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A Novel Dewar-Like Reactor for Maintaining Constant Heat and Enhancing Product Yields during Microwave-Assisted Organic Syntheses

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Abstract:

A novel microwave reaction vessel is herein proposed for maintaining constant heat during microwave-assisted organic syntheses. The structure of the vessel is Dewar-like in that it prevents conduction of microwave-generated heat in dielectric substrates into the surroundings. The potential of the double-walled vacuum-filled vessel has been examined for the absence of thermal gradients in aqueous media (homogeneous media) and in the synthesis of biphenyl in a nonpolar solvent (heterogeneous media) involving the Suzuki−Miyaura coupling reaction. The efficiency of the microwave-assisted organic synthesis was enhanced significantly (6- to 7-fold) with this double-walled vessel relative to the conventional single-walled reactor vessel currently used in commercial microwave chemical devices.

1. Introduction

Traditional chemistry has typically involved thermal energy to drive chemical reactions. In the 20th century, photochemical, catalytic, sonic, and high pressure techniques have been exploited to drive chemical reactions.[1] They have required the development of suitable reaction vessels in the advancement of these newer technologies. The first organic syntheses that used microwave radiation as the principal heating source were performed in the mid-1980s in a domestic microwave oven.[2] Since then, several commercial microwave devices have appeared[3] along with various specially designed photochemical/microwave reactors,[4] high-pressure/-temperature reactors,[5] large-scale flow reactors,[6] and continuous flow capillary reactors.[7]

It is now well-known that microwave-generated heating in microwave-assisted processes progresses outward from the center of the reactive vessel to the inner reactor walls, thereby creating temperature gradients that give rise to concentration gradients in substrates. Such thermal gradients result from thermophoretic migration, a process now referred to as the Ludwig−Soret effect.[8] As an example, preventing the inner walls of a microwave reactor from becoming soiled is normally achieved by placing a metallic thin film on the internal wall of the vessel in microwave-assisted synthesis of nanoparticles as the process begins at the center of the reaction vessel.[9] The latter synthesis provides a clear example of microwave-generated internal heating, unlike the case of conventional organic syntheses where initiation of the process within the reactor is rather unclear. Often temperatures measured at different positions within the reactor show variations as a result of thermal gradients generated in the reaction medium.[10] Such temperature variations may at times be due to the technique used in the measurements between the infrared method, which measures temperature at the inner wall of the reactor, and the fiber-optic thermometer often used to measure temperatures at the center of the solution or dispersion. The less expensive infrared thermometer is often provided in some commercial microwave chemical apparatuses because of cost considerations relative to a fiber-optic thermometer.

This article reports on a novel microwave reaction vessel which has been especially designed to insulate and thereby contain the microwave-generated heat from being transmitted to the surroundings during the organic syntheses. Normally, one makes use of heat insulating materials (e.g., fiberglass) wrapped around the external wall of a reactive vessel to prevent escape of heat to the surroundings. However, such materials will attenuate the microwave radiation reaching the reacting substrates in the vessel. The proposed reactor system consists of a double-walled glass vessel in which the double wall is vacuum-

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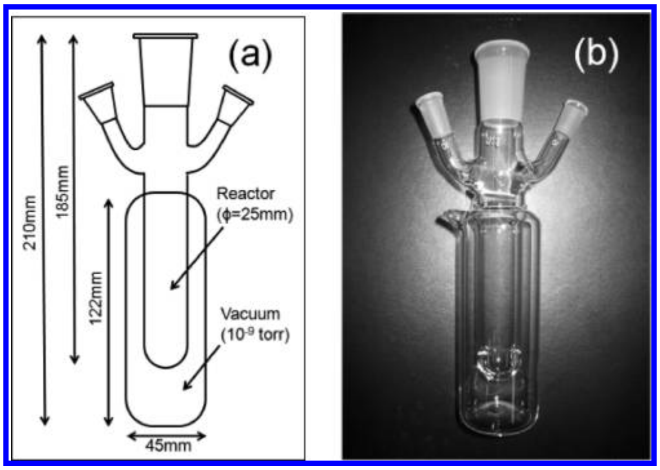

Figure 1. **(a) Sketched image and dimensions of the double-walled reactor; (b) photograph of the microwave Dewar-like vacuum vessel.**

filled that typifies a Dewar-like structure[11] used to preserve cold fluids, e.g. liquid helium. A somewhat similar reaction vessel (viz. a Dewar-ampoule device) was used by Villanueva et al.[12] to synthesize inorganic solid MPS_3 materials (M = Mn, Cd) for which the vessel consisted of a silica ampoule divided into a Dewar zone (*hot* zone) and a noninsulated part (*cold* zone) operated inside a conventional domestic microwave oven. The double-walled vacuum-filled structure of the reaction vessel ensures the containment and sustainment of microwave-generated heat during the syntheses. An attractive feature of this vessel is that it does not attenuate in any way the transmission of microwave radiation to the reacting substrates. The characteristics of this microwave reactor were examined by probing the temperature distribution in an aqueous medium (water; an example of a homogeneous system) and by carrying out the synthesis of biphenyl in toluene solvent as a model reaction of a heterogeneous system in the presence of Pd/activated carbon (Pd/AC) as the catalyst.

2. Experimental Section

2.1. The Proposed Reactor. The vacuum-filled Dewar-like double-walled microwave vessel is illustrated in Figure 1a. It consists of a Pyrex glass cylinder with a double-wall structure; the inner pressure in the vacuum-filled double wall is 10^{-9} torr (i.e., 133.3×10^{-9} Pa). The total capacity of the three-neck cylindrical vessel is 76.5 mL. An actual photograph of the microwave vessel is shown in Figure 1b. The attractive features of this microwave reactor are evidenced on comparison with a conventional single-walled microwave vessel having the same volume, shape, and size.

2.2. Preparation of the Pd/C Catalyst. An aqueous solution (50 mL) of acidified palladium(II) chloride ($PdCl_2$) (0.034 g) was added to a 50-mL aqueous dispersion of activated carbon (Wako Pure Chemical Industries, Ltd.; 1.0 g; mesh size, 0.74 mm) maintained under constant stirring. The pH of the dispersion was brought to pH 14 with an aqueous NaOH solution, after which an aqueous $NaBH_4$ solution (0.0363 g, 50 mL water) was added to the dispersion. The dispersion was stirred for 3 h and then heated at 60 °C for 2 h with continued stirring. Filtration of the dispersion gave solid particles of deposited palladium on activated carbon particles that were washed with ultra pure water, filtered, and then dried in air. The quantity of palladium on carbon was 1.5 wt % ascertained by atomic emission spectroscopy using the Shimadzu ICPE-9000 apparatus.

2.3. Synthesis of Biphenyl by the Suzuki−Miyaura Coupling Reaction. The synthesis of biphenyl by the Suzuki−Miyaura coupling reaction was carried out by a procedure reported by Guillén and co-workers.[13] Thus, the Pd/AC catalyst (0.15 g), phenylboronic acid (0.8 mmol; 0.0975 g), bromobenzene (0.6 mmol; 0.0942 g), K_2CO_3 as the base (1.2 mmol; 0.165 g), and toluene (5 mL) as the nonpolar solvent were mixed and subsequently added under an argon atmosphere to the double-walled microwave vessel and to the conventional single-walled microwave vessel. The syntheses were performed by placing the respective reactors in a commercial multimode microwave chemical apparatus (Tokyo Rikakikai Co. Ltd., MWO-1000S system) equipped with a fiber-optic thermometer (Anritsu Meter Co., Ltd., FL-2000). Unless noted otherwise, the microwave-applied power was kept constant at 80 W. The temperature−time profiles of the heterogeneous dispersion were determined by recording the temperatures at the center of the dispersions kept stirred with a magnetic stirrer during the microwave irradiation period. To determine the reaction yields of biphenyl by gas chromatographic analyses (Shimadzu model 2014 equipped with Ultra alloy-1 capillary columns) with a biphenyl standard (Wako Pure Chemical Industries, Ltd., 100% GC standard) eight dispersion samples were prepared: four for the Dewar-like reactor and four samples for the conventional single-walled reactor. The eight samples were then microwave-irradiated for the times reported in Figure 3. Thus, a total of eight experiments were carried out. The product yields were then assessed by filtration of a microwaved toluene dispersion (solution 1), followed by a further extraction with 5 mL of toluene of any biphenyl product that might have remained adsorbed on the Pd/C catalyst particles (solution 2). Solutions 1 and 2 were then mixed and subjected to GC analyses.

3. Results and Discussion

3.1. Temperature Distribution in the Homogeneous Aqueous Medium. The temperature distributions in the doubled-walled and in the conventional single-walled vessels were examined by recording the increase in the temperature of water (20 mL) at various times following continuous irradiation of the dielectric medium with 120-W microwaves in the commercial multimode microwave chemical apparatus (Tokyo Rikakikai Co. Ltd., MWO-1000S system) equipped with a fiber-optic thermometer (Anritsu Meter Co., Ltd., FL-2000). The

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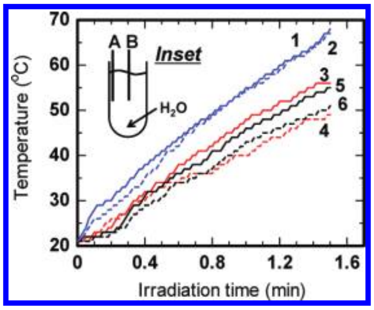

Figure 2. **Temperature−time profiles for water in the microwave Dewar-like vacuum vessel under nonstirring conditions (blue curves 1,2) and in the conventional microwave vessel also under nonstirring conditions (red curves 3,4) and under conditions where the aqueous medium was stirred (black curves 5,6). (Inset) Positions of temperature measurements in water ((A) inner wall positions - dashed curves 2,4,6; (B) center positions - solid curves 1,3,5).**

temperature−time profiles for water in the microwave Dewar-like double-walled reactor and in the conventional vessel are illustrated in Figure 2. The temperature of the water was measured at the center position B (solid curves 1,3,5; inset Figure 2) and at the inner wall side position A (dashed curves 2,4,6; inset Figure 2) of the vessels. The temperatures at the end of the 1.5-min microwave irradiation period between positions A and B in the microwave conventional vessel under nonstirring conditions varied by as much as 7 °C (i.e., 49 and 56 °C, respectively; curves 4 and 3), whereas in the Dewar-like reactor the temperatures were nearly identical (67 °C at position A and 68 °C at position B; curves 2 and1). The corresponding rates of increase of temperature in water for the conventional and Dewar-like reactors were, respectively, 18.7 ± 0.2 °C min^{-1} and 30.2 ± 0.3 °C min^{-1} (positions A), and 25.3 ± 0.3 °C min^{-1} and 28.8 ± 0.3 °C min^{-1} (positions B).

The extent of heat that escapes from the reactors will depend on the temperature difference between the atmosphere surrounding the reactor vessels and the heated water. Interestingly, when the aqueous medium was stirred with a magnetic stirrer, the temperatures between positions A and B in the microwave conventional vessel varied by as much as 4 °C at the end of the 1.5-min microwave irradiation period. Evidently, stirring narrowed the temperature gradient between the two positions in the aqueous medium, with the temperature at position A increasing and at position B decreasing. Under these conditions, the rates of temperature rise for the conventional reactor were 21.8 ± 0.2 °C min^{-1} (A; dashed curve 6) and 24.3 ± 0.2 °C min^{-1} (B; solid curve 5), indicating relatively little difference at the center position B but significantly different when determined at the inner wall position A in comparison with rates under nonstirring conditions.

Herrero and co-workers[10] have noted that uneven temperature distributions within a reactor are the result of uneven microwave heating. In the present instance, temperature fluctuations in the microwave conventional vessel showed a similar tendency. By contrast, the microwave Dewar-like, vacuum-filled, double-glassed vessel achieved uniform constant heating owing to the insulation provided by the double-walled structure. In summary, the attractive feature of the proposed microwave Dewar-like reaction vessel for a high dielectric medium such as water is not so much an improvement in heating efficiency as a sustained, constant, higher temperature throughout the whole medium.

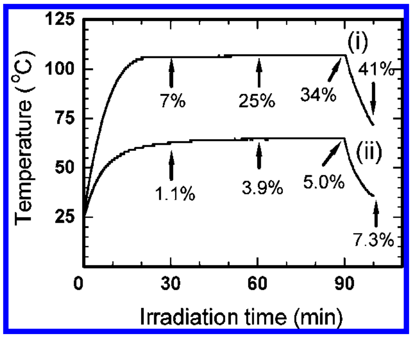

Figure 3. **Temperature−time profiles and percent reaction product yields of biphenyl at various times in (i) the microwave Dewar-like, vacuum-filled vessel and (ii) in the microwave conventional vessel; temperatures measured at the center position of the dispersion (see inset 1 of Figure 2).**

3.2. Temperature−Time Profiles in the Heterogeneous System and Product Yields. The temperature−time profiles and the reaction product yields in the synthesis of biphenyl carried out in the microwave Dewar-like vessel and in the microwave conventional vessel are reported in Figure 3. The initial rates of increase of temperature in the stirred dispersions were ∼8 °C min^{-1} for the double-walled reactor and ∼4.5 °C min^{-1} for the conventional single-walled vessel, i.e. a nearly 2-fold greater rate of increase of temperature with heat insulation provided by the vacuum double-walled design. Continued microwave irradiation beyond 10 min for both reactor vessels led the heterogeneous system to reach a temperature of 106−107 °C for the Dewar-like vessel, but only 63−65 °C for the conventional vessel. The main absorber of microwave radiation in this heterogeneous system was the activated carbon, which subsequently imparted most of its heat to the surrounding toluene solvent. For the single-walled conventional vessel, the heat was also dissipated into the surrounding atmosphere, contrary to the constant heat maintained within the double-walled glass reactor. At approximately 90 min into the reaction, microwave irradiation was terminated, resulting in a drop of temperature in both vessels.

The chemical yields of biphenyl from the Suzuki−Miyaura coupling reaction were 7% after a 30-min irradiation period, 25% after 60 min, and 34% after 90 min when using the microwave Dewar-like vacuum vessel. The corresponding chemical yields of biphenyl in the conventional vessel were 1.1% (30 min), 3.9% (60 min), and 5.0% (90 min) under otherwise identical irradiation conditions. The large difference in the reaction temperature between the Dewar-like vessel and the conventional vessel is no doubt the principal cause for the different yields. Even 10 min after the termination of the microwave irradiation the chemical yields continued to increase to 41% and 7.3%, respectively. Most importantly, the product yields increased by as much as a 6- to 7-fold margin when using the proposed double-walled reactor.

The heating efficiencies assessed at the center position of the medium in the microwave Dewar-like, vacuum-filled vessel and in the conventional vessel (see Figure 2) showed no variations in the case of water (homogeneous dielectric medium). However, significant differences in heating efficiency

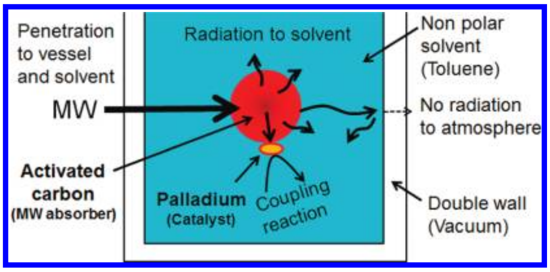

Figure 4. **Schematic image illustrating the propagation of microwave heating in a Pd/AC toluene dispersion in the microwave Dewar-like, vacuum vessel.**

(see Figure 3) were seen when the medium consisted of a microwave absorber (activated carbon) and a nonpolar solvent (toluene). The progress of microwave heating in the Pd/AC-toluene heterogeneous system is schematically illustrated in Figure 4. Toluene has a low dielectric loss factor ($\varepsilon'' = 0.07$) and consequently will absorb few 2.45-GHz microwaves, as evidenced in an exploratory experiment in which the temperature rise of the solution without the Pd/AC catalyst was ∼4 °C following a 10-min microwave irradiation period, whereas in the conventional reactor the rise in temperature was only 3 °C following this 10-min irradiation period. Accordingly, the microwave radiation is selectively absorbed by the Pd/AC particles, in accord with the study by McGill and Walkiewicz [**14**] who reported a high microwave heating rate in activated carbon (1283 °C min^{-1}). In our case, the heated activated carbon radiates some of its heat to activate the supported Pd catalyst, thereby allowing the Suzuki−Miyaura coupling reaction to take place. However, since the quantity of Pd catalyst deposited on the AC support was only 1.5 wt %, most of the heat of the activated carbon was absorbed by the cold toluene solvent. Therefore, it is imperative that the temperature of the toluene heated by the activated carbon be maintained relatively constant during the reaction. In the conventional single-walled reactor, the heat of the activated carbon will decrease rapidly if the temperature of the toluene solvent continuously decreases by conduction of heat through the single wall to the surrounding atmosphere. Keeping the temperature of the toluene constant, therefore, will maintain the temperature of the activated carbon, and in turn sustain the activity of the Pd catalyst.

4. Concluding Remarks

A novel Dewar-like, vacuum-filled, double-glassed reaction vessel has been described and proposed for potential use in carrying out organic syntheses in commercially available microwave chemical apparatuses. The absence of thermal gradients in this reactor vessel has been ascertained in homogeneous media using water with no attenuation of the microwave energy. The synthesis of biphenyl by the Suzuki−Miyaura coupling reaction in a toluene/Pd/AC heterogeneous system has evidenced some attractive features of the proposed reactor, namely higher reaction temperatures and greater reaction product yields *vis-à-vis* the conventional single-walled reactor currently in use in many of the commercial microwave chemical syntheses apparatuses.

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