

Confirmation of Heat Generation during Hydrogenation of Oil

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I show you new result that excess heat generation under high H₂ pressure and high temperature to use the reactant as phenanthrene of heavy oil fraction and metal catalyst.

Method

- **Reactant:** phenanthrene and hydrogen gas. *The fluorescent grade*

(99.5%) of phenanthrene was supplied by Kanto Chemical Co. LTD.

- **Catalyzer:** Platinum wire and mesh, Ni Cylindrical block. *The Pt catalyzer was a high purity Pt mesh (99.99%) supplied by Tanaka Noble Metal Co. LTD. It is rectangular, 5 cm ×10 cm, 50 g.*

- **Condition:** Higher than 530°C and high H₂ gas pressure.

We used a 99.5% pure phenanthrene and a metal catalyzer such as a high purity Pt mesh or Ni block.

At the beginning of this series of experiments, the catalyzer were activated once in hydrogen gas at high temperature.

Condition for generate the heat is needed high temperature and pressure.

Contents

- Measurement procedures.

Heat and gamma generation.

- Experiment results.

Heat generation, Gamma emission.

- Analysis

Peak analysis of intensity spectrum of gamma emission, Coincidence between gamma and heat.

- Conclusions.

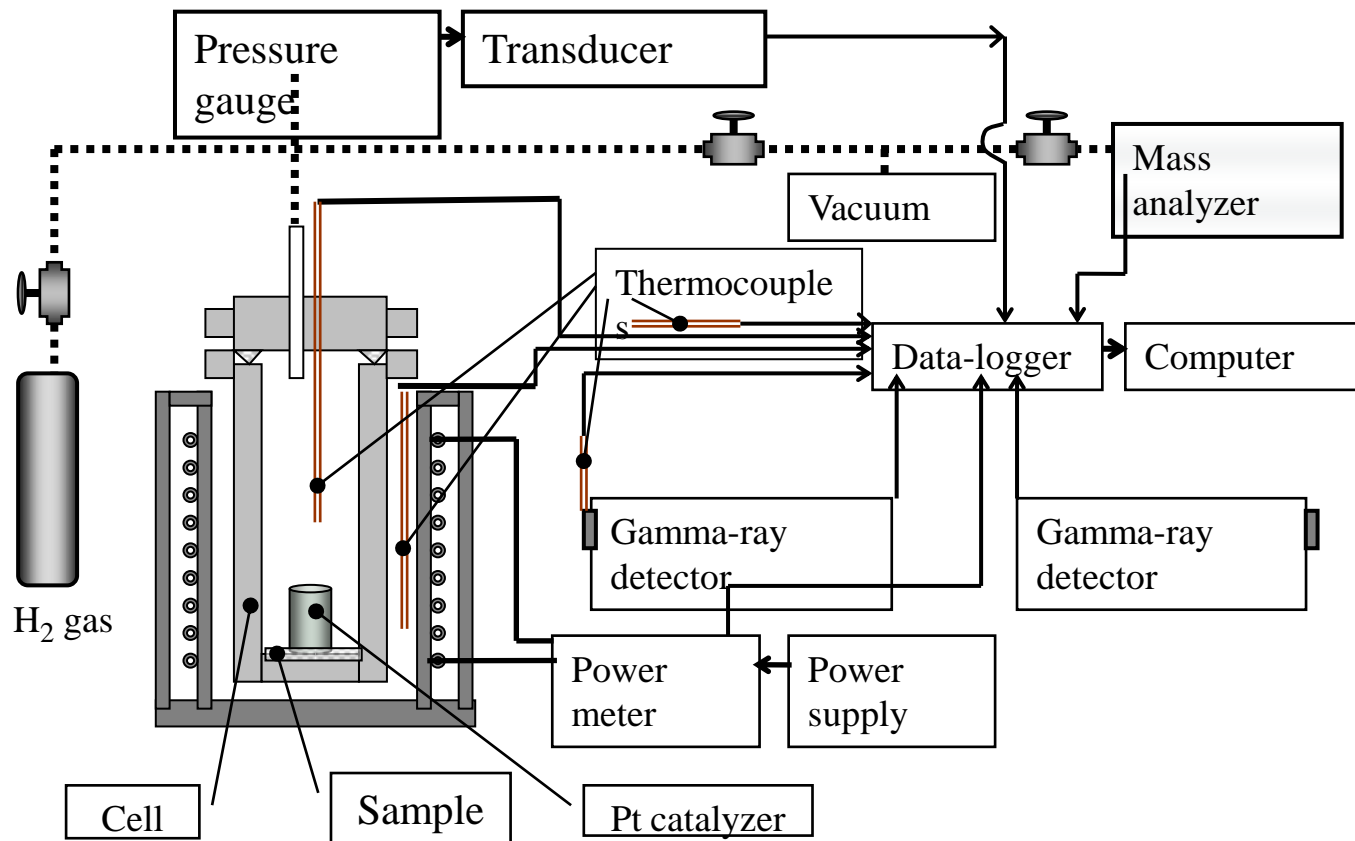
Factor of reaction control.

First of all, the measuring method, the heat measurement, the mass spectrometry, and the radiation detection method, are described.

The analysis method of the detection of abnormal generation of heat and the γ ray and products is described in the result.

In addition, the controlling method and the devised mechanism are shown in the result.

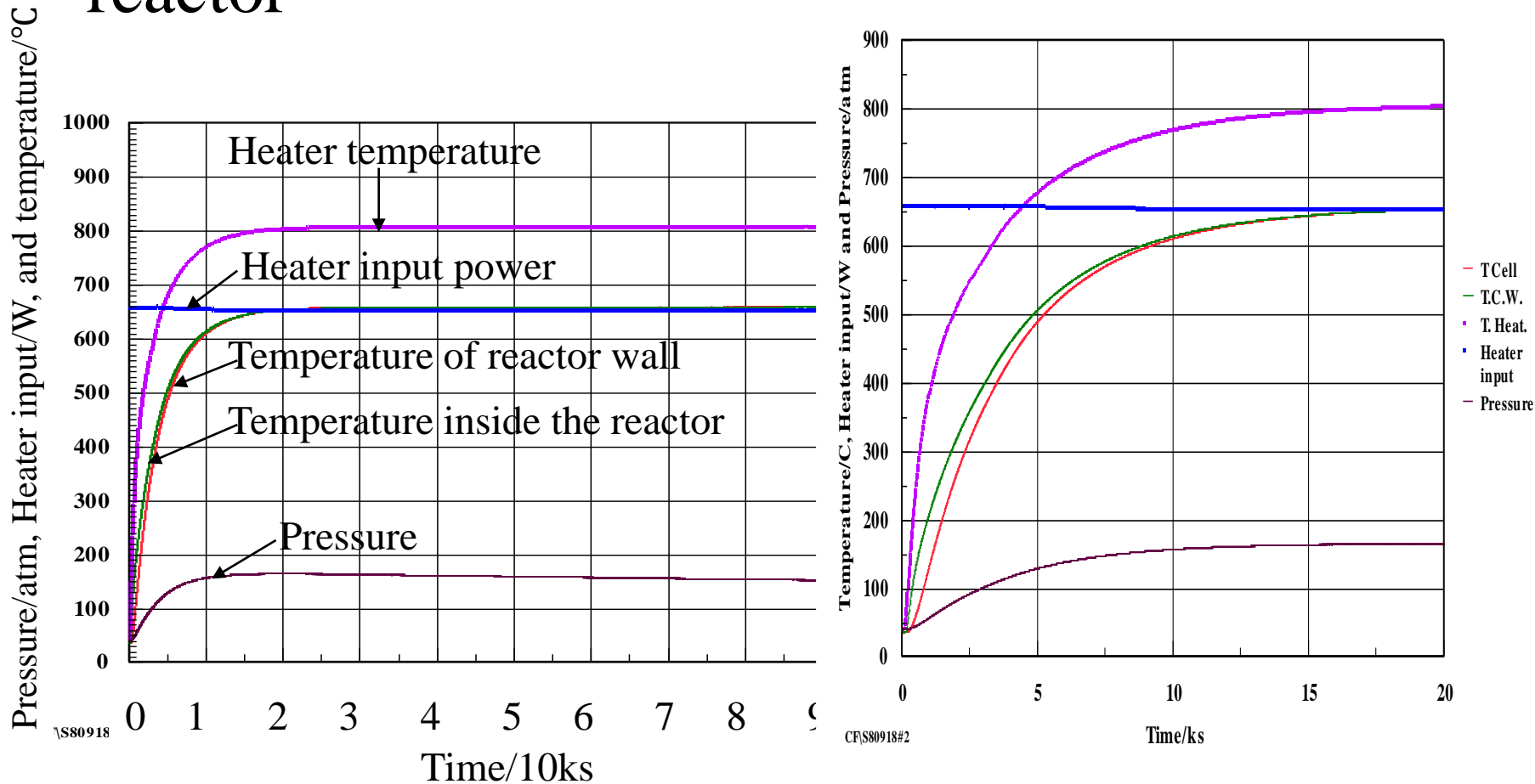
Schematic of the reaction cell and the experimental set up



The reaction chamber is cylindrical. It is constructed from Inconel 625. It has a 16-mm outer diameter, a 10-mm inner diameter, a 300-mm height, and has a 0.01-l capacity. It can sustain a pressure of 500 atm, and it can be heated to 850° C. The reactor has a plug for the hydrogen inlet and housing for an internal temperature sensor. A platinum catalyst is placed inside the cell. The temperature inside the cell is measured with an R-type thermocouple, 1.6 mm in diameter, 30 cm long, which is enveloped in a 0.3 mm thick SS314 stainless steel shield and grounded to reduce noise. The thermocouple range is from -200 to 1,300° C. Moreover, another thermocouple of the same type measuring the temperature outside wall of the reactor. Thermocouple data is collected by a data logger, with a temperature sensitivity of 0.1° C. *The error ranges of the temperature measurement system is determined by the resistivity of the thermocouples (4 Ω), the insulation (100 MΩ), and the data logger (100 MΩ). In this case, the error works out to be 0.03% of the instrument reading. At a temperature of 800° C the error is 0.03° C.*

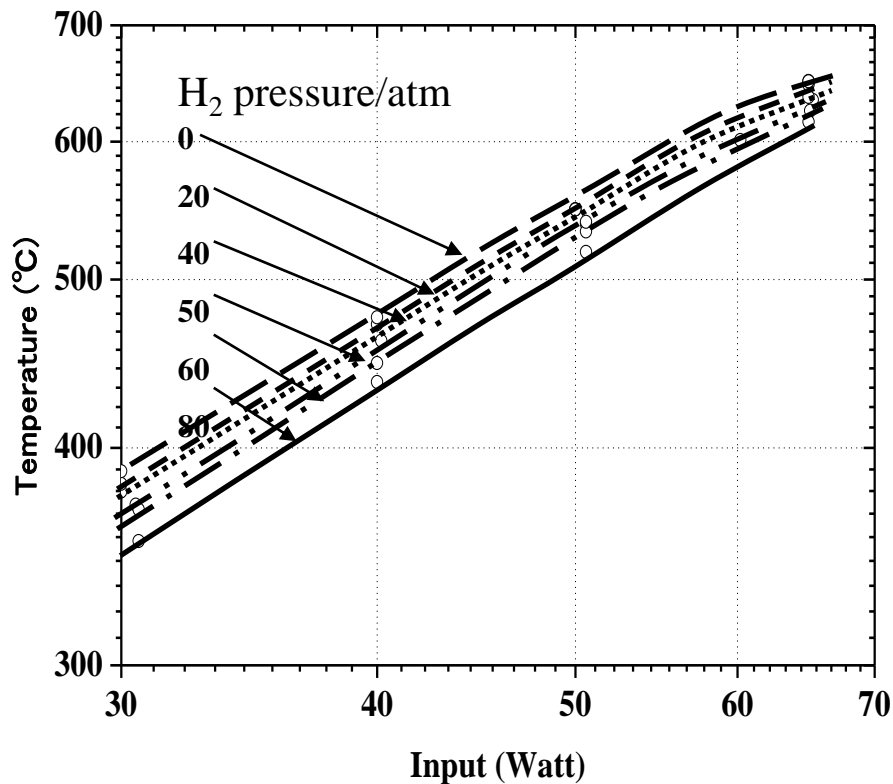
Measurement of heat and γ

Calibration for input and temperature: Inconel reactor



The furnace heater input was set to 650 W, and the hydrogen pressure was set to 50 atm. The reactor contained the platinum catalyst, but did not contain a sample. The change in temperature of the outside wall of the furnace, the inside wall of the furnace, the in-furnace temperature and pressure, all as a function of time, are shown.

Temperature dependence on heater power at different H₂ gas pressure

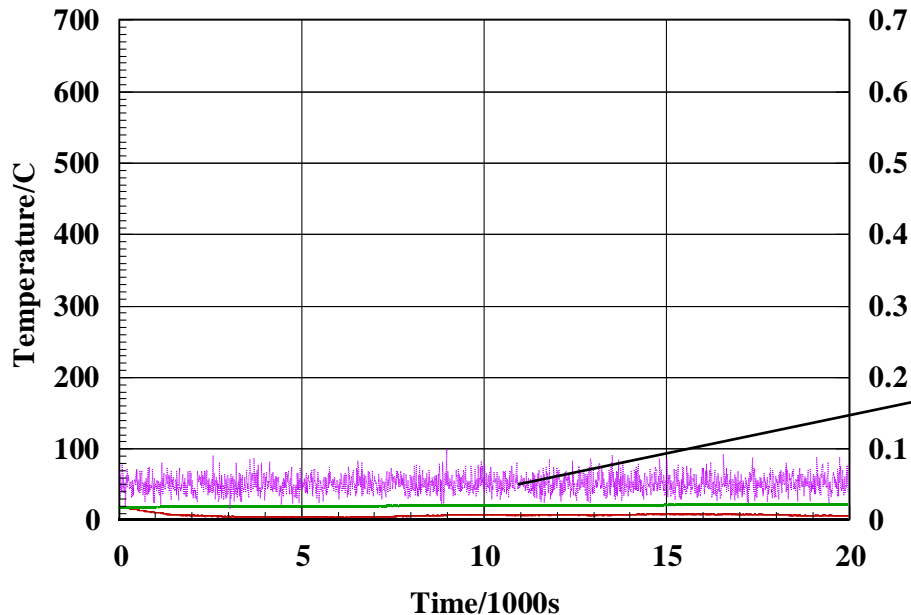


The amount of excess heat is determined by comparing input heater power to a stable temperature in the cell on a calibration curve. Figure shows the relationship between heater power and the cell temperature. These data points were taken with the phenanthrene sample in the cell but no Pt catalyst present. They were taken after the temperature stabilizes: the values shown are cell temperature minus ambient temperature.

Calibration for gamma emission

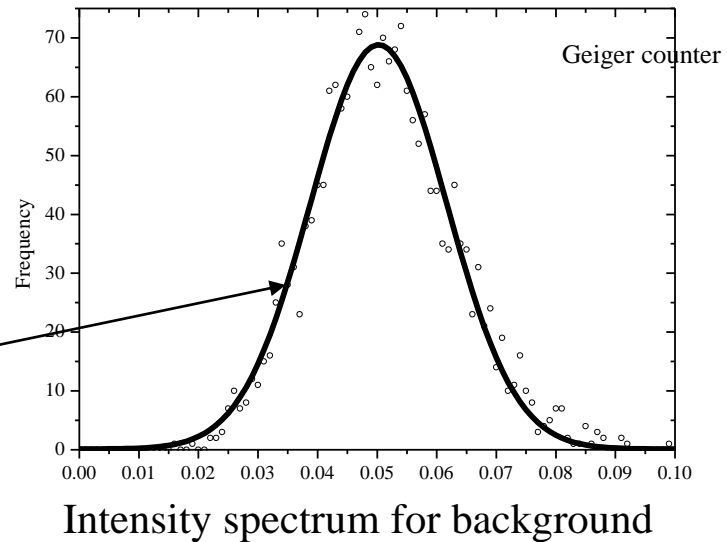
Computer software for peak analysis: Origin pro 8

Background gamma



$$f(x) = \frac{1}{\sqrt{2\pi}} \exp\left(-\frac{x^2}{2}\right)$$

$$\text{psn}(x:\lambda) = e^{-\lambda} \lambda^x / x! \quad (x=0,1,2,\dots)$$



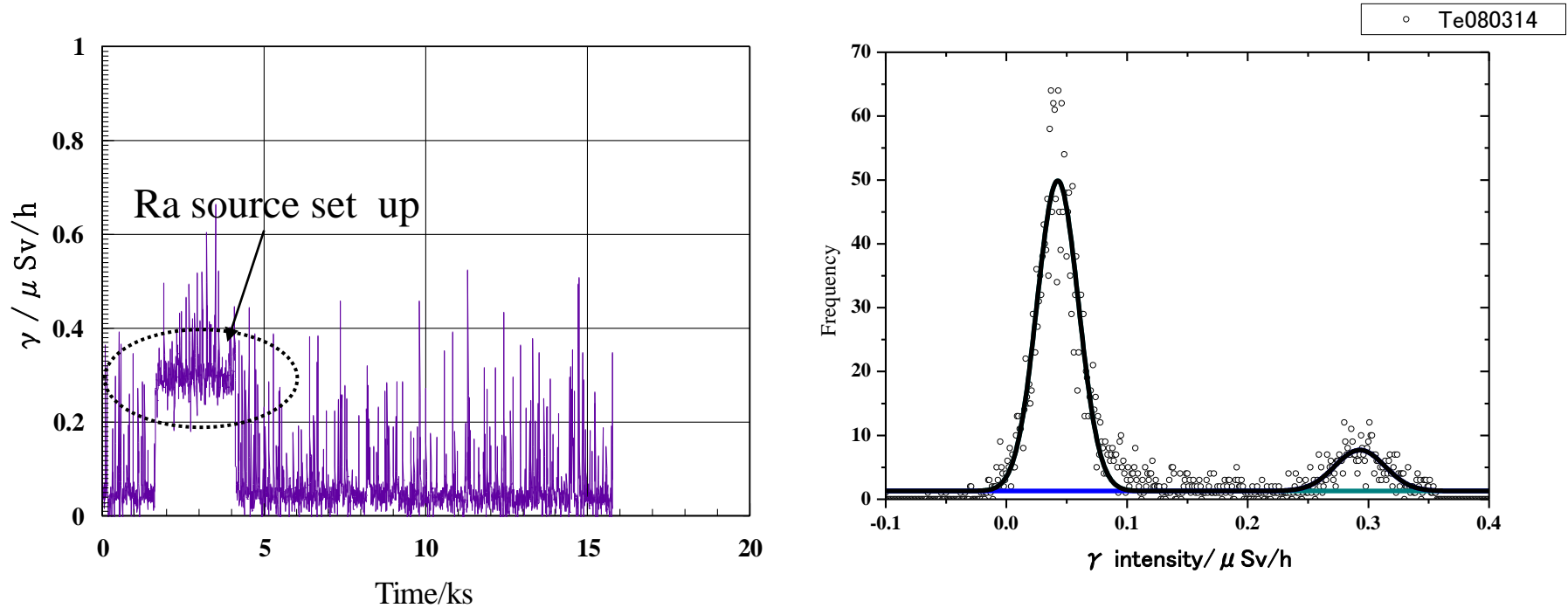
Left figure shows the change in gamma-ray emissions for the background. It changes around 0.05 $\mu\text{Sv/h}$, but the average intensity is constant. The intensity distribution shown by the open circle in a right graph. It is clear normal distribution, since the background change is a process of the Poisson. Moreover, these points is analyzed by multi peak presentation by a computer software of Origin professional. It is understood that the peak is only one normal distribution shown as solid line in right graph.

Peak analysis

- Multiple peak analysis: A Gaussian distribution analysis.
- $y = y_0 + A(w(\pi/2)^{-1/2})\exp(-2(x-x_0)^2/w^2)$
- Where,
- $y_0 =$ Baseline offset
- $A =$ Total area from baseline to curve
- $X_0 =$ Midpoint of peak
- $W = 2\sigma$. Half bandwidth $\cong 0.849$
- The midpoint X_0 is the average, where $w/2$ is the standard deviation.
- Reducing the difference between the fitted curve and original data.
- Definition of additional peaks multiple peaks.
- $y_1 = f(x_1, x_2, \dots, a, b, c, \dots)$
- $y_2 = f(x_1, x_2, \dots, a, b, c, \dots)$
- $y_3 = f(x_1, x_2, \dots, a, b, c, \dots)$
- \dots
- $y_n = f(x_1, x_2, \dots, a, b, c, \dots)$
- The Gaussian peaks derived with these functions are closest to the original data.

The radiation data was further processed with OriginPro software (OriginLab) to analyze multiple peaks. A Gaussian distribution analysis was performed to fit of multiple peaks, with the following equation. To reduce the difference between the fitted curve and original data, additional peaks were plotted, and the following peak analysis was performed. To analyze multiple peaks, a function with multiple dependent variables and independent variables was defined in the following equations. The Gaussian peaks derived with these functions are closest to the original data.

Gamma calibration



This graph shows when the check source was located 10 cm from the detector for 1.8s to 4 ks. The periods before 1.8 ks and after the 4 ks indicate only background. The gamma-ray emissions increase six times from 0.05 to 0.3 $\mu\text{Sv/h}$, when the isotope source was moved closer to the detector. The calibration of the gamma-ray emission detector was performed to change the set up time and distance to locate the source position from the detector by using a standard Ra radiation source. Right figure shows the intensity distribution of gamma. Two peaks are shown in this intensity distribution figure. These peaks at the 0.04 and 0.3 $\mu\text{Sv/h}$ positions are caused by the background and the source, respectively. The solid line in figure shows the calculated intensity distribution. In this case, the peak of the gamma-ray emission from the source clearly differs from that of the background. However, when the position of the source was far from the detector and the data accumulation time was short, it is difficult to distinguish the foreground peak from that of the background.

Changes of reactor temperature and gamma emission

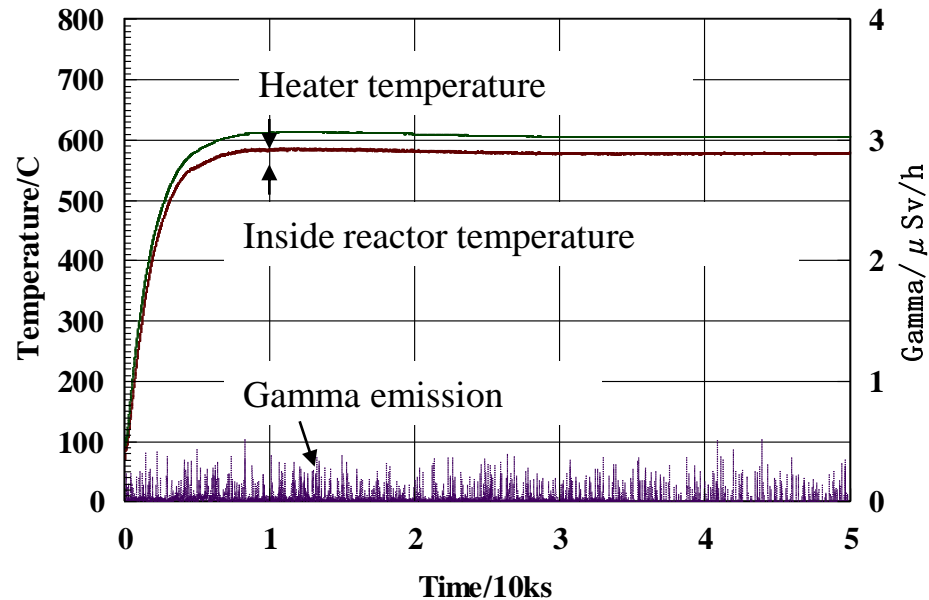
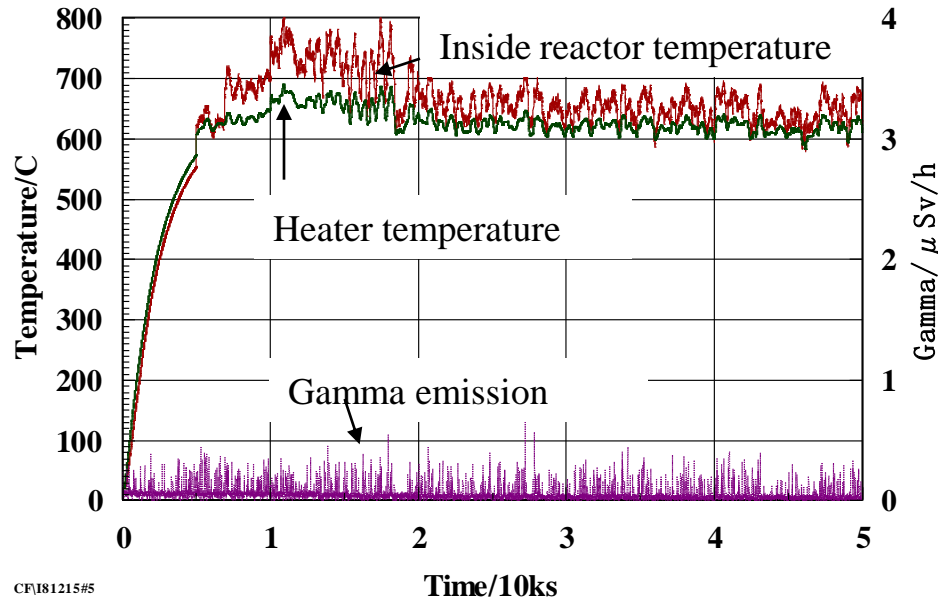


Figure shows an example of a test with no excess heat. 1 g of phenanthrene was exposed to a 70 atm of hydrogen gas, and furnace heater power was set for 60 W. However, the Pt catalyst was not placed in the cell. By 10 ks, the temperature stabilized at about 600° C. After that the temperature remained stable and settled.

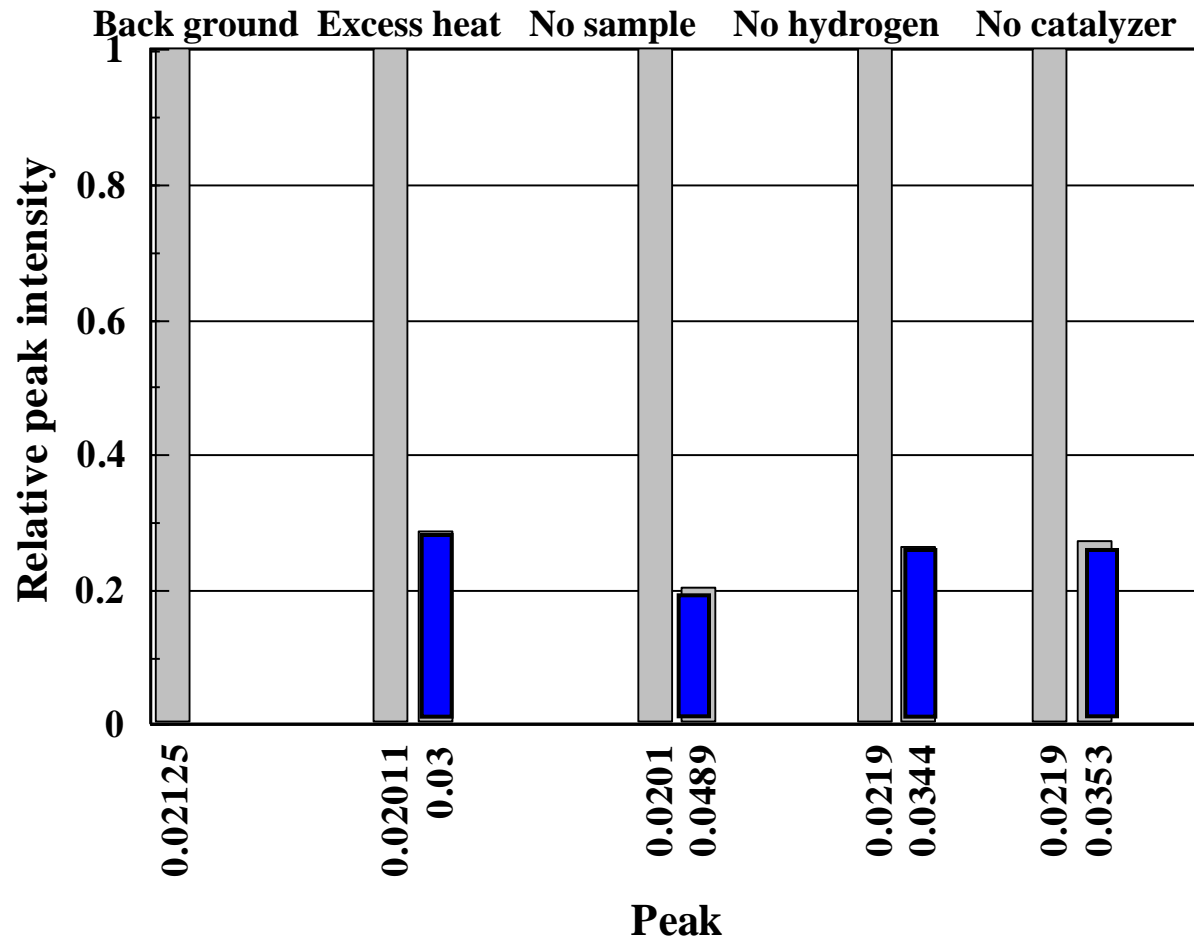
Right figure shows the intensity distribution of gamma-ray emission. Only the background peak is observed. Calculated peak analysis reveals no other peaks.

Changes of reactor temperature and gamma emission



Furnace heater power was set for 60 W. The furnace heater temperature rose faster than the cell temperature. As shown in the calibration curve when there is no anomalous heat, by 10 ks both temperatures stabilize at around 640°C . However, in this test they both soon begin to rise above the stabilization point. After 5 ks, large perturbations begin and the temperatures continue rising. Also, at this point the cell temperature exceeds the furnace heater temperature. This temperature reversal is proof that heat was being produced inside the cell. The cell temperature reaches 800°C , which is 200°C higher than the calibration curve predicts. Since input power is 60 W, based on the calibration curve. We extrapolate that roughly 60 W of anomalous heat is being produced. Because of the extreme fluctuation in heat, total energy is more difficult to estimate than power, but because the excess power persisted for 10 ks it was at least 120 kJ in this test. Right figure shows the intensity distribution of gamma-ray emission from the ionization chamber detector. Two peaks are shown, $0.05\ \mu\text{Sv/h}$ and $0.09\ \mu\text{Sv/h}$ of the background by calculated peak analysis. These are clearly differentiated from the background of $0.02\ \mu\text{Sv/h}$. Gamma-ray emissions were rare in but they were observed when intense excess heat was generated. Total heat production can be estimated from the calibration curve and total duration of excess heat production which started around 18 ks and continued to 50 ks. Over this period, the average temperature was 50°C above the calibration point continuing for 40 ks. Based on the calibration point of 600°C the excess was roughly 5 W on average, so total heat production was roughly 160 kJ for the entire run.

Peak distribution of gamma at various conditions



The peak analysis result in the previous graph is synthesized and this graph is shown. The peak from 2 to 3 with the Gauss distribution comes in succession from each calculation result. The biggest peak is having the position of 0.02, and has a secondary peak in the position of 0.08-0.1. A peculiar peak appears at the position from 0.023 to 0.05 excluding this. This peculiar peak appears clearly at where is generation of heat. However, the peak is admitted when there is no hydrogen. The hydrogen atom is included in Phenanthrene (C₁₄H₁₀) of the sample though the hydrogen gas is not here.

The radiation emission peak position and intensity under various conditions.

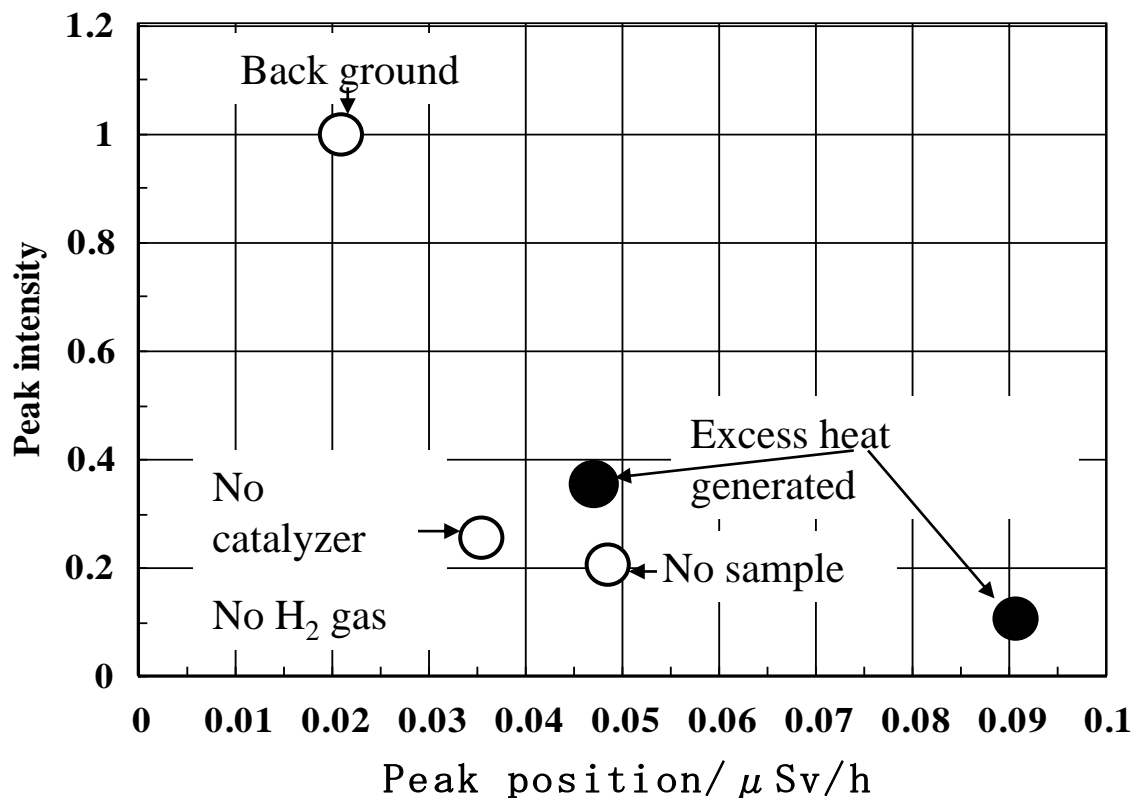
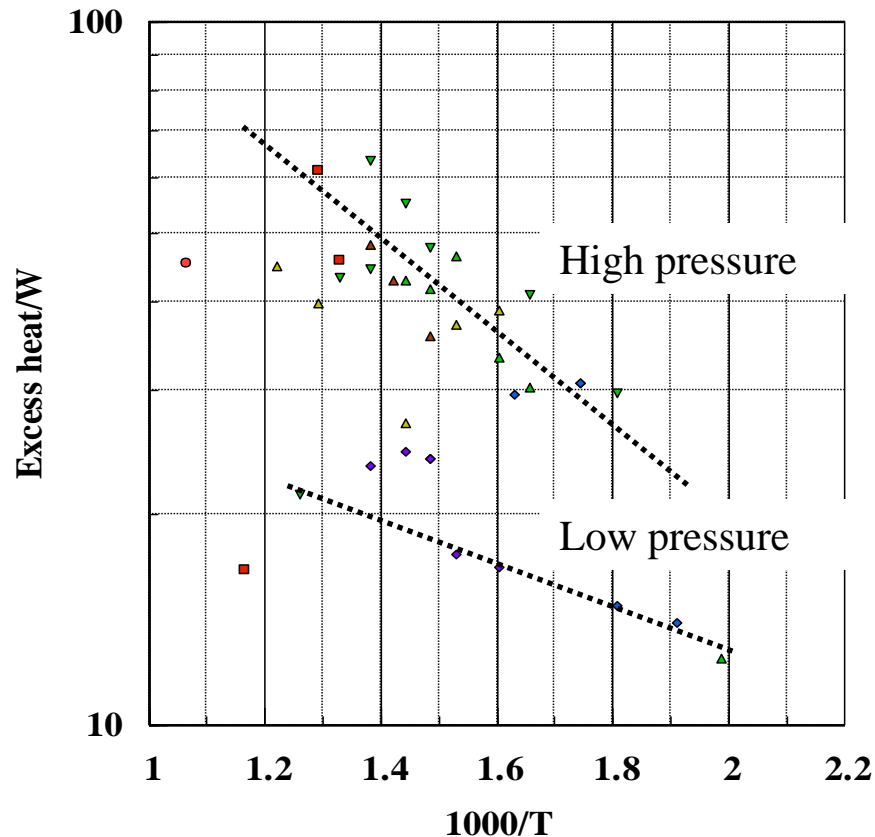


Figure shows various conditions under which heat is produced or not produced, and the associated radiation peaks relative intensity compared to the background. The 0.02 $\mu\text{Sv/h}$ peak is the background; the others are normalized to it.

Even when there is no excess heat, in other words when the catalyst, hydrogen gas, or the phenanthrene sample is removed from the cell in a blank test, there is a peak 0.034 ~ 0.048 $\mu\text{Sv/h}$. But, when there is excess heat, two peaks appear at the same time (at 0.04 and 0.09 $\mu\text{Sv/h}$) and the intensity of the first one is stronger than the blank test peaks.

Changes in heat production in response to different gas pressure and temperature.



The effects of changes in hydrogen pressure and temperature on excess heat production are summarized before figure. The horizontal axis shows the temperature setting, the vertical axis shows the highest level of excess heat. Pressure settings were from 1 to 100 atm, and they were split into two domains for the purposes of this graph: low pressure from 1 to 10 atm, and high pressure above 10 atm. A trend is observed: higher pressure tends to produce more excess heat.

Conclusions

- Anomalous heat generation was confirmed during the heating of phenanthrene in high-pressure H₂ gas.
- Sporadic radiation emissions (probably gamma rays) were confirmed during the high temperature experiments.
- A weak correlation was observed between the anomalous heat generation and the radiation emissions.

The reaction is reliably triggered by raising temperatures above the threshold temperature of ~600°C and the hydrogen pressures above 70 atm. It can be quenched by lowering the temperature inside the cell below ~600°C. When the necessary conditions are achieved, generation of heat is observed with high reproducibility. However, the amount of heat generated is not stable. Only a small amount of reactant is consumed during the experiment, presumably by conventional chemical reactions. We conclude the following: Anomalous heat generation was confirmed during heating of phenanthrene in high pressure of H₂ gas. Sporadic gamma emission was confirmed during high temperature experiment. A weak correlation was observed between heat and gamma ray emissions.