The Decomposition of Hydrogen Iodide and Separation of the Products by the Combination of an Adsorbent with Catalytic Activity and a Temperature-swing Method

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The decomposition of hydrogen iodide and the separation of the products by the combination of a column packed with an adsorbent with catalytic activity(platinum-supported active carbon, 2.3 wt%) and a temperature-swing method (450—900 K) are carried out, and the features and the problems of the method are examined. A one-step conversion of hydrogen iodide, 70%, is obtained at 450 K, where the equilibrium conversion is 13%. It is shown that the products of the decomposition of hydrogen iodide containing water are separated from each other.

The decomposition of hydrogen iodide serves as the hydrogen-evolution step in several thermochemical water-splitting cycles,[1-3] including the Magnesium–Iodine cycle[4,5] previously proposed by Kondo *et al.* Suitable catalysts for the catalytic decomposition of hydrogen iodide were searched for,[6] and the kinetic analysis of the reaction over a platinum-supported active carbon catalyst and an active carbon catalyst which had been found effective was carried out.[7] The results showed that hydrogen iodide could be decomposed rapidly enough by the use of those catalysts in the range of comparatively low temperatures (500—700 K) and in the presence of water vapor that might coexist in the actual cycle. However, the equilibrium conversion of hydrogen iodide is low (0.13—0.20 at 450—700 K)[6] when all the components, including the products, are in the gaseous phase. Therefore, the separation of the product mixture into its components, *i.e.*, hydrogen, iodine, undecomposed hydrogen iodide, and water, is necessary. However, iodine and undecomposed hydrogen iodide cannot be separated from each other easily, since iodine readily dissolves in the hydriodic acid formed from hydrogen iodide and water. On the other hand, the amount of undecomposed hydrogen iodide which has to be recirculated should be minimzied in order to increase the thermal efficiency of the whole cycle.

Therefore, from the standpoint of the thermochemical water splitting, the problems in the decomposition of hydrogen iodide can be summarized as follows: the elevation of a one-step coversion, and the development of an effective separation method of the product mixture. Various decomposition-separation methods have been proposed, *i.e.*, methods in which hydrogen iodide is decomposed, when iodine is in the liquid phase[8] or hydrogen iodide is in the liquid phase,[8] a method with porous membrane,[9] a method with MgO,[10] *etc.* However, each method has its own problems. Therefore, the present author considered that the development of a new method was necessary.

Principle

An adsorbent with catalytic activity is prepared by the addition of catalytic activity to an adsorbent which has very different adsorption characteristics toward the reactant, hydrogen iodide, and the products, hydrogen and iodine. Under the conditions that a column packed with the adsorbent with catalytic activity is heated in the temperature range where hydrogen iodide is decomposed rapidly, and that hydrogen iodide is fed in intermittently, there is a possibility that a one-step conversion higher than the equilibrium one can be obtained.

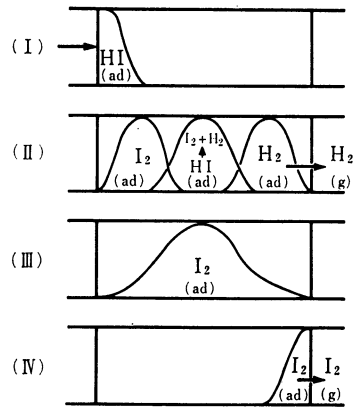

Fig. 1. Conceptual drawing of the decomposition of hydrogen iodide and the separation of the products by the use of a column packed with an adsorbent with catalytic activity.

Figure 1 is the conceptual drawing of the method. As a certain amount of hydrogen iodide fed intermittently proceeds in the column, it decomposes on the surface of the adsorbent, thus forming hydrogen and iodine. If it is hard for the adsorbent to adsorb hydrogen, while it readily adsorbs iodine, the hydrogen formed on the surface of the adsorbent desorbs into the gaseous phase, while the iodine formed remains adsorbed. Since the iodine formed is continuously removed from the reaction system, the undecomposed hydrogen iodide is decomposed further as it proceeds in the column (Figs. 1-I, II). Thus, if the decomposition of hydrogen iodide is rapid enough, a one-step conversion higher than the equilibrium one is obtained. The iodine remaining in the adsorbent is desorbed, and the adsorbent is regenerated (III, IV). In the present method, the one-step conversion of hydrogen iodide will be dependent

on both the catalytic activity of the adsorbent and the difference in the adsorption characteristics of the adsorbent toward hydrogen iodide, hydrogen, and iodine. If a higher one-step conversion is obtained, the thermal efficiency of the whole cycle is expected to become higher, since the amount of the undecomposed hydrogen iodide which has to be recirculated decreases. This method may be divided into two kinds of procedures. One is a procedure in which the decomposition of hydrogen iodide and the desorption of iodine are carried out at a constant temperature (Pressure-swing Method). The other is one in which they are carried out at different temperatures (Temperature-swing Method).

As has been mentioned above, the platinum-supported active carbon catalyst has been found to reveal high catalytic activity for the decomposition of hydrogen iodide. On the other hand, active carbon, which is the support of the catalyst, is known to exhibit markedly different adsorption characteristics toward hydrogen, iodine, and hydrogen iodide.[11,12] Therefore, it seems that it is possible for the platinum-supported active carbon (abbreviated as Pt/C) to behave as the adsorbent with catalytic activity mentioned above. With this in view, the present author has attempted the decomposition of hydrogen iodide and the separation of the products by the combination of a column packed with a Pt/C and a temperature-swing method; he has also examined the features and the problems of the present decomposition-separation method.

Experimental

Materials. The Pt/C's (1.1 wt%, 2.3 wt%) were prepared by an impregnation-calcination method (1000 K, 6 h, in an argon stream) from $H_2PtCl_6 \cdot 6H_2O$ (WAKO, Sp. Gr.) and active carbon (PITTSBURG ACTIVATED CARBON, BPL, 12-30 U. S. Sieve Series). Six grams of the Pt/C (2.3 wt%) was used in each run, unless otherwise stated. One ml of hydriodic acid (WAKO, Sp. Gr., 7.52 mol dm^{-3}, $d=1.70$) was fed in in each run.

Apparatus. Figure 2 shows the experimental apparatus. The inside diameter of the quartz reaction tube (b) was 12 mm. The length of the quartz wool layer (c) was 20 mm, while that of the adsorbent layer (d) was 165 mm.

Procedure. The quartz reaction tube was heated in an argon stream at 900 K for 2—3 h, after which the water, oxygen, and so on adsorbed on the quartz wool and the Pt/C were desorbed. After the reaction tube had been cooled, it was set up and 1 ml of hydriodic acid was added to the quartz-wool layer by means of a transfer pipet from the end. After the Pt/C layer only had been heated at the reaction temperature in an electric furnace, the quartz-wool layer also was moved into the electric furnace. The hydriodic acid contained in the quartz-wool layer was evaporated in an argon stream within 10 (450 K) —0.5 min (900 K) and fed into the Pt/C layer. The step of the iodine desorption followed the step of the decomposition of hydrogen iodide. The flow rate of argon in both the steps was usually 27 ml/min.

Thermogravimetry. The Pt/C (2.3 wt%, 100 mg, ground into a diameter less than 0.3 mm and heated at 1000 K for 6 h in an argon stream) and the samples prepared from the Pt/C by the addition of a certain amount of water, hydriodic acid, or iodine were used in the measurements. The sample containing iodine was prepared by the adsorption of iodine into the Pt/C at 373 K in a glass ampoule. After a reduced-pressure treatment (660 Pa, 30 min) of the samples in the sample chamber, argon was introduced and the samples were analyzed by means of thermogravimetry (CHYO, TRDA3-L). The flow rate of argon was 100 ml/min, while the heating rate was 5 K/min.

Analyses. All the components of the product-gas mixture except for hydrogen and argon were condensed at the back part of the reaction tube or trapped in the scrubber. The hydrogen concentration of the exhaust gas was determined by means of gas-chromatography (YANACO 180G, Molecular Sieve 13A). The amount of hydrogen iodide or iodide, condensed or trapped, was determined by titration.[13,14]

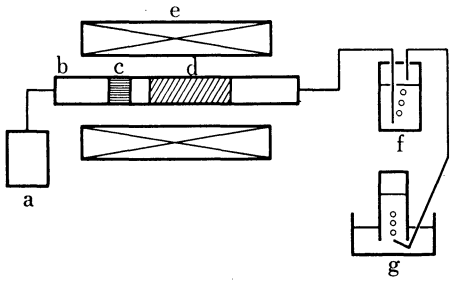

Fig. 2. Schematic drawing of apparatus employed: a, argon bomb; b, quartz reaction tube; c, quartz wool; d, adsorbent with catalytic activity; e, electric furnace; f, scrubber; g, gas reservoir.

Results and Discussion

Thermogravimetry. Figure 3 shows the results of the thermogravimetric analyses of the Pt/C samples. The weight of the Pt/C itself which had been treated at 1000 K remained almost constant up to 1000 K. The water added desorbed almost completely in the pre-measurement operation composed of a reduced-pressure treatment and an argon introduction at room temperature. The iodine added began to desorb around 450 K and finished its desorption at 900 K. In the case of hydriodic acid, about 40% of the weight of the hydriodic acid added was reduced in the pre-measurement operation, after which the residue was reduced in weight in a manner similar to that of the iodine added. The weight loss in the pre-measurement

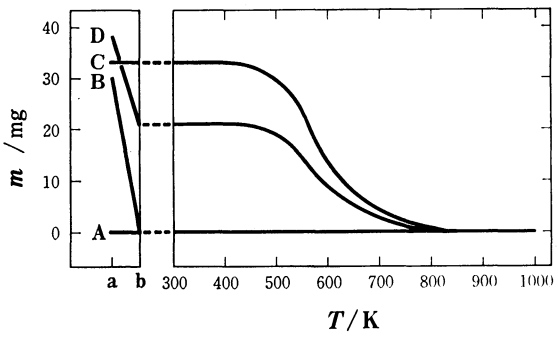

Fig. 3. Thermogravimetric analyses of the Pt/C samples: (a) before and (b) after the pre-treatment; A, Pt/C; B, Pt/C with H_2O; C, Pt/C with I_2; D, Pt/C with HIaq: heating rate, 5 K/min; argon flow rate, 100 ml/min.

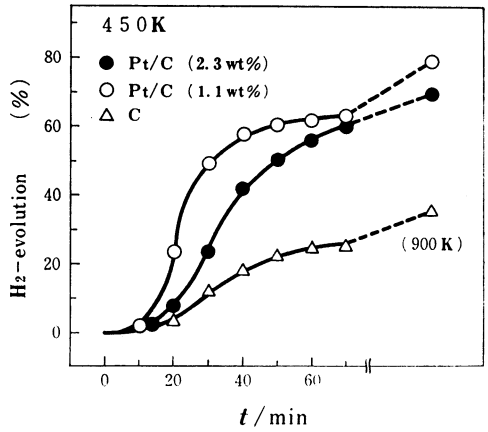

Fig. 4. Influence of the addition of platinum to active carbon on the hydrogen evolution. Six grams of the adsorben twas used. The points above (900 K) corres ponds tothe sum of the amount of hydrogen evolved in the course of the reaction at 450K and that evolved in the hightemperature after-treatment at 900 K for 30 min.

operation was almost equal to the weight of the water contained in the hydriodic acid. This fact suggested the possibility of a selective removal of water from hydriodic acid.

Influence of the Addition of Platinum to Active Carbon on the Hydrogen Evolution. Figure 4 shows the hydrogen evolution (equals the conversion of hydrogen iodide; 100% corresponds to 84 ml (STP) of hydrogen). The points above (900 K) correspond to the sum of the amount of the hydrogen evolved in the course of the reaction at 450 K and that evolved in the high-temperature after-treatment (iodine desorption) at 900 K for 30 min. The amount of hydrogen evolved after the after-treatment was negligibly small, even at 1000 K. The hydrogen evolution obtained with the active carbon itself was remarkably lower than that obtained with the two kinds of Pt/C. This fact indicates that the catalytic activity of the adsorbent is one of the important factors that affect the hydrogen evolution.

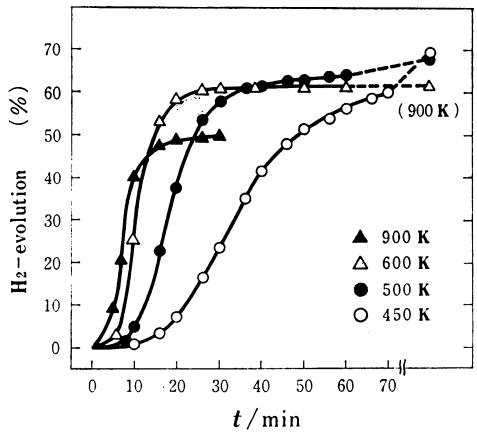

Fig. 5. Influence of the reaction temperature on the hydrogen evolution. The points above (900 K) corresponds to the sum of the amount of hydrogen evolved in the course of the reaction at each temperature and that in the high temperature after-treatment at 900 K for 30 min.

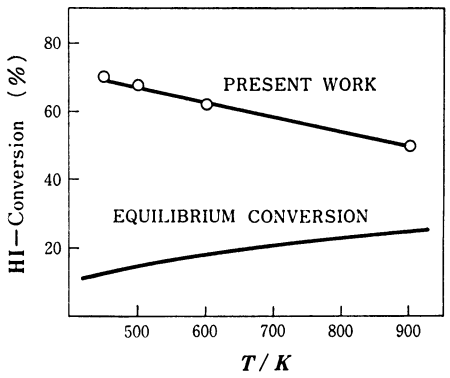

Fig. 6. Comparison of the one-path conversion with the equilibrium one.[6]

Influence of the Reaction Temperature on the Hydrogen Evolution. Figure 5 shows the hydrogen evolution at various temperatures. In the case of the reaction temperature of 900 K, the hydrogen evolution stopped within 30 min. Figure 6 shows that a one-step conversion fairly higher than the equilibrium one was obtained at each temperature. In the temperature region employed in the present experiment, lower temperatures gave higher hydrogen evolutions. This fact may be explained as follows. When the reaction temperature was low, the hydrogen formed was easily desorbed, while the iodine remained adsorbed and the reaction conditions favorable for the elevation of one-step conversion which have been mentioned in the "Principle" section were satisfied. However, as the reaction temperature increased, the desorption of the iodine became easier, as is shown in Figs. 3 and 7. Thus, the removal of the iodine formed from the reaction system by the adsorption became more difficult. Therefore, the one-step conversion decreased as the reaction temperature increased. At higher temperatures, the one-step conversion is expected to approach the equilibrium conversion. However, of course, higher temperatures required a shorter reaction time.

There was a reproducibility for each hydrogen evolution when fresh (not used) Pt/C was used. On the other hand, the hydrogen evolution obtained with a used Pt/C was lower than that obtained with a fresh Pt/C, even if the adsorbates had been fully desorbed from the used Pt/C: for example, the hydrogen evolutions were 61.5% for the first use, 58.6% for the second use, and 54.1% for the third use at 600 K. This fact suggests that the Pt/C gradually deteriorates on repeated runs through the interaction with hydrogen iodide, hydrogen, iodine, and water.

Influence of the Desorption Temperature on the Recoveries of Iodine and Hydrogen Iodide. As Fig. 7 shows, the undecomposed hydrogen iodide began desorbing at 500 K, the iodine formed did so at 600 K, and the total iodine ($HI+I_2$) finished desorption at 900 K. This is in fairly good agreement with the results of the thermogravimetric analyses (Figs. 3-c and d). The maximum temperature available in the thermochemical water splitting is expected to be around 1200 K (High Temperature Gas Cooled Reactor). The fact that the

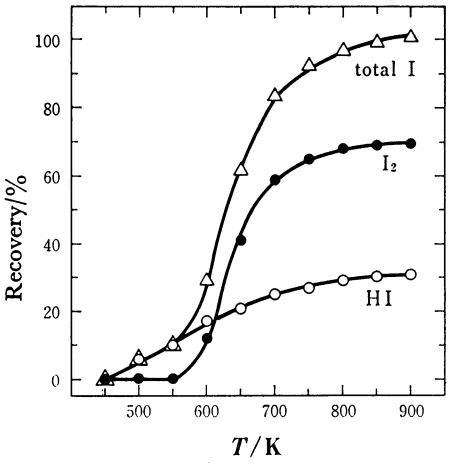

Fig. 7. Influence of the desorption temperature on the recoveries of iodine and hydrogen iodide. Column was kept at each temperature (in the direction of higher temperature) for 30 min: total $I=HI+I_2$.

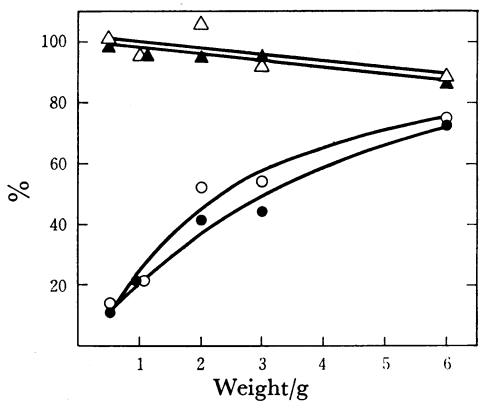

Fig. 8. Influence of the amount of the Pt/C on the hydrogen evolution, the iodine evolution, the total H recovery, and the total I recovery. Each value was obtained in one hour's reaction and thirty minutes' after-treatment at 900 K.
H_2 evolution (○), I_2 evolution (●), total H recovery (△), total I recovery (▲).

iodine desorption, which requires the maximum temperature of this method, is completed around 900 K indicates that this method may be used in the thermochemical water-splitting cycles.

Selective Removal of Water from Hydriodic Acid. As Fig. 7 shows, the undecomposed hydrogen iodide began desorbing around 500 K. On the other hand, a colorless and transparent liquid was already found to condense in the back part of the reaction tube at 450 K. As has been mentioned in the "Thermogravimetry" section, it may be suggested that the liquid was water and that the amount of it corresponded to that of the water contained in the hydriodic acid initially added on the basis of the behavior of the sample D in Fig. 3. The following experiments were carried out in order to confirm this idea. A Teflon tube packed with about 10 g of calcium chloride was attached to the back part of the reaction tube. After 1 ml of hydriodic acid had been added to Part c and the reaction tube had been maintained at 450 K for one hour in an argon stream, the weight of the Teflon tube (kept at room temperature) increased 0.72—0.73 g, with a good reproducibility. The results of titration showed that the total iodine ($HI+I_2$) present in the calcium chloride after the reaction was negligibly small. As no other colorless and transparent liquid except for water and hydriodic acid was included in the system, the liquid was confirmed to be pure water. The amount of 0.72—0.73 g corresponds to 97—98% of the amount of water (0.739 g) contained in 1 ml of the hydriodic acid. On the basis of these experiments, it was found that the water in the hydriodic acid could be removed selectively and almost completely by the use of the Pt/C.

It is well known that active carbon is consumed through the water-gas reaction with water vapor at elevated temperatures. The amounts of hydrogen evolved in the reaction of the Pt/C (2.3 wt%, 6.0 g) with water vapor (0.738 g, corresponding to the amount of the water contained in 1 ml of hydriodic acid) were as follows: 0 mmol(450 K), 0(600 K), 0(700 K), and 0.0982(900 K). On the basis of these results, it is concluded that the consumption of active carbon attributable to the water-gas reaction can be prevented when the water in the hydriodic acid is desorbed at temperatures below 750 K.

Influence of the Amount of the Pt/C on the Hydrogen Evolution. Figure 8 shows the dependence of the hydrogen evolution, the iodine evolution, the total H recovery (H_2+HI), and the total I recovery (I_2+HI) on the amount of the Pt/C. When the amount of the Pt/C was large, a high hydrogen evolution and a high iodine evolution were obtained. On the other hand, the total H recovery and the total I recovery were low in that case, since the time devoted to the desorption was not long enough. As Fig. 7 shows, if enough long time is devoted to the desorption, a total I recovery of almost 100% will be obtained. The optimum amount should be found to obtain a high hydrogen evolution, a high iodine evolution, a high total H recovery, and a high total I recovery, all at the same time.

As has been described above, it was confirmed that a fairly higher one-step conversion of hydrogen iodide than the equilibrium one could be obtained by the combination of the adsorbent with the catalytic activity, namely, the platinum-supported active carbon, and the tempreature-swing method. By the use of this method, the hydrogen formed and almost all the water contained in hydriodic acid could be separated from the product mixture through the operation at 450 K. By removing the water completely from the product mixture, the iodine and the undecomposed hydrogen iodide that desorbs below 900 K can be separated from each other easily. Therefore, the author could show the possibility of the solution of both the subjects mentioned in the introduction; the elevation of the one-step conversion and the development of an effective separation method. However, the method proposed above has two problems which remain unsolved: the rate of the process is low in the temperature region employed; and the process must be driven between the two separated temperatures. It remains necessary to undertake the research

and development of new adsorbents which do not deteriorate, their activation, and that of the pressure-swing method at elevated temperatures, where the rate of the decomposition of hydrogen iodide and the desorption of the adsorbates are high enough, from the standpoint of thermochemical water splitting.

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