduced by adsorbed hydrogen successively, or the microscopic electrochemical reaction.



Reaction (7) is favorable thermodynamically, since the free-energy change is calculated to be -124 kcal/mole. As can be seen in reaction (6), the pH of the solution becomes higher as the reaction proceeds. Experiments were performed at various initial pH values by adjusting the pH of the solution with NaOH or HCl. It was found that the reaction proceeded faster as the initial pH of the solution was lowered.

Oxidation of SH^- Ion by Oxygen

Oxygen gas was bubbled through a solution containing 0.4 mole/liter NaSH (initial pH ≈ 11) at a flow rate of 1 N liter/min and at a temperature of 80°C . Figure 4 shows

the reaction profile from a typical experiment with the water-repellent active carbon catalyst (C-PTFE). It is seen that SH^- was completely consumed within an hour and $\text{S}_2\text{O}_3^{2-}$ was formed in an amount equivalent to the initial SH^- . The formation of SO_3^{2-} was observed, but the amount was less than 5% of $\text{S}_2\text{O}_3^{2-}$. The unidentified sulfur compounds indicated in Fig. 4 are merely the difference between the initial SH^- and the measured oxidation products, i.e., $\text{S}_2\text{O}_3^{2-} + \text{SO}_3^{2-}$. Polysulfide ions could account for the unidentified sulfur compounds at least partly, since the solution showed reddish-brown color at the maximum unidentified sulfur compound concentration.

Experiments were performed using C-PTFE catalyst loaded with Pt or Pd. It was found that the reaction rate was not enhanced in the presence of Pt or Pd. It seems that active carbon itself forms active sites for the reaction. The oxidation of SH^- by oxygen proceeds slowly in the absence of a catalyst, or in the presence of a hydrophilic catalyst. The reaction rate was found

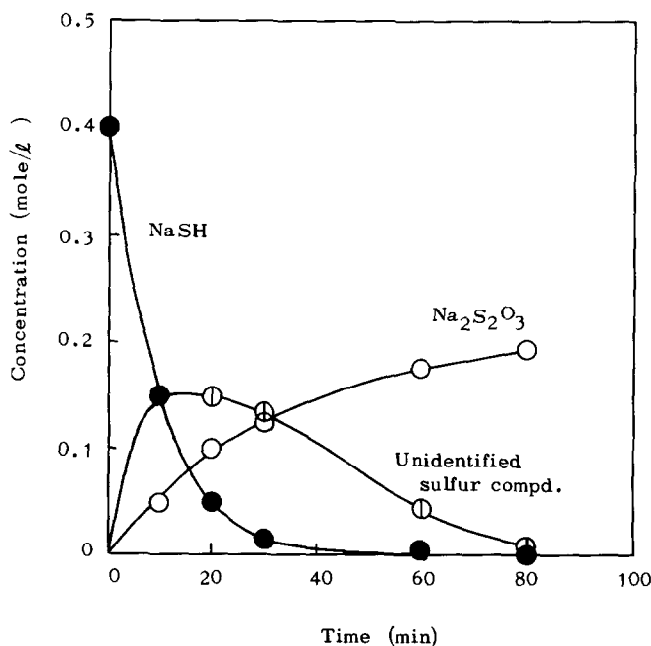


FIG. 4. Oxidation of NaSH solution by O_2 gas. Catalyst: C-PTFE. Temperature: 80°C .

to be about one-tenth of that in the presence of the water-repellent active carbon catalyst.

The overall reaction of the oxidation of SH^- by oxygen is given by



The free-energy change of reaction (8) is calculated to be -178 kcal/mole. It is of interest to note that the oxidation of SH^- by oxygen is accelerated only by the C-PTFE catalyst which is composed mainly of electroconductive carbon among the catalysts used in the present study. The experimental result is in agreement with that described in the patents (6, 7).

Further work is obviously needed to elucidate the reaction mechanism in the presence of a water-repellent catalyst and will be published later.

REFERENCES

1. Gulick, H. M., *et al.*, U.S. Patent 2,687,449 (1954).
2. Tsukada, T., *et al.*, *Denki Kagaku (J. Electrochem.)* **47**, 240 (1979).
3. Enright, I. T., and Chuang, T. T., *Canad. J. Chem. Eng.* **56**, 246 (1978).
4. Butler, J. P., *et al.*, "Separation of Hydrogen Isotopes," ACS Symposium Series, Vol. 68, p. 93. Amer. Chem. Soc., Washington, D.C., 1978.
5. Yamashita, H., *et al.*, *J. At. Energy Soc. Jap.* **25**, (1983), in press.
6. Smith, G. C., *et al.*, Canada Patents 959,628 and 959,821 (1974) (to Mead Corp.).
7. Smith, G. C., *et al.*, Japan Patents 876,447 (1975) and 910,151 (1978) (to Mead Corp.).
8. Yeager, E., and Kozawa, A., in "Proceedings, 6th AGARD Meeting, Cannes, 1964." Pergamon, Oxford, 1965.
9. Kunz, H. R., and Gruver, G. A., *J. Electrochem. Soc.* **122**, 1279 (1975).
10. Weast, R. C. (Ed.), "Handbook of Chemistry and Physics," D-111. Chem. Rubber Pub. Co., Cleveland, Ohio, 1973.