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Heat Generation by Hydrogenation of Carbon Hydride

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Summary

We observed anomalous heat generation during heating a small quantity of phenanthrene that was put in a cylinder with a Pt catalyzer and filled with high pressure hydrogen gas. It is very difficult to explain the total energy generation by a conventional mechanism of a chemical reaction. Because almost of all phenanthrene and hydrogen gas remained as it was after experiment. The heat generation sometimes reached to 0.1kW and continued for several hours. Moreover, we have confirmed γ ray emission at the same time. The correspondence between the heat generation and the gamma emission was not good but sometimes they showed good correlation. We have confirmed same result with high reproducibility by controlling the temperature and the pressure.

Introduction

We observed unusual reaction when hydrocarbon (a heavy oil fraction) was reacted under high pressure and high temperature with a metal catalyzer. It produces excess heat and weak radiation, specifically x-rays and gamma-rays. It is very difficult to explain the total energy generation by a conventional mechanism of a chemical reaction. Many studies concerning the hydrogenation of hydro-carbon have been performed for a long time (1-10). We have motivated the idea of this reaction by following facts. Alkali hydride is made to react with the hydrogen gas at high temperature and high pressure. The hydride of Li is made at one atmosphere of hydrogen pressure in the reaction container made of the stainless steel at 725℃. LiH is made to react in melting Paraffin with hydrogen. NaH is made at high-pressure hydrogen to add the Phenanthrene and Anthracene in the mineral oil, and to distribute the sodium metal powder at 280℃. It has been reported that an extremely abnormal reaction in the process of such the hydrogenation. Such a report motivates us to vivificate the reaction.

Material and Methods

Figure 1 shows a schematic drawing for the measurement set up. Two types of reactor cylinders have been used in this study. The one is made from Inconel 625. Inconel reactor has 56mm outer diameter, 26mm inner diameter, 160mm height and the volume is 0.1l. The other one is made from SUS316L, 15mm outer diameter, 9mm inner diameter and 300mm height with 0.02l capacity. The inconel cylinder can sustain 500 atm of pressure, while the SUS one is limited under 200 atm. Both can be heated up 850°C. The reactor is set in an electric furnace. It has hydrogen inlet, gas outlet and housing for a sensor of internal temperature measurement. Moreover, a thermo-couple for the measurement of the temperature of the outside wall of the reactor cylinder has been inserted between reactor walls and the inner wall of the heater.

The reactor is put in the heater. And there is an electric power supply described in right bottom of the graph, data logger and a recorder is set on them. After the metal catalyzer is put in the reactor, 1g weight of phenanthrene is put in and the cover is closed. And then, the reactor is evacuated to 10^{-3}mmHg with a vacuum pump. The hydrogen gas is supplied from the gas cylinder of 150atm pressures up to a constant pressure through a pressure regulator.

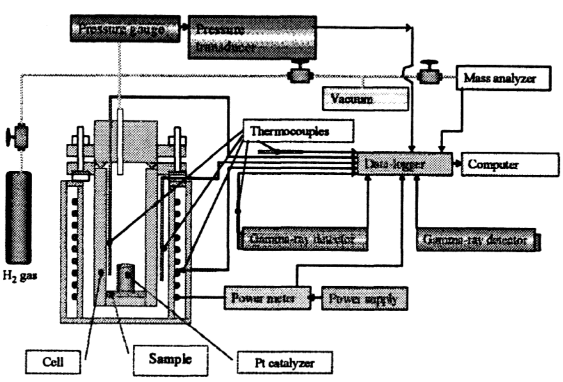

Fig.1: Schematic drawing for the measurement set up.

The electric furnace is supplied by a regulated electric power of 2-kW power supply. Temperatures of the space between the reactor and the furnace, and the inside of the reactor are continuously measured by R-type of sheath thermocouples. The temperature resolution of estimation through the system is 0.1degree.

Gamma-ray emissions are detected by a γ-ray detector (Aloka TCS-161) that is located 15 cm from the reactor. Its output is recorded continuously by the computer through a digital multimeter (Advantest, TR-6845). Temperatures of the furnace heater wire, of the inside of the reactor, of the outer reactor wall, of the surface of the gamma-ray detector, and of the room are also recorded by the computer through the multimeter. The mass spectrometer used in this study (ULVAC REGA201) can detect mass numbers up to 400.

Results and Discussion

We can estimate anomalous heat caused from the calibration curve obtained from the relationship between input power and the stable temperature of the reactor cylinder. We obtained the relationship between heater input and these temperatures to change the conditions of the sample presence, hydrogen pressure and the reactor. The temperature deviations stay in ±3°C if the hydrogen gas pressure increased from 1 to 100atm. It can be understand that the heat release caused by gas in the reactor is not noticeable when the case of inconel reactor.

Figure 2 shows an example of anomalous excess heat. In this test, 1g of phenanthrene was exposed to a mixture of 1 atm of hydrogen and 70 atm of helium gas. Heater power is initially set for 1.4kW, then after 3ks it is reduced to 700W. Finally, it is reduced to 640W. The heater temperature (T_2) rises faster than the cell temperature (T_1). At 10ks they both stabilize at around 640°C, which is where the calibration curve predicts they will settle if there is no anomalous heat. However, they both soon begin to rise above the calibration point. At 9ks the cell temperature T_1 stabilizes for about 2ks as the heater temperature continues to rise. Then the cell temperature begins rising again and at 12ks it exceeds the heater temperature T_2. This temperature reversal is definitive proof that heat is being produced inside the cell. When power is turned off, at 16ks, the heater temperature T_2 peaks at 670°C and the cell temperature T_1 has reached 690°C, 20°C higher than T_2. Input heater power is 640W. The temperature at T_2 peaks at 670°C which is only as high as the calibrated point for this power level; it does not indicate any excess heat. Total energy is even more difficult to estimate than power, but given that the excess power persisted for 6ks (100min) it was at least 120kJ, for this test. Other tests have produced more energy.

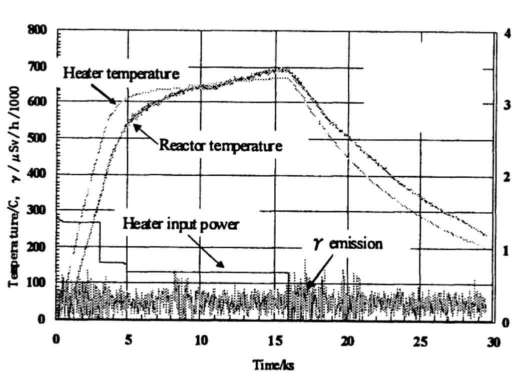

Fig. 2: An example of anomalous excess heat.

Figure3 shows the intensity distribution of gamma emission with the ionization chamber type detector. There are two peaks are shown at 0.11μSv/h and at 0.05μSv/h of the background by a peak analysis. Gamma emission stronger than the background is admitted when an excess heat had generated. Generation of heat was confirmed in the inconel reactor as above described. It has been understood that there was the generation of γ emission from these results. However, the temperature was measured by only a part of inside the reactor having large volume as 0.1l. It can not be understood where in the system the heat generation has occurred. We took the correspondence of the temperature and the Gamma emission with a small reactor. As for the measurement that uses the SUS reactor, the inside diameter is small as 9mm, and we puts the sample and the platinum catalyst in the bottom in the reactor, the thermo-couple touched the catalyst directly, then we can promptly measure the temperature. Thus, the correspondence of the γ emission and the temperature change can be seen directly.

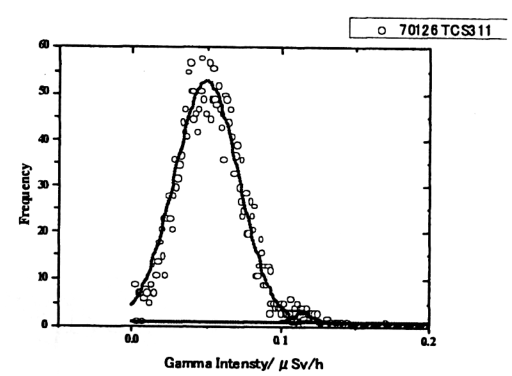

Fig.3: Intensity spectrum for the foreground γ emission in fig2.

Figure 4 shows the measurement result in the SUS reactor. This shows the temperatures and the gamma emission that 1g of sample is heated with the platinum catalyst at 50atm H_2 pressure. The interval between each point showed the data collection is 5s. The heater input was 55W, and then the preset temperature was 595°C. The figure is shown the first 30ks-82ks interval.

It is understood that the reactor and the wall temperatures rose gradually though the initial temperature setting was 595°C. Moreover, it is understood that the temperature in the reactor, in this case, goes up previously, and the outside wall of the reactor goes up afterwards. Meanwhile, heater temperature has exceeded 700°C though that is not shown here. Moreover, it is understood that the temperature change in the reactor is extremely large.

It can be seen that the temperature rises rapidly after the emission of γ ray occurs. Especially, a strong γ emission corresponds to the rise of the heat. It is also admitted to correspond to the rise of the temperature at a weaker γ ray emission. Here, it shows rapid temperature change because the temperature returns to the preset temperature of 600°C again even if the temperature of the reactor goes up temporarily.

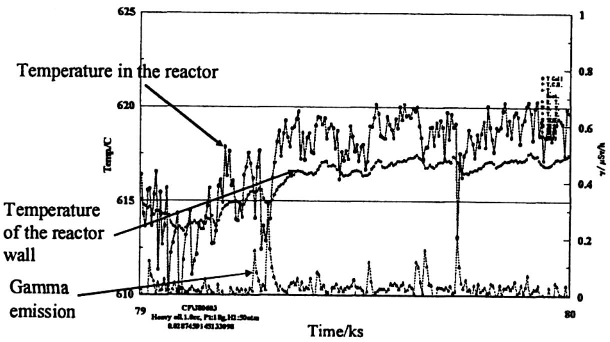

Fig. 4 : Gamma emission at the onset of anomalous heat.

Moreover, the following result was obtained by the ICP Mass analysis. In the analysis result of the solid was 99% ^{12}C in the carbon of the sample before experiment, and 50% or more was $^{13}C^{+}$ in the sample after experiment that excess heat had been occurred. Usually the reaction of hydrogenation of carbon hydride is exothermic, and heat is released corresponding to the ΔE. For example, ΔE is around -125 kJ/mole. But the enthalpy of the hydrogenation reaction of Phenanthrene is different depending on the temperature. It is a reaction of heat generation less than 300℃[11]. However, it is an endothermic reaction as kJ/mol at higher than 300℃. We observed the weight loss due to the reaction of phenanthrene in the high pressure of H_2 gas was under 0.01g. So, the molar of the phenanthrene was only 5.6×10^{-5}. Then the typical heat can be estimated as 11.2J. On the other hand, total heat observed was the order of 100 kJ; the heat was 10^4 times higher comparing with the calculation. Therefore, generation of heat is thought for the possibility of causing by the chemical reaction not to exist. In addition, the γ emission was observed during the experiment. It is shown that there was a generation of a certain kind of nuclear reaction through the correlation of the heat generation and the γ emission.

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