Chemical Reaction under highly Precise Microwave Irradiation

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Abstract: Chemical reactions conducted under microwave irradiation have high reaction rates and high selectivity, but these reaction rates are not always reproducible. To achieve reproducibility, a solid-state microwave source with an ultra precise oscillator, high power amplifier module (HPA), and elliptical applicator is developed. This HPA has up to 141 W average power and generates pure 2.45-GHz sine signal. With these features, reproducible reactions can be conducted. We also demonstrated methanol decomposition as a solid-gas reaction with a Pd/C catalyst under microwave irradiation using this HPA and applicator. The reaction rate under microwave irradiation was more than three-fold of that under electric furnace heating.

Keywords: SAW oscillators, microwave heating

1. Introduction

Chemical reactions carried out under microwave irradiation often have high reaction rates and high selectivities, which enables compact reactor sizes and energy-conservation processes. Hence, microwave chemical processing and chemical synthesis have attracted considerable interest as they will be employed for greatly improving process efficiencies and conserving energy for realizing “Green Chemistry or Green Engineering” [1]. In thermal reactions driven under conventional heating such as the use of electrical heating furnaces and steam heaters, the reactor is heated by heat conduction through the reactor wall. On the other hand, microwave heating provides internal and homogeneous heating of reaction systems. In general, heating with microwave irradiation displays the following features: rapid and high-efficiency heating, rapid thermal response, and selective heating. Furthermore, there have been a lot of works showing unusual enhancement in the reaction rates and selectivities, called “non-thermal effects” [2]. Because of these features, microwave heating has been widely employed in studies on organic synthesis, inorganic synthesis, hydrothermal synthesis, and high-temperature firing [3, 4]. Tsukahara et al. successfully observed the phenomenon of nonequilibrium local heating of the dimethylsulfoxide molecules that were in proximity to Co particles under microwave irradiation by using real-time, in situ Raman spectroscopy [5]. They also reported on a rapid and highly productive synthetic microwave irradiation protocol for transition-metal-catalyzed carbon-carbon coupling for a wide range of benzylic/allylic alcohols with ß-diones, ß-keto esters, and dialkyl malonates [6]. However, it is often pointed out that microwave irradiated reactions have a very low reproducibility. Our opinion is that one of reason is low reproducibility comes from broad spectrum of microwave source. Most of chemists usually employed a magnetron as microwave source [7]. Because a magnetron is cheaper than that of a solid-state amplifier, and has high power and high efficiency generation of microwave. On the other hands, silicon RF lateral diffused metal-oxide technology has progressed to meet the demand of the mobile phone base station and achieves a high power gain of 13dB and a high power of 130W [8].

In this study, we developed a microwave irradiation system with a precise and stable high power of microwave using a LDMOS-FET and as a diamond surface acoustic wave (SAW) resonator and studied the methanol decomposition reaction for extracting hydrogen from methanol using Pd/C as a solid catalyst under highly precise microwave irradiation as a model solid-gas reaction.

2. Development of high power amplifier module and applicator

We have successfully developed microwave irradiation system with a solid-state microwave source, a slug tuner, power meter and an ellipsoid applicator for chemical synthesize. Fig. 1 and Fig. 2 show a photo and block diagram of an entire system. The solid-state microwave source consists of a voltage-controlled SAW oscillator (VCSO) that employs a diamond SAW resonator and a three-stage high power amplifier module (H.P.A.).

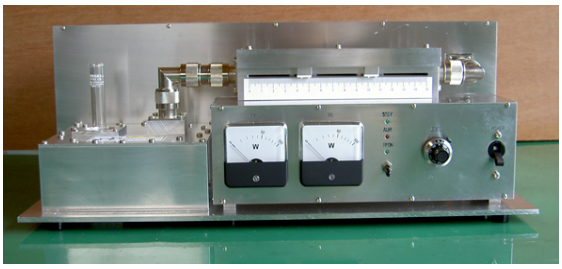

Figure 1. Photo of overview of the microwave irradiation system

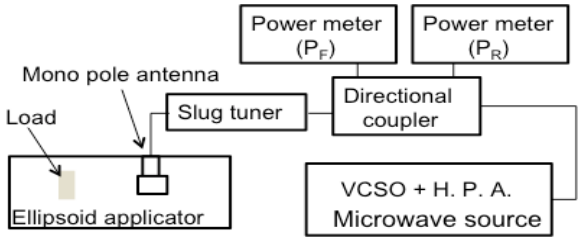

Figure 2. Block diagram of the microwave system

2.1 Voltage-controlled SAW oscillator

The diamond SAW resonator operating at high frequency from 2 to 10 GHz with outstanding temperature stability were developed using a SiO_2/IDT/ZnO/diamond structure and a SiO_2/IDT/AlN/diamond structure [9, 10]. The VCSO was successfully developed and has several advantages such as a low phase noise (-90 dBc/Hz at 1 KHz offset), low floor noise (-160 dBc/Hz at 10 MHz offset), no spurious signal, and a low temperature deviation of the center frequency [11]. Because of these characteristics, there is no redundancy in a circuit design of high power amplifier to obtain safety for human.

2.2 High power amplifier module

Our design concept of HPA is completely different from that of a base station power amplifier in modern wireless communication system. Doherty, Envelope elimination restoration and class F topology design technique of high power amplifier are useful for a base station power amplifier in order to obtain high efficiency, linearity, and wide band [12-14]

A HPA for chemical synthesis should have a capability of a continuous microwave with precise and stable power and without any spurious signal and distortion. We employed class AB amplifier using the LDMOS FET (Infineon Technologies) as a power transistor in the final-stage amplifier module. The final stage amplifier module was realized by using a step impedance transformer method. Fig. 3 and Fig. 4 show circuit design and photo of this module. This module has a 13dB gain, a maximum output power of 141W and a drain efficiency of 48% with a continuous wave signal and an output impedance of 50 Ω at 2.45GHz. The final amplifier module has good specifications. When 500W power is generated, four modules are combined using a simple combiner technique. Owing to these features, the HPA can serve as a highly stable and suitably precise microwave source as compared to a magnetron. Fig. 5 and Fig. 6 show the relative output power spectra of the developed microwave source and a magnetron, respectively, for various output power values. Although the magnetron was expected to show frequency stability for over 500 W of output power, a 5 MHz fluctuation was still observed. On the other hand, good frequency stability can be achieved using a diamond SAW resonator, even for an output power of over 100 W.

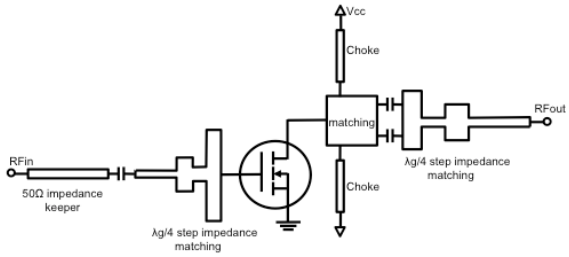

Figure 3. Circuit design of the final stage power amplifier module

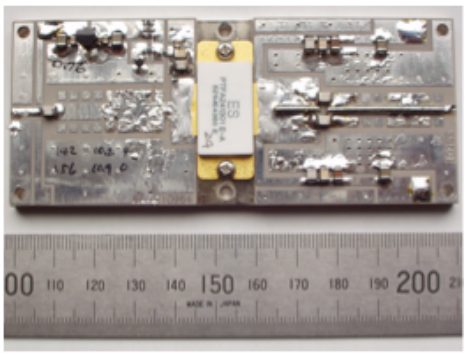

Figure 4. Photo of the final stage power amplifier module

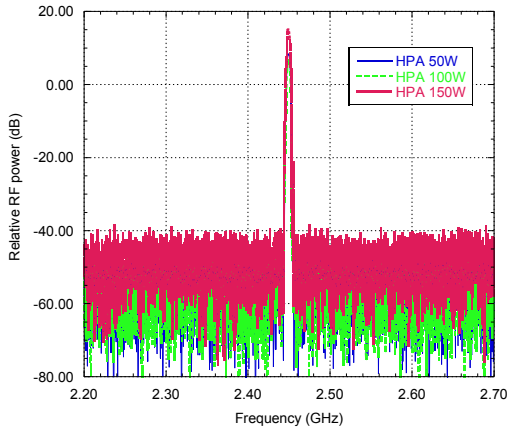

Figure 5. RF power spectrum of HPA for 50, 100, and 150 W

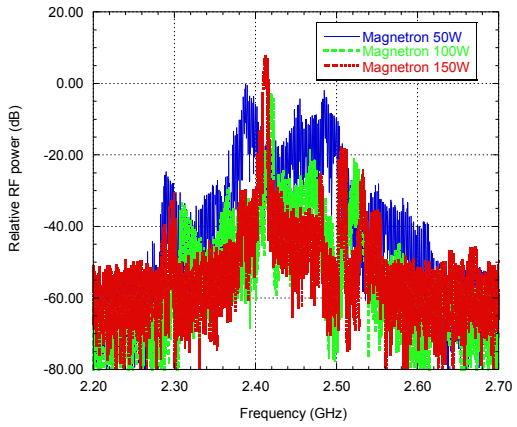

Figure 6. RF power spectrum of Magnetron for 50, 100, and 150 W

The output power can only be precisely measured if the output signal shows high frequency stability, purity, and low noise. Fig.7 shows phase noise of the VCSO with 6dBm and the developed microwave source with 100W output power measured by the Agilent E5052A systems. From the measurement, the phase noise of the developed microwave source is still small, reaching as small as -80dBc/Hz at a 1KHz offset. The floor noise of this microwave source is degraded with 20dB, but is still small value, -150dBc/Hz.

2.3 Elliptical Aplicator

The cylindrical cavity with TM mode is well known to measure material property and also was used to sintering silicon-based composites [15]. The cylindrical cavity usually has high Q-

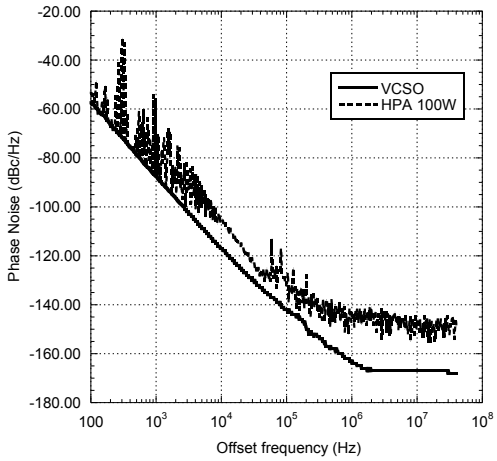

Figure 7. Phase noise of the VCSO and the HPA with 100W output power measured by the Agilent E5052 system.

value. The material property during chemical reaction has drastically or suddenly changed. On the other word, resonant frequency easily changed and it's difficult to continue microwave irradiation. Kretzschmar studied on an elliptical wave-guide and resonator by using a computer simulation [16, 17]. Komarov et al. studied on an elliptical applicator with two ports by using a 3D-FDDT method in order to expand a zone of interaction between the electrical field and the product; in their applicator, the microwave-irradiated body is placed away from the focal point [18]. And they also showed uniformity of the dissipated power within the cylindrical samples in the simulation result. When the resonance frequency due to changing the material property during reaction using a cylindrical applicator, the electrical field at a load is also changed. But we can't apply this structure to our system in order to use the fixed pure frequency. We also realized an original elliptical applicator with one port for use in chemical synthesis processes in order to continue microwave irradiation at first time. In our applicator, a quarter-wavelength monopole antenna is placed at one focal point of the ellipsoid and the microwave-irradiated body is placed at the other focal point. Fig. 8 shows the structure of the elliptical applicator made of aluminum. This applicator has the elliptical ratio of 0.867, and the height of 36mm. When the microwave-irradiated body has some loss tangent or conductivity, TM110 mode generates easily and electromagnetic wave energy can be easily

concentrated at the focal point. Using our applicator and the microwave source, the center of the electrical field at a load is not changed due to the changing of material property and only input energy become just low. These features of the HPA and applicator enable chemical synthesis reactions to proceed with high reproducibility. Our HPA and applicator are highly suitable for investigating chemical synthesis reactions under microwave irradiation.

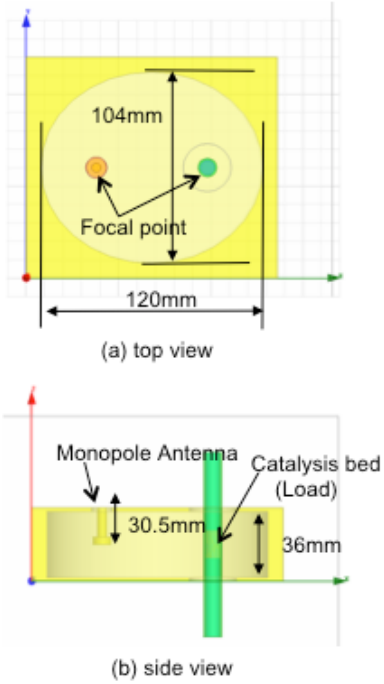

Figure 8. The drawing of the elliptical applicator with catalyst (a) top view and side view

3. Use of COMSOL Multiphysics

Chemical reaction rate greatly depends on reaction temperature. Electromagnetic (EM) wave and heat transfer simulations of the applicator with an irradiation body were performed using COMSOL Multiphysics in order to investigate heat spots.

Before the EM simulation was performed, the relative permittivity and the loss tangent of a powder of the active carbon catalyst in powder form were determined by the cavity perturbation method.

The simulation was performed in two steps. First, the simulation was performed to obtain the impedances of applicators with a 50 Ω input port for varying depths of the catalyst bed under the antenna and for a frequency range of 2–3 GHz. Next, in order to compare the results of the electromagnetic wave and the electric loss density results for varying depths of the active carbon catalyst bed, the simulation was performed under a normalized output power of 1 W and a matching input port. Fig. 9 shows the distribution of the power loss density around the active carbon catalyst bed with 5, 10, and 15 mm depth. It was found that there was no region of high power loss density except the edges of the catalyst bed.

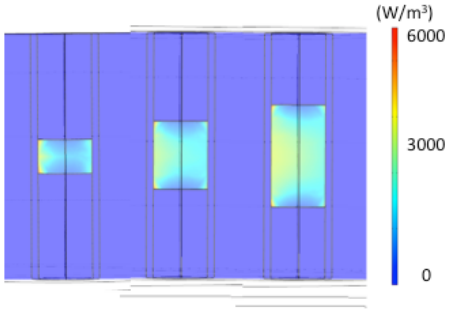

Figure. 9 The distribution of the power loss density around the active carbon catalyst bed with (a) 5mm, (b) 10mm, and (c) 15 mm depth

The temperatures at the six points in the Pd/C catalyst bed under microwave irradiation were measured with a fiber-optic thermometer. Fig. 10 shows the six positions (a-f) at which the measurements were carried out. The gradual increase of temperatures was recorded under MW irradiation shown in Fig. 11. At a given position, the temperature increased with increasing the microwave power, and attained a steady state. The steady temperatures thus obtained are summarized in the right part of Fig. 8, from which an observation follows that there is no region of high temperature in the catalyst bed and that the temperature of the upper region of the catalyst bed, i.e., 157 °C, is 70 °C lower than the temperature of the lower middle region. It was suggested that the nitrogen gas acts as a carrier gas and cools the upper region of the catalyst bed. When the catalyst bed is heated, the matching point for the lowest reflection power does not change. This indicates that the dielectric parameters of materials do not change for temperatures less than 250 °C. This catalyst system was confirmed to be suitable for comparing the catalyst performances under microwave irradiation and for an electrical heating furnace.

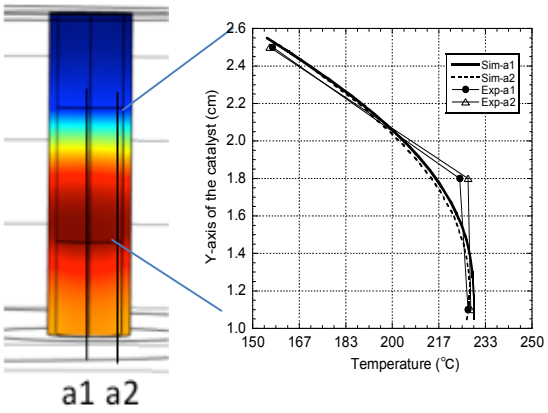

Figure 10. Temperature distribution within Pd/C catalysts bed with 15mm depth under microwave irradiation; lines of Sim-a1 and Sim-a2 calculated by the COMSOL Multiphasics : Exp-a1 and Exp-a2 measured by the optical fiber.

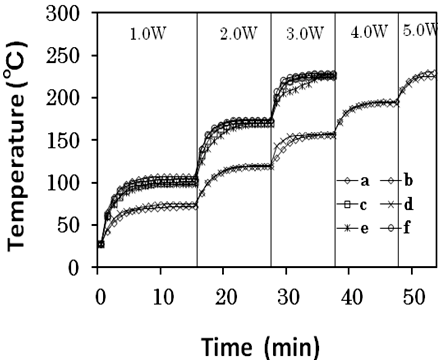

Figure 11. Change in the Pd/C-catalyst bed temperature with time during which the microwave power was successively increased in a stepwise way.

4. Methanol Decomposition Reaction

In this experiment, the conversion of methanol was carried out to demonstrate a model gas-solid catalytic reaction under microwave irradiation, which gives hydrogen (H_2) and carbon monoxide (CO) as products.

First of all, the reaction was carried out using an electric furnace (500 W) as a heater of the reactor. Fig. 10 shows the rate of evolved H2-amount as a function of time measured from the start of feeding methanol into the catalyst bed. At each reaction temperature, which was once increased from 225 °C to 300 °C and then decreased back to 225 °C, H_2 evolution attained a steady state. The H_2 rates observed for the decreasing-temperature region showed the same rates observed for the increasing-temperature region at the same temperatures. This shows that the catalyst was not deactivated throughout the reaction, despite commonly observed phenomena that the CO produced together with H_2 adsorbs on a Pd surface leading to a deactivation of the catalytic sites. Therefore, methanol decomposition on was found to be a suitable selection of the reactions giving good reproducibility in the reaction experiments. Fig. 10 shows the rate of evolved H_2-amount as a function of time measured from the start of feeding methanol into the catalyst bed. At each reaction temperature, which was once increased from 225 °C to 300 °C and then decreased back to 225 °C, H_2 evolution attained a steady state. The steady amounts at a decreasing-temperature region resumed that obtained at an increasing one. This shows that the catalyst was not deactivated throughout the reaction, despite a commonly observed phenomena that the CO produced together with H_2 adsorbs on a Pd surface leading to a deactivation of the catalytic sites.

During the reaction at a given temperature, power of microwave irradiating the catalyst bed was kept constant. The energy supplied from the microwave, absorbed by carbon material in Pd/C catalyst, and consumed by the catalytic reaction was balanced, assuring the each four constant temperatures of 225, 250, 270, and 300 °C.

The conversion of methanol was maintained under 5% with the aim of investigating the reaction rate. This condition is realized for the reaction carried out in a short time, namely methanol flows through the Pd/C catalyst bed immediately. Thus, the contact time, *W/F*, where *W* and *F* represents the weight of the catalyst and the flow rate of methanol plus accompanied inert gas of argon, respectively, should be small as shown in Fig. 12.

The reaction was conducted at a temperature of 225 °C in the catalyst bed (length 15mm) under microwave irradiation. Further, for comparison, this reaction was also performed under the same conditions using an electrical heating furnace.

Fig. 13 shows the dependence of the hydrogen generation rate on contact time, for hydrogen generated by the methanol decomposition reaction using microwave irradiation and the electrical heating furnace.

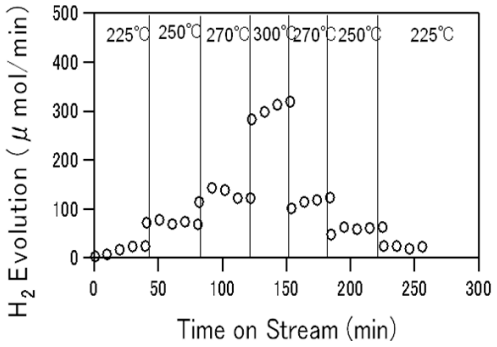

Figure 12. Rate of H_2-evolution at various temperatures.

From Fig. 13, we can see that the production rate of hydrogen through the methanol decomposition reaction under microwave irradiation was approximately three times greater than that in the case of the electrical heating furnace. This striking difference in the rate might arise from a phenomenon of "nonequilibrium local heating" caused by microwave, recently reported by authors including one of us [3]. Thus, a metal particle such as cobalt (0.1-3.0 μm in diameter) dispersed in an organic solvent of dimethylsulfoxide, DMSO, was selectively heated by receiving microwave irradiation, the temperature of which exceeded that of DMSO liquid-phase, where heat has a room for dissipation through the liquid phase. In contrast to this condensed-phase experiment, the present gas-solid reaction system has practically no mediator or carrier for heat transfer, owing to small heat capacity of gas compared with that of liquid. The present study has demonstrated such a peculiar example of "nonequilibrium local heating".

5. Conclusion

With the aim of obtaining high reproducibility of chemical reactions, a microwave high power amplifier (HPA) module with an ultra precise oscillator and elliptical applicator has been successfully developed. This HPA module has an average power of up to 500 W, and the output is a pure sine signal with 2.45 GHz frequency. The microwave energy can be concentrated at the focal point of the elliptical applicator. Because of these features, high reproducibility of the chemical reaction can be achieved. We also demonstrated methanol decomposition reaction as a model gas-solid reaction using Pd/C as a catalyst under microwave irradiation. The reaction rate under microwave irradiation was enhanced three-fold as compared with that under electric furnace heating.

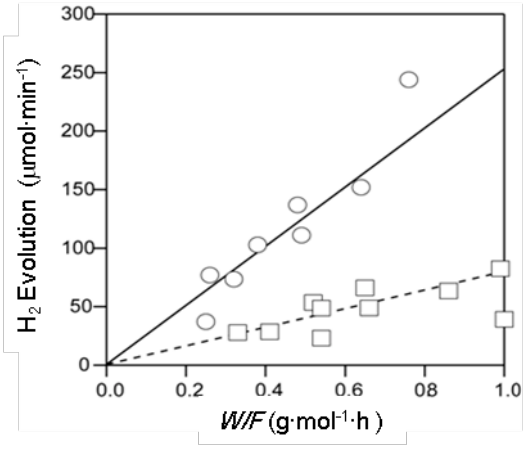

Figure 13. Rate of hydrogen generation rate by methanol decomposition under microwave irradiation (○) and electrical furnace heating (□)

8. References

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9. Acknowledgements

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