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Hydrogen Evolution from Alkaline Formaldehyde Solution

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Synopsis. Hydrogen is evolved from an alkaline solution of formaldehyde in the presence of a tungsten carbide catalyst at room temperature under atmospheric pressure. Neither platinum nor palladium shows any catalytic activity to this reaction. The hydrogen evolution competes with the Cannizzaro reaction.

Much attention has been paid to hydrogen as a fuel of a post-petroleum clean energy system. If hydrogen could be made available in desired quantities without great effort or equipment, this energy system would become more feasible. Formaldehyde in an alkaline solution has been found to yield hydrogen at room temperature under atmospheric pressure when tungsten carbide (WC) is used as a catalyst. This new type of reaction might satisfy some of the above requirements. Moreover, a hydrogen energy system including formaldehyde is related to an efficient utilization of coal since formaldehyde is produced from coal. The present note describes and discusses experimental results of a preliminary investigation on the new reaction.

When WC (0.5 g) was added to a formaldehyde (1 mol dm^{-3}) solution containing 2 mol dm^{-3} NaOH at around room temperature under atmospheric pressure, a gas was evolved after an induction period of about 1 min as shown in Fig. 1. The evolved gas was identified with pure hydrogen gas by gas chromatography (with molecular sieves 5A column and TCD). As Fig. 1 shows, the hydrogen evolution rate decreases with increasing reaction time. This tendency is more predominant at higher reaction temperatures. The hydrogen evolution rate calculated from the amount of hydrogen evolved for 5 min after the beginning of the evolution was greater for the higher temperature. An activation energy estimated was about 36 kJ mol^{-1}.

No change was observed in the X-ray diffraction of WC after the reaction, indicating that it worked as a catalyst.

The relation between the hydrogen evolution rate and the hydroxide ion concentration under conditions where the initial formaldehyde concentration was 2 mol dm^{-3} and the reaction temperature was maintained at 20 °C, is shown in Fig. 2. The evolution rate increased linearly until the concentration was increased to 2 mol dm^{-3}. Above this value, the rate decreased slightly.

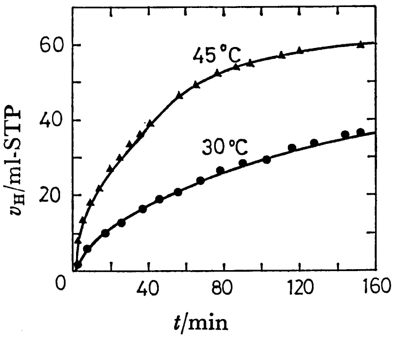

Fig. 1. Hydrogen evolution volume *vs.* time under at mospheric pressure.
v_H: Hydrogen evolution volume in ml-STP, formaldehyde concentration: 1 mol dm^{-3}, hydroxide ion concentration: 2 mol dm^{-3}, WC weight: 0.5 g.

The dependence on the formaldehyde concentration of the evolution rate observed at 20 °C with the hydroxide ion concentration of 2 mol dm^{-3}, is shown in Fig. 3. The rate increased when the formaldehyde concentration was increased up to 2 mol md^{-3}. However, further increases in the concentration decreased the rate.

No hydrogen was evolved when benzaldehyde, acetaldehyde, paraldehyde, acetone, methanol, or formic acid was used in place of formaldehyde. No hydrogen evolution was observed either in an acidic formaldehyde solution. Thus, the hydrogen evolution must occur only in an alkaline formaldehyde solution. Therefore, the conceivable reaction is written as

$$HCHO + OH^- = HCOO^- + H_2. \qquad (1)$$

The total amount of hydrogen evolved from a solution containing 26 mmol formaldehyde and 26 mmol NaOH was 10 mmol. If only reaction 1 proceeded

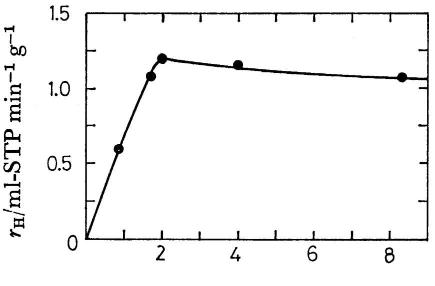

Fig. 2. Dependence of hydrogen evolution rate on hydroxide ion concentration at 20 °C.
r_H: Hydrogen evolution rate measured at 5 min after the beginning of the evolution, formaldehyde concentration: 2 mol dm^{-3}.

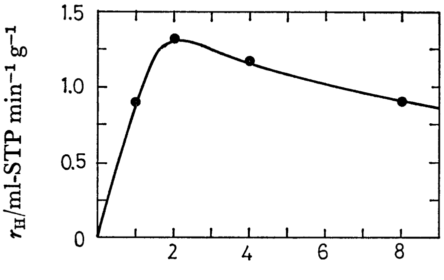

Fig. 3. Dependence of hydrogen evolution rate on formaldehyde concentration at 20 °C.
Hydroxide ion concentration: 2 mol dm^{-3}.

in the reaction solution, the total hydrogen amount must have been 26 mmol. This discrepancy can be explained as follows. In the reaction system, the Cannizzaro reaction

$$2HCHO + OH^- = CH_3OH + HCOO^- \qquad (2)$$

must compete with the hydrogen evolution. Thus, the total amount of hydrogen is smaller than that calculated on the basis of only reaction 1.

Sodium formate and methanol were found except for formaldehyde in the reaction solution by Raman spectroscopy. This is consistent with reactions 1 and 2.

The standard Gibbs energy difference of reaction 1 is -47.7 kJ mol^{-1}.1) Therefore, the forward reaction in reaction 1 is thermodynamically easy to proceed. With an acidic formaldehyde or alkaline methanol solution, the standard free energy difference is positive or slightly negative as follows:1)

$$HCHO + H_2O = HCOOH + H_2 \quad \Delta G^0 = 10.9 \text{ kJ mol}^{-1}, \qquad (3)$$

$$CH_3OH = HCHO + H_2 \quad \Delta G^0 = 44.9 \text{ kJ mol}^{-1}, \qquad (4)$$

$$CH_3OH + OH^- = HCOO^- + 2H_2 \quad \Delta G^0 = -0.7 \text{ kJ mol}^{-1}. \qquad (5)$$

Thus, the forward reactions in reactions 3—5 are thermodynamically almost difficult to proceed. By comparing the free energy difference in reaction 1 with that for reaction 3, the motive force for hydrogen evolution is considered to be the heat of neutralization

$$OH^- + HCOOH = HCOO^- + H_2O \quad \Delta G^0 = -58.6 \text{ kJ mol}^{-1}. \qquad (6)$$

To find catalysts effective to the hydrogen evolution other than WC, carbides, nitrides, borides, oxides, sulfides, and transition metals of all the groups from III B to VIII B were tested at room temperature with an aqueous solution of 2 mol dm^{-3} formaldehyde concentration and 1.6 mol dm^{-3} hydroxide ion concentration. It was found that Mo_2C, W_2C, (Mo,W)C, Mo_2N, W_2B_5, WB_4, WB_2, Mo, and W were active. It can be pointed out that only the compounds of the VI B group elements have catalytic activities. Among them, WC was most active. It was interesting that platinum black and palladium black were inactive. WC often behaves as a platinum-like catalyst2,3) due to its similar catalytic activity and electronic structure. However, WC catalyzes the reaction that platinum does not. Since WC is known to be a catalyst for the anodic oxidation of hydrogen,4) ammonia synthesis,5) and other reactions,6) it is a very promising material to replace precious metal catalysts.

References

1) W. M. Latimer, "Oxidation Potentials," 2nd ed, Prentice-Hall, Inc., N. J. (1952).

2) R. B. Levy, and M. Boudart, *Science*, **181**, 547 (1973).

3) L. H. Bennett, J. R. Cuthill, A. J. McAlister, N. E. Erickson, and R. E. Watson, *Science*, **184**, 563 (1974).

4) H. Binder, A. Koeling, and G. Sandstede, *Am. Chem. Soc., Div. Fuel Chem., Prepr.*, **13**, 99 (1969).

5) G. S.-Ekloff, D. Baresel, and W. Salholz, *J. Catal.*, **43**, 353 (1976).

6) For example, ethylene hydrogenation: I. Kojima, E. Miyazaki, Y. Inoue, and I. Yasumori, *J. Catal.*, **59**, 472 (1979); hydrogen oxidation at rt: R. B. Levy and M. Boudart, *Science*, **181**, 547 (1973); liquid phase hydrogenation: G. Horányi, G. Vértes, and Gy. Fézler, *Z. Phys. Chem. N. F.*, **83**, 322 (1973).