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# Organic syntheses by microwave selective heating of novel metal/CMC catalysts – The Suzuki–Miyaura coupling reaction in toluene and the dehydrogenation of tetralin in solvent-free media

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#### 1. Introduction

#### ABSTRACT

The present study examines carbon microcoils (CMCs) as a novel support for Pt and Pd nanocatalysts and compares it with activated carbon nanoparticles as support for Pt and Pd metal deposits in two model microwave-assisted organic syntheses: (i) the Suzuki–Miyaura coupling reaction between phenylboronic acid and 1-bromo-4-methylbenzene in toluene solvent to produce 4-methyl-biphenyl and (ii) the dehydrogenation of tetralin (1,2,3,4-tetrahydronaphthalene) in solvent-free conditions. The microwave absorption capacity of the CMCs was more effective than the ACs support from the viewpoint of dielectric parameters (dielectric constant, dielectric loss, and loss tangent). Possible generation of microplasma (i.e., hot spots) on both supports that can impact on the progress of the reactions was monitored visually and photographed with a high-speed camera. Conventional heating (oil bath or heating mantles) of the Pd(Pt)/CMCs and Pd(Pt)/ACs system led to significantly lower product yields.

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Carbon microcoils (CMCs) present unique physical characteristics, electric properties, electromagnetic properties, chemical properties, and bio-activation properties as expected of innovative materials [1]. As such, CMCs are good candidates as absorbers of electromagnetic waves, as field emitters, as microsensors, as hydrogen storage materials, and as electrode materials, among others. CMCs look like microsized springs made of carbon that has attracted considerable attention in the stealth technology of the military establishment owing to its high absorption of radio-waves. Particularly significant, these carbon microcoils display a double 3D-helix chiral structure with a coil diameter typically 1–10-µm and a 0.1–10-mm coil length. CMCs can effectively absorb electromagnetic waves in the 2–18 GHz microwave regions [2].

Recent studies on heterogeneous metal catalyst reactions have shown that microwave radiation as the heating source is particularly advantageous in many processes [3]. Microwave heating utilizes the polarization ability of molecules to transform electromagnetic energy into thermal energy. As such, in a hetero-

\* Corresponding authors. E-mail addresses: horikosi@sophia.ac.jp (S. Horikoshi), nick.serpone@unipv.it, nickser@alcor.concordia.ca (N. Serpone). geneous catalyzed reaction system in a nonpolar solvent, it is possible to heat selectively only the catalysts by microwave irradiation [4]. Therefore, in the construct of the reaction system, the microwaves must interact solely with the solid catalyst, a feature that cannot be attained by existing conventional heating methods. To attain such a microwave/catalyst reaction system requires that the catalyst be supported on a material that is a strong absorber of microwave radiation. Activated carbon (AC) has proven in the past to be a good catalyst support and a useful microwave absorber.

In the present study, we examine the carbon microcoils as a microwave absorber and as a possible catalyst support. Features of the heat developed on microwave irradiation of CMCs are compared with those of the conventional activated carbon support. Palladium nanoparticles used as the metal catalysts were deposited on the CMC surface and used in the Suzuki–Miyaura coupling reaction as a model of an organic synthesis in toluene solvent; this solvent is a poor microwave absorber. As well, platinum nanoparticle deposits on the CMCs were examined in the dehydrogenation of tetralin as another model reaction and compared with the same deposits on activated carbon; tetralin is also a poor microwave absorber. Interestingly, in the hydrogen storage field, tetralin has been considered as a sort of cycloalkane material for hydrogen storage [5].



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#### 2. Experimental section

#### 2.1. Preparation of metal deposits on carbon microcoils

A sample of carbon microcoils was a gift from Dr. Motojima of the Toyota Physical and Chemical Research Institute. CMCs were prepared by a thermal chemical vapor deposition (CVD) method at a temperature of 770 °C using Ni powder as the catalyst placed on a graphite substrate setting within a horizontal quartz reaction tube into which a gas mixture consisting of  $C_2H_2$ ,  $H_2$ ,  $H_2S$ , and  $N_2$  was introduced that ultimately led to the growth of the carbon microcoils [6]. Granular activated carbon particles of ca. 0.95 mm in size were used for comparison with the CMCs. The particle size of the ACs was greater than the size of the CMCs (see Fig. 2 for the size of CMCs). BET measurements (Bel Japan, Micrometrics Tristar surface analyzer) revealed that the activated carbon sample had a specific surface area (ca. 1095 m<sup>2</sup> g<sup>-1</sup>) nearly fivefold greater than the surface area of the as-prepared CMCs (ca. 231 m<sup>2</sup> g<sup>-1</sup>).

In the case where the Pd/CMCs catalyst was used in the reactions, the surface of the CMCs (1 g) was washed in an aqueous  $HNO_3$  solution (10 M, 100 mL) with stirring for 3 h at an 80 °C temperature. Note that CMCs were synthesized using nickel as the catalyst, such that the initial CMCs contained 1.2% nickel that upon washing with the HNO<sub>3</sub> solution fell to 0.095% Ni content. The microcoils were subsequently washed further with ultrapure water and quantities of NaOH (2 M, 50 mL) for 24 h under room temperature conditions, after which the CMCs were washed once again with ultrapure water and dried for a few hours at 100 °C. The so-washed CMCs (1 g) were introduced into an aqueous PdCl<sub>2</sub>

a quartz cylindrical reactor (height, 24 mm; diameter, 16 mm). Since the dielectric loss factor of toluene ( $\varepsilon'' = 0.07$ ) is significantly smaller than that of pure distilled water ( $\varepsilon'' = 9.4$ ), so that by comparison, toluene solvent was not heated by the microwave radiation. Nonetheless, microwaving the toluene solution in the absence of the catalyst led to a 7 °C increase in temperature after 30 min of irradiation. Therefore, this reactive system can be taken as a solvent-free system from the viewpoint of absorption of microwave radiation. A condenser was connected to the microwave cylindrical reactor. Reaction yields of 4-methylbiphenyl (reaction (1)) were determined by gas chromatographic analyses (Shimadzu model 2014 equipped with Ultra alloy-1 capillary columns) from samples appropriately prepared from the various dispersions; a sample of 4-methylbiphenyl was used as the calibration standard (Wako Pure Chemical Industries, Ltd., 100% GC standard).

Tetralin dehydrogenation: The dehydrogenation of tetralin (1,2,3,4-tetrahydronaphthalene; reaction (2)) was carried out by a procedure similar to the one given earlier [8]. Accordingly, the Pt/CMCs powder (150 mg) and a pure tetralin sample (5 mL) were introduced, under an Ar atmosphere, into a quartz cylindrical reactor (height, 24 mm; diameter, 16 mm). Note that since the dielectric loss factor of tetralin ( $\varepsilon''$ ) is 0.12, it too is a poor microwave absorber when compared to water. Microwave irradiation of the tetralin system in the absence of the Pt/CMCs catalyst increased the temperature by only 33 °C after a 30-min period. The extent of tetralin conversion was also determined by gas chromatography using a Shimadzu Model 2014 Chromatograph equipped with a Zebron ZB-624 column.



(0.034 g) and HCl (1 M) solution (50 mL), following which the solution was brought to pH 14 by addition of NaOH. Subsequently, NaBH<sub>4</sub> (0.016 M) was added to the solution and stirred for 3 h; stirring was then continued for an additional 2 h at 60 °C. Finally, the colloidal Pd/CMC solids in the solution were filtered, washed with ultrapure water, and then dried at 100 °C overnight. In the preparation of Pt/CMCs, the aqueous 50 mL solution contained H<sub>2</sub>PtCl<sub>6</sub>·H<sub>2</sub>O. The quantity of Pd deposited on the CMC and on the AC was ca. 0.7 and 1.5 wt.%, respectively, ascertained by atomic emission spectroscopy using the Shimadzu ICPE-9000 apparatus.

#### 2.2. Chemical model reactions and microwave apparatus

#### 2.2.1. Suzuki-Miyaura coupling reaction

The synthesis of 4-methylbiphenyl by the Suzuki–Miyaura coupling reaction was carried out by a procedure similar to the one given earlier [7]. The Pd/CMCs and Pd/ACs catalyst (150 mg), phenylboronic acid (0.80 mmol; 0.0975 g), 1-bromo-4-methylbenzene (0.60 mmol; 0.1026 g),  $K_2CO_3$  as the base (1.2 mmol; 0.165 g), and the nonpolar toluene solvent (5 mL) were mixed and subsequently added under an Ar atmosphere to



**Fig. 1.** Details of the experimental setup and position of the reaction samples in the single-mode microwave resonator. Sample set at the maximal *E* field position.



Fig. 2. (a) Low-resolution SEM image of Pt/CMCs (Hitachi scanning electron microscope S-3400N) and (b) TEM image of Pt deposits on CMCs at greater resolution (Hitachi Transmission Electron Microscope, Model U-3310).

#### 2.2.2. Microwave apparatus setup

The continuous microwave irradiation setup operated in the single-mode cavity  $TE_{103}$  (transverse electric 103 mode) is schematically illustrated in Fig. 1. Note that a TE mode is a mode whose electric field vector is normal to the direction of propagation, that is, no electric field in the direction of propagation (for further information see http://en.wikipedia.org/wiki/Transverse\_mode).

The resonance of the microwaves was adjusted with the iris and the plunger at 1.5 cycles ( $TE_{103}$ ). Both reactions were performed by placing the respective quartz cylindrical reactor in the single-mode resonance microwave apparatus of Fig. 1 at positions of maximal electric field density (*E* field) within the waveguide, namely at 11.04 cm from the iris [9]. The exact position of the electric field maximum in the waveguide was ascertained by an electric field monitor. The wavelength of propagation of the microwaves in the  $TE_{103}$  mode within the waveguide was estimated from Eq. (3) as being 14.78 cm [9]:

$$\lambda = \frac{\lambda_0}{\sqrt{1 - (\lambda_0/2b)^2}} \tag{3}$$

where  $\lambda$  is the wavelength in the waveguide;  $\lambda_o$  (2.45 GHz) = 12.24 cm is the wavelength in vacuum given by c/f (c being the speed of light, 2.9979 × 10<sup>10</sup> cm s<sup>-1</sup>, and f being the microwave frequency 2.45 × 10<sup>9</sup> s<sup>-1</sup>, i.e., 2.45 GHz); and b is the height of the waveguide, 10.92 cm. The maximal position of the E field from the iris was at 3/4 the wavelength of the standing wave in the waveguide, namely at 11.09 cm [9].

Unless noted otherwise, continuous microwave radiation irradiated the sample in a setup that employed a short plunger, an iris, a three-stub tuner, a power monitor, and an isolator. Microwaves were generated from a 2.45-GHz microwave semiconductor generator equipped with a metal-oxide semiconductor field-effect transistor (MOSFET; Fuji Electronic Industrial Co. Ltd.; GNU-201AA; maximal power, 200 W). For the conventional magnetron generator, the frequency of the microwaves was distributed in a broad range (e.g., between 2.39 and 2.52 GHz) [7]. The microwave input power distribution is reflected in the widely dispersed frequency distribution. Thus, the actual power output of the 2.45-GHz microwaves from the magnetron generator was smaller than the input power. By contrast, the semiconductor generator produced microwaves within a very narrow frequency distribution centered at 2.45000 ± 0.00250 GHz [7]. In the latter case, the microwaves can resonate in single-mode apparatuses because the microwave power is concentrated within this narrow 2.45000 GHz frequency. Heating the reaction samples with a microwave semiconductor generator is more effective than with a magnetron generator, under identical microwave output conditions. The microwave input power was fixed at 50 W for the conditions of the data reported in Fig. 3, 70 W for Fig. 4, and 80 W for Fig. 5. The temperature of the heterogeneous sample solution was measured with an optical fiber thermometer (FL-2000, Anritsu Meter Co. Ltd.). The frequency distribution of the irradiating microwaves was assessed with an Agilent Technologies N9010A EXA signal analyzer.



**Fig. 3.** Temperature–time profiles in the heating microwave heating of a toluene solution (5 mL) containing dispersed Pd/CMCs and Pd/ACs (150 mg; 0.6 mm and 0.95 mm diameter) under continuous microwave irradiation at a 50-W microwave input power.



**Fig. 4.** Product yields of 4-methylbiphenyl (MB) at 110 °C in toluene solvent under microwaves heating (MW) and conventional oil bath heating (CH). Closed circle, Pd/ CMC-MW; open circle, Pd/CMC-CH; solid triangle, Pd/AC-MW; open triangle, Pd/ AC-CH.



**Fig. 5.** High-speed camera photographs of the electrical arc discharge occurring on the Pd/AC catalyst surface during the Suzuki–Miyaura coupling reaction under microwave irradiation.

#### 3. Results and discussion

#### 3.1. Morphology of metal deposits on the CMCs

An SEM image of the carbon microcoils with the Pt deposits (Pt/ CMCs) is shown in Fig. 2a. The morphology of the CMCs has both helical and twisted forms with small and large coil pitch in accord with earlier reported SEMs [2]. Some broken-up CMCs were also contained in the sample. A TEM image of the tip of Pt/CMCs is reported in Fig. 2b, which shows the Pt nanoparticles nicely dispersed about the CMC surface. Close examination of (on average) 50 such Pt nanodeposits in the TEM images indicated an average particle size of ca. 3 nm. In some cases, we also observed larger aggregated Pt nanoparticles. In the case of Pd/CMC systems, TEM observations also showed that Pd/CMC is in the same state as Pt/ CMC, that is, adsorbed state and particle size. The highly dispersed Pt nanoparticles (ca. 4 nm) on the activated carbon support were also examined by TEM microscopy.

## 3.2. Microwave selective heating of dispersed CMCs in nonpolar solvent

Microwave heating processes of substances can be classified as dielectric loss heating, conductive loss heating, and magnetic loss heating for a magnetic molecule [10]. On absorption of microwave radiation by polar molecules, the electric field component (E) of the microwaves causes the permanent and induced dipoles to rotate as they align themselves with the alternating E field. The resulting molecular motion of the molecules has, in effect, converted microwave energy into heat through dipolar polarization. By contrast, charged particles in dielectric solids free to move within a delimited region of the solid, for example,  $\pi$ -electrons as found in carbonaceous materials, induce a current that travels in phase with the microwaves' E field [12,13]. Along similar lines, Ohgushi and coworkers have investigated microwave heating of three different zeolites-A containing Na<sup>+</sup>, K<sup>+</sup>, and Na<sup>+</sup>/Ca<sup>2+</sup> cations and found that the zeolite-A with the lower activation energy of cation movement (i.e., the more mobile cations) was more easily heated by microwave radiation [11].

In carbonaceous materials, the electrons do not couple with the phase changes of the *E* field, so that the microwave energy is dissipated into heat through the Maxwell–Wagner effect. In some cases, free-to-move electrons on the surface of carbon materials receive enough kinetic energy that they induce a current flow through normally nonconductive media such as air causing an electrical breakdown observed as a plasma discharge (arcing) [14].

In the model reactions examined in this study, both the toluene solvent and tetralin are poor microwave absorber such that they are not heated by the microwaves. As a result, the heating of the reaction systems must be left to the capacity of microwave heating of the CMCs and AC catalyst supports. In this regard, a heating profile of dispersed CMCs and ACs in pure toluene solvent was assessed under microwave irradiation; the microwave input power was 50 W of continuous irradiation. We hasten to note, and we confirmed that the heating rate of pure AC was unaltered in the presence of metal deposits on the AC surface. Powder-activated carbon particles with size less than 0.6 mm were also used for comparison to assess the particle size effect.

The CMCs were promptly heated at a rate of  $0.43 \circ C s^{-1}$  or about 30% greater than the heating rate  $(0.33 \circ C s^{-1})$  of AC particles whose size was ca. 0.95 mm, which in turn was 50% greater than the heating rate  $(0.22 \circ C s^{-1})$  of the 0.6-mm AC particles (see Fig. 3). Thus, the microwave heating of CMCs was more efficient than of the ACs. Hence, the smaller the particle size of the ACs is, the slower is the microwave heating rate. However, although the carbon microcoils are smaller than the activated carbon particles (Fig. 2), the heating efficiency was nevertheless higher than for the ACs. That is, conduction loss heating of the coil structure of the CMCs is remarkably greater than that of AC particles. It is known that electrical resistance is generated by the coil structure under an alternating current [15]. Accordingly, since the frequency of the microwave radiation (*f*) is remarkably high (2.45 GHz), the ensuing electric current (*I*) is relatively small:

$$I = \frac{V}{2\pi f L} \tag{4}$$

where *V* is the voltage (the electric field) and *L* is the inductance.

The dielectric constants  $(\varepsilon'_r)$  and dielectric loss factors  $(\varepsilon''_r)$  of naked CMCs and ACs were measured by the resonant-cavity method; results are summarized in Table 1. The loss tangent  $(\tan \delta)$  was calculated by the ratio of dielectric loss  $(\varepsilon_r'')$  to dielectric constant  $(\varepsilon_r)$ . The dielectric constant of the carbon microcoils was 1.5-fold greater than for the activated carbon particles, while the dielectric loss of the CMCs was ca. 1.5-fold greater than that of the ACs. This brought the loss tangent of CMCs to be 3.0-fold greater than for ACs. Clearly, from the viewpoint of dielectric parameters, the CMCs should prove far better catalyst supports for the microwave-assisted catalyzed organic syntheses. Note that even if the metal catalysts were deposited on CMCs and ACs supports, the difference in the dielectric parameters was less than 5%, nearly the error in measuring the dielectric parameters of CMC and AC. No enhancement of the heating efficiency occurred by the presence of a metal catalyst on the supports.

The characteristics of CMCs as catalyst supports in the organic synthesis were evaluated by examining the Suzuki–Miyaura coupling reaction. After microwave irradiation of the reactants for 150 min, the chemical yield of the 4-methylbiphenyl (4-MB) product using the Pd/CMCs catalysts was 1.7-fold greater than with the Pd/ACs catalysts. For the case of Pd/CMCs, the solution temperature reached the boiling point (110 °C) of toluene in about 2.5 min; it took 4.8 min to reach the boiling point of toluene in the case of Pd/ACs. No correlation exists between the heating rates and the

#### Table 1

Dielectric constants ( $\varepsilon'$ ), dielectric loss ( $\varepsilon''$ ), and loss tangent ( $\varepsilon''_r/\varepsilon'_r = \tan \delta$ ) of carbon microcoils (CMCs) and activated carbon particles (ACs) at a microwave frequency of 2.45 GHz.

Support	Dielectric constant $(\mathcal{E}'_r)$	Dielectric loss $(\varepsilon_r'')$	Loss tangent $(\tan \delta)$
Carbon microcoil (CMC)	53	107	2.0
Activated carbon (AC)	35	36	1.1

product yields. Heating the reaction mixture by the conventional method of an oil bath (CH), the chemical yield of 4-MB with Pd/ ACs was 1.2-fold higher compared to the Pd/CMCs (Fig. 4). Evidently, no selective heating of the catalysts occurred by the CH method. Therefore, we ascribe the greater yield of the product with the Pd/ACs relative to Pd/CMCs from conventional heating to the larger surface area of the AC support.

An interesting contradiction to expectations is worth noting in Fig. 4, as we expected the ACs support to be more effective than the CMCs support under otherwise identical temperature conditions by microwave irradiation of Pd/CMCs catalyst and Pd/ACs catalyst. As the Fig. 4 emphasizes, the Pd/CMCs catalyst was far more effective. In an earlier study [7], we observed formation of hot spots (i.e., arcing or so-called microplasma) on the Pd/ACs surface for the Suzuki-Miyaura coupling reaction in the toluene solvent under high microwave electric field conditions. Related to these observations. Menéndez and coworkers [14] identified two different types of microplasmas formed on microwave heating of activated carbon: ball lightning plasma and arc discharge plasma. Apparently, ball lightning plasmas were more abundant initially when the temperature of the carbon bed was still relatively low (<400 °C), whereas arc discharge plasmas were seen at higher temperatures (400–700 °C) in accord with our observations [7].

The high-temperature hot spots had a deleterious effect on the product yields from the Suzuki-Miyaura coupling reaction as they caused the metal catalyst Pd on the ACs support to aggregate and reduce reaction efficiency [7]. In the current study, generation of hot spots was confirmed through photographs taken with a highspeed camera for the Pd/ACs system (see Fig. 5). By contrast, no arc discharge plasma was observed for the Pd/CMCs system. It is plausible that the smaller electrical conductivity of the CMCs (6.4-fold smaller) relative to the ACs (see Table 1) controls the generation of such microplasma. Another factor that could impact formation of the plasmas is the helical structure of the CMCs that may be unsuitable in forming the hot spots. The dielectric polarization induced by the microwaves' E field on the CMCs with low electrical conductivity is smaller than that of the ACs and thus moderates the electric discharge. Additionally, the generation of hot spots on the Pd/AC catalyst can cause the aggregation of the metal catalyst on the support (Fig. 5), so that hot spots can have a negative influence on the progress of the reaction [7].

The temporal course of the dehydrogenation of tetralin using Pt/CMCs and Pt/ACs catalysts is shown in Fig. 6. After 90 min of microwave irradiation, the conversion yield in the presence of Pt/CMCs was 50% greater than the yield with Pt/ACs. In this case also,



**Fig. 6.** Temporal course of the dehydrogenation of tetralin in the presence Pt/CMCs and Pt/ACs catalysts subjected to microwave dielectric heating (MW) and conventional mantle heating (CH) at a temperature of 207 °C (closed circles, Pt/CMC-MW; open circles, Pt/CMC-CH; solid triangles, Pt/AC-MW; open triangles, Pt/AC-CH).

hot spots were seen on the Pt/AC surface. Once again, no hot spot formed when using the Pt/CMCs system, at least none were observed. However, in spite of the formation of the microplasma and plausible aggregation of the Pt on the ACs support, the extent of dehydrogenation of tetralin with Pt/AC under microwave irradiation is relatively significant (ca. 16%) but lower than with Pt/CMCs (ca. 25%). Under conventional heating, the yields were significantly lower, respectively, 3% and 5%. As the reaction temperature of the tetralin dehydrogenation was considerably higher (boiling point, 207 °C) than that of the Suzuki-Miyaura coupling reaction (bp. of toluene, 110 °C), the high-temperature microplasma generated on the ACs surface likely aided in the heating of the tetralin. In the dehydrogenation of tetralin with Pt/CMC, ca. 98% of the reaction products were composed of hydrogen and naphthalene (reaction (2)) with the remaining 1–2% consisting of hydrocarbon impurities (substrates), whereas using the conventional heating mantle method to drive the reaction, the amount of hydrocarbon substrates was ca. 2%. No doubt generation of hot spots contributed to formation of impurities; however, the increase was negligible under our conditions. The amount of hydrocarbon impurities increased somewhat to ca. 5% when using the Pt/AC catalyst.

#### 4. Conclusions

The present study has demonstrated that carbon microcoils (CMCs) are indeed effective catalyst supports in microwave organic chemistry, despite the fact that the available surface area is significantly less than the activated carbon particles. In revenge, however, the carbon microcoils proved to be better microwave absorbers than the ACs and thus optimal for the selective heating of the metal catalysts. In addition, somehow the CMCs were able to prevent generation of the microplasmas that have proven to impact negatively on reaction yields [7]. Recent years have witnessed fabrication of equipment for the continuous synthesis of CMC in industry. Production of CMCs continues to improve every year. If CMCs were to attract attention as a catalyst support in chemical syntheses, no doubt the manufacturing technique would see further improvement.

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