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Local Thermal Nonequilibrium on Solid and Liquid Interface Generated in a Microwave Magnetic Field

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Dehalogenation of (2-haloethyl)benzene using Fe particles was carried out in the electric and magnetic fields in a microwave single mode cavity. Microwave irradiation in a magnetic field enhanced the conversion of (2-haloethyl)benzene compared with heating by a mantle heater and microwave in an electric field, while the ethylbenzene selectivities were comparable. Larger Fe particles generated sparks under microwave irradiation, resulting in the increase of ethylbenzene selectivities. These data suggested the reaction acceleration by a local thermal nonequilibrium in the solid–liquid system by the selective microwave heating of the solid.

Microwave heating is applied in various areas such as plasma generation[1–3] and extraction[4,5] and ceramic sintering.[6–8] Since Gedye[9] and Giguere[10] first used microwave heating in organic synthesis in 1986, many studies have reported chemical syntheses using microwave heating. Many reports on reduced reaction time and improved product selectivity in microwave-assisted chemical syntheses have been published, in which the authors claimed that these syntheses were conducted under the same temperature conditions as in conventional syntheses.[11–13] This effect is called the nonthermal effect and is considered to differ from the thermal effect, which features rapid, uniform internal heating. However, no definite proof of the existence of such a nonthermal effect distinct from the thermal effect of microwaves has been provided to date.

Local thermal nonequilibrium, which is defined as the phenomenon of heating domains at much higher temperatures than a bulk solution temperature, is one of the special features of microwave heating.[14–17] Microwaves heat materials directly, and their heating efficiency depends on the electrical conductivity, dielectric constant, and magnetic permeability.[18] When microwaves are applied to a solution consisting of a solvent that is heated inefficiently by microwaves and a solid that is heated highly efficiently, we expect selective heating of only the solid, resulting in local thermal nonequilibrium.[19] Tsukahara et al. directly observed such local thermal nonequilibrium by Raman spectroscopy.[20] They found that the surface temperature of cobalt particles became 50 °C higher than that of the solvent. Furthermore, dechlorination of halo-organic compounds was accelerated by microwave irradiation. In general, metal particles do not get heated in an electric field because they reflect microwaves; however, magnetic metal particles such as cobalt were heated by magnetic loss of microwaves. Therefore, when the solution is irradiated by only the microwave magnetic field, the local thermal nonequilibrium is probably accelerated. Conversely, recent reports show that microwaves generate sparks in a metal–liquid reaction systems and accelerate the reaction.[21–24] Thus, this study attempts to explain this acceleration of local thermal nonequilibrium in metal particles irradiated by the microwave magnetic field in comparison with acceleration by sparks.

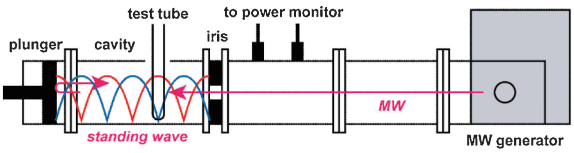

Figure 1. Experimental setup in the single-mode microwave resonator.

A single-mode irradiation device is shown in Figure 1. In a waveguide, traveling waves and returning waves interfere with each other and form a standing wave, producing a microwave intensity distribution in the waveguide. The phase difference between the electric and magnetic fields of the standing wave is $\pi/2$. Where the electric field intensity is the strongest, the magnetic field intensity is the weakest, and vice versa. The electric field and magnetic field intensity distributions of microwaves due to these standing waves are calculated theoretically in the Supporting Information.[25] Therefore, microwave irradiation, primarily by the electric or magnetic field, can be realized by changing the location at which the specimen is inserted, although it is not possible to provide irradiation purely by the electric field or the magnetic field alone. Magnetic material, which has a large magnetic loss coefficient, is heated rapidly in the magnetic field, whereas solvents are not easily heated by microwaves because their magnetic loss coefficient is relatively small. That is, local thermal nonequilibrium is expected to occur at the interfacial surface of the solvent and the magnetic metal. In this study, we use iron(II) particles as the magnetic metal and verify the local thermal nonequilibrium effect by microwave irradiation with the magnetic field in a single-mode microwave device.

The microwave system is shown in Figure 1. A magnetron was used as a microwave power source at the frequency of 2.45 GHz. The electric field intensity distribution in the waveguide showed sinusoid pattern (Figure S1),[25] indicating the formation of standing wave in the cavity. Fe particles (1.125 g) were dispersed in decalin (10.6 mL) in a three-necked test tube and were subjected to microwave irradiation at the points where the electric or magnetic field intensity was strongest. After they were heated to a given temperature, (2-chloroethyl)benzene (0.112 g, 0.7 mmol) was infused. The time of infusion was set to 0 min, and samples were taken at regular intervals thereafter. The reactants and product materials were analyzed using gas chromatography. The same procedure was followed using a mantle heater for comparison. Because a magnetic stirrer cannot stir Fe particles evenly, agitation during the experiment was

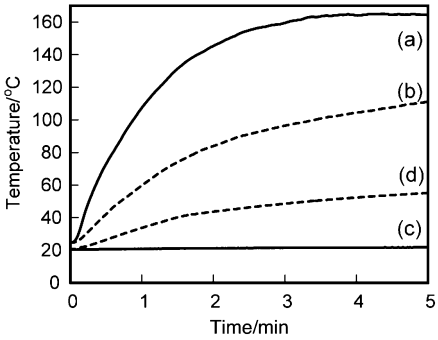

Figure 2. Temperature profiles for a sample of decalin heated by microwave irradiation in (a) magnetic and (b) electric field with Fe particles and (c) magnetic and (d) electric field without Fe particles.

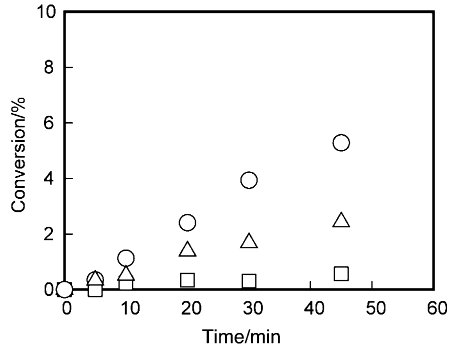

Figure 3. Conversions of (2-chloroethyl)benzene by microwave heatings in magnetic (○) and electric field (△) and a mantle heatings (□).

Table 1. Conversions and ethylbenzene selectivities of (2-chloroethyl)benzene by changing particle size and heating method

Particle size /μm	Heating mode	Conversion /%	Ethylbenzene selectivity /%[a]
45	Mantle	0.6	72
	MW(E field)	2.4	71
	MW(H field)	5.3	69
150	Mantle	0.7	72
	MW(E field)	7.7	89
	MW(H field)	8.3	88

[a]Ethylbenzene selectivity was calculated by dividing the ethylbenzene yield by the conversions of (2-chloroethyl)benzene.

achieved by a mechanical stirrer (800 rpm). Moreover, to consider the differences between materials, similar experiments were performed with (2-bromoethyl)benzene and (2-iodoethyl)-benzene.

To examine the heating properties in the area where the electric or magnetic field intensity is strongest, a test tube containing Fe particles and decalin was inserted, and the temperature profile associated with microwave heating was measured (Figure 2). A test tube containing decalin only was heated to 58 °C under electric field irradiation but only to 22 °C under magnetic field irradiation after microwave irradiation for 5 min. When Fe particles were added to the decalin, the test tube was heated to 110 °C under electric field irradiation and 162 °C under magnetic field irradiation, indicating that the heating efficiency improved significantly. Because the increase in heating efficiency resulted from heat generated by the Fe particles, formation of nonequilibrium local heating under magnetic field irradiation was confirmed. The increase in heating efficiency under electric field irradiation is thought to result from the weak magnetic field that intrudes around the point where the electric field intensity is strongest.

To obtain the dechlorination reaction, while controlling the microwave intensity and keeping the solution temperature at 190 ± 3 °C, a reactant was added after the solvent temperature reached 190 °C to avoid possible variations in reactivity because of different heating rates (Figure 3). Dechlorination of (2-chloroethyl)benzene progressed linearly, indicating a stable reaction rate. After 45 min of reaction, the conversion was 0.6% with mantle heater heating, 2.4% with electric field irradiation, and 5.3% with magnetic field irradiation. Ethylbenzene was detected as the main product, and its selectivity after 45 min was calculated to be 72%, 71%, and 69% with mantle heater heating, electric field irradiation, and magnetic field irradiation, respectively (Table 1). The similar conversions suggest that the reaction mechanism is the same for microwave heating and mantle heating. Conversely, the significant increase in the dechlorination conversion is the result of acceleration of the reaction by microwave heating, supporting the occurrence of nonequilibrium local heating.

The effect of differences in the reaction substrate was examined by changing the halogen groups. Regardless of the heating method, the reaction conversion rate exhibited an increasing trend as the halogen atom was changed from chlorine to bromine or iodine. In addition, the reaction rate was highest under magnetic field irradiation for all the reaction substrates. This was attributed to the predicted selective heating of iron particles by the microwave magnetic field, which caused a high temperature on their surfaces. Furthermore, for (2-chloroethyl)-benzene and (2-bromoethyl)benzene, the reaction was also accelerated under electric field irradiation. This is attributed to the effect of selective heating, i.e., heating of iron particles by the electric field and the weak magnetic field coexisting at the maximum point of the electric field.

Because of the low yield and linearity of the reaction regardless of the heating method, the reaction rate is proportional to the initial concentration. The reaction rate equation is, therefore, expressed as in eq 1.

$$v = k[\mathrm{Fe}]_0[\text{(2-iodoethyl)benzene}]_0 \qquad (1)$$

A kinetic analysis based on the Arrhenius plot was applied to (2-iodoethyl)benzene, which showed the highest reaction rate (Figure 4). Regardless of the heating method, the activation energy in the reaction was the same. Thus, the reaction mechanism did not change under different heating methods. The reaction under the magnetic field was accelerated because Fe particles were selectively heated, and their surface temperature exceeded the bulk temperature. Local thermal nonequilibrium showed a temperature difference of about 15 °C according to a calculation of the Arrhenius parameter. Previous work on cobalt particles showed a higher temperature difference; the

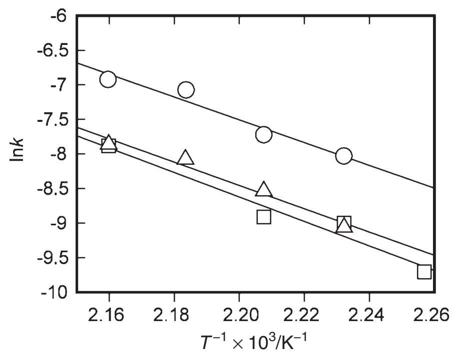

Figure 4. Arrhenius plots for the dehalogenation reaction of (2-iodoethyl)benzene by microwave heatings in magnetic (○) and electric field (△) and a mantle heatings (□).

reason for the difference was probably that Fe particles have a lower magnetic loss than cobalt particles.

In recent years, accelerated reactions have been attributed to sparks produced by microwave irradiation on the solid surface.[21–24] In this study, the effect of sparks was also examined by changing the particle size. Because it is known that sparks tend to occur as the particle size increases,[23] we conducted an experiment in which sparks were intentionally produced by increasing the iron particle size from 45 to 150 µm. An observation window located beside the waveguide was used. No sparks were observed when 45-µm iron particles were used, but sparks were seen every few seconds with 150-µm particles. In the conversion of (2-chloroethyl)benzene using 150-µm iron particles by mantle heating, little change occurred compared with that in conversion using 45-µm iron particles; however, irradiation of the 150-µm iron particles by microwave magnetic heating and microwave electric heating enhanced conversion by 7.7% and 8.3%, respectively. Sparks were often accompanied by a change of the morphology and surface appearance of the metal, resulting in the enhancement of the reactions.[21–24] Use of 150-µm iron particles also increased the ethylbenzene selectivity for microwave heating to 89% and 88%, respectively. The increase in the ethylbenzene selectivity compared with the results for small particles indicates that the reaction mechanism changed owing to spark production. Conversely, the ethylbenzene selectivity with 45-µm particles was the same for microwave heating and mantle heater heating. This can be understood as a result that little or no spark was produced therein.

Dehalogenation of (2-haloethyl)benzene using Fe particles was performed in the electric or magnetic field in a microwave single-mode cavity. The microwave magnetic field enhanced the dehalogenation; this result is attributed to the presence of local thermal nonequilibrium. The dehalogenation mechanism in microwave heating is comparable to that in conventional heating, whereas sparks generated by microwave irradiation of larger Fe particles produced a different reaction mechanism. The local thermal nonequilibrium produced by the microwave magnetic field accelerates the reaction at the liquid–solid interface.

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