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A New Hydrogen Generation Process from Water Using Decomposition of Metal Ammonium System under Metal Pile or Alloy Catalysis[1)]

Different from the hitherto developed direct electrolysis of water, this new method generates hydrogen gas from water easily, smoothly and immediately through an indirect processes, *i.e.* so-called double pre-catalytic decomposition consisting of two pre-catalytic processes. One of them consists of a metal-pile or alloyed catalyzer and the other of an ammoniac aqueous solution of metallic ammonium complex salts or hydroxides. These two pre-catalytic agents generate hydrogen gas from water by mutual contact reaction, producing aside ammine coordinate compounds from the ammonium complex salts or hydroxides in a redox-cyclic system introducing the environmental thermal energy from the outside atmosphere. These catalyzers are effectively useful for several days after once settled and only by supplying the decomposed amount of water from outside.

Keywords——double pre-catalytic decomposition; pre-catalytic process; ammonium complex hydroxide; ammine coordinate compound; redox-cyclic system; environmental thermal energy

Water and electricity are fundamental and essential factors to keep the human life in healthy conditions for ever. Meanwhile the modern livelihood of mankind needs more and more a larger amount of them, as well known, and nowadays there happens already water famine in the world. This new method may be easily utilized to produce simultaneously electricity and drinking-water either by using thermal or explosive energy obtained by combustion of the hydrogen with the air-oxygen. The water used for the double pre-catalytic decomposition may be easily obtained from the sea-water under heat-exchanging with steam vapour exhausted from the hydrogen-oxygen combustion turbine and then desalting by ion-exchange treatment.

Different from that developed hitherto, this new method is composed of two pre-catalytic processes, *i.e.* one of the pre-catalytic processes consists of metal-pile which provides a necessary electric voltage and current, and the other consists of an ammoniac aqueous solution of metallic ammonium complex salts or hydroxides, which are decomposed smoothly, actively and immediately in the case of use on contact with metal-pile into hydrogen gas and metallic ammine compounds. These ammine compounds are inactive, but easily re-activated on contact with their metallic oxides and then with the metal powders, producing their original active metallic ammonium complex salts or hydroxides, outside this reactive hydrogen gas generation system. And thus this hydrogen gas generation method is completely cyclic creation system and able to provide both sufficient amounts of clean energy in form of electricity and of drinking-water economically. Naturally these two pre-catalytic agents do not act and generate hydrogen gas by themselves in separate condition but when combined each other, it will become a complete catalytic system and produce hydrogen gas, and thus named these two separate processes as pre-catalytic processes and this whole system as a "double pre-catalytic decomposition" system.

Example of Experimental Device and Data

According to the principle of hydrogen gas generation from water by double pre-catalytic method, the following device or apparatus, for example, is made at present in small scale experiment as one of the most efficient or effective and convenient procedures.

a) Apparatus: A cylindrical plastic vessel has *ca.* 50 ml in volume, 3.3 cm in inner diameter and 6.2 cm in height. A gas outputting guide pipe is settled in the top-cap which

1) Preliminary report: O. Ishizaka, Proceedings 12th Anniversary of the F.A.P.A. and the 6th Asian Congress of Pharmaceutical Sciences Nov. 21—26, 1976 (Jakarta), 1978, pp. 334—343.

may put out *ca.* 0.05 ml of generated hydrogen gas in one bubble into a detergent solution and the bubbles are collected in a volumetric gasometer, and then analyzed by an ordinary gas analyzer.

b) Metallic Aluminium Plate Catalyzer: A basic metallic aluminium plate is of a scale $3.5\times40\ \mathrm{cm}^2$ and 0.3 mm in thickness. Catalytic activation: According to the principle of catalytic reaction, it has been revealed from a series of experiments that a two metallic combined pile catalyzer based on such above described aluminium spiral plate ($3.5\times40\ \mathrm{cm}^2$) is made by coating and activating in accordance with a special formulation using finally zinc ammonium complex hydroxide obtained from supernatant on or filtered through zinc oxide and metallic zinc powders for over ten munites. The re-activation method of inactive or wasted solution is almost the same as that of metallic plate catalyzer and thus the wasted solution can be used repeatedly by filtering through zinc oxide and then through metallic zinc powders for over ten minutes, recovering the inactive ammine compounds in the initial, active ammonium complex hydroxides. Experimental data of hydrogen gas generation and the duration of activity: An example of data obtained from a series of repeated experimen-

Table I. Generation Activity of Hydrogen Gas by Al=Zn–ZnO Pile System (23—25°)

Time	I	0	5′	15′	30′	50′	I	0	5′	15′	30′
(H_2) ml/min	(1)	0	1.6	1.2	0.2	0.1	(2)	0	1.6	3.0	0.3
Time	I	0	5′	40′	I	0	15′	40′	I	0	10′
(H_2) ml/min	(3)	0	3.0	1.2	(4)	0	0.8	0.2	(5)	0	0.4
Time	30′	50′	60′		II	0	5′	30′	50′	II	0
(H_2) ml/min	0.8	0.4	0.5		(1)	0	1.0	1.5	1.0	(2)	1.0
Time	1h 10′	1h 30′	2h	2h 30′	3h	6h	7h	8h	9h	10h	15h
(H_2) ml/min	2.4	3.6	5.2	6.4	6.0	7.2	7.2	6.0	6.2	5.8	5.0
Time		20h	25h								
(H_2) ml/min		4.9	4.0								

(H_2) generated: 7.20 L (*ca.* 0.64 g), Al consumption: 0.85 g.
N.B. I (1)—(5): Preliminary pile-preparing processes by using Zn ammonium complex hydroxide.
II (1): Preliminary and II (2): Main actual (H_2) generation processes only by treating with 5% NH_4OH solution.

tation may be summarized as such in Table I. The hydrogen gas generation continues for over twenty five hours efficiently or effectively, *i.e.* during this term, the loss in weight of aluminium plate is less than 1 g so that it may generate over a volume of hydrogen gas more than that stoichiometrically equivalent to 3 (H_2): 1 mol of aluminium consumption.

From the results of over 5000 times of repetitive small scale experiments, the following reactive formulation (Chart 1) may be theoretically and from experimental practice presented between two metals Al (aluminium) and M (metals of di-valent series to make six coordinate ammine compounds):

1. $[\mathrm{Al(NH_3)_6H_6}]\mathrm{X_2Y_4} + 2\mathrm{MO} \longrightarrow \underline{2\mathrm{M}} + 2\mathrm{H_2O} + [\mathrm{Al(NH_3)_6H_2}]\mathrm{X_2} + 4\mathrm{Y}$

2. $[\mathrm{M(NH_3)_6H_2}]\mathrm{X_2} + 4\mathrm{Y} + 2\mathrm{H_2O}\,(\text{from outside}) \xrightarrow[\text{atmospheric thermal energy}]{\text{intake of the outside}} \mathrm{MO} + [1/2\mathrm{O_2}] + \underline{2\mathrm{NH_4X}} + \underline{4\mathrm{NH_4Y}}$

3. $\mathrm{M} + 2\mathrm{NH_4X} + 4\mathrm{NH_4Y} \longrightarrow [\mathrm{M(NH_4)_6}]\mathrm{X_2Y_4}$ (under the outside atmospheric thermal energy)

4. $[\mathrm{M(NH_3)_6H_6}]\mathrm{X_2Y_4} \xrightarrow[\text{ammoniac medium}]{\text{metal-pile or alloyed catalyzer}} [\mathrm{M(NH_3)_6H_2}]\mathrm{X_2} + [2\mathrm{H_2}] + 4\mathrm{Y}$

Consequently: [(1)→(2)→(3)→(4) cyclic system] ⟶ [H_2]

Chart 1. Proposed Chemical Reactions in the Process [Al=M–MO]

Al: aluminium.
M: metals of di-valent series to make six coordinate ammine compounds.
Underline: reclamation
X and Y: inorganic or hydroxide anions, and in case of Al=Zn–ZnO pile system only hydroxide anion.
Metal-pile or alloyed catalyzer: made of Zn, Mn, Ni, Cr, Co, Fe, Cu, *etc.*

From the results of the repetitive small scale experiments, by using an usual apparatus described above, concerned with Al=Zn–ZnO or Al=Co–Zn=ZnO, for instance, hydrogen gas is generated catalytically in accordance with the Al=M–MO redox cyclic system, independent of the original Al–M system and scarcely consuming Al (aluminium). The Al=M–MO or Al=M_2–M_1=M_1O redox cyclic system, *e.g.* either Al=Zn–ZnO or Al=Cu–Zn=ZnO or Al=Mn–Zn=ZnO or Al=Ni–Zn=ZnO or Al=Co–Zn=ZnO *etc.* seems practically to be ideal catalytic metal-pile effective for several days' use.

This catalytic hydrogen gas generation in total is an exothermic reaction and the thermic Qh energy directly generating hydrogen gas is calculated from an amount of the thermal energy balance sheet between Q1 input and Q2 output energies. That is *ca.* 18.5 (gas) or 6.6 (liquid) [kcal/mol-H_2] and almost the same amount calculated from the experimental heat balance data, which is *ca.* 1/4 amount of thermic energy produced by consumption of one mole hydrogen gas with half a mole of oxygen, and thus the rest amount of energy may be supplied by the electric pile in a form of electricity. The best thermal condition for the generation of hydrogen gas is *ca.* 30° and below this temperature the generation velocity decreases in accordance with the decrement in environmental temperature.

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