

# **An Effect of Microwave Irradiation on Pd/SiC Catalyst for Prolonging the Catalytic Life**

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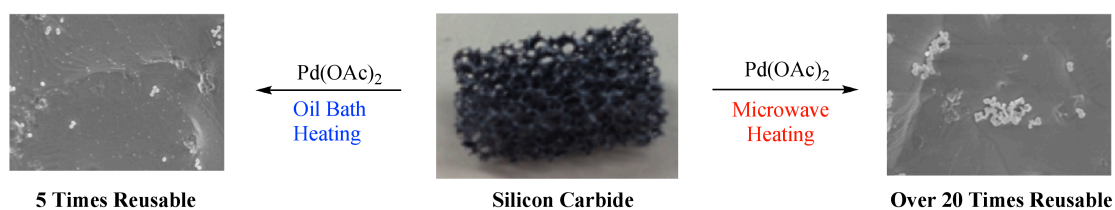
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**Running title:** An Effect of Microwave on Pd/SiC Catalyst

**Abstract:** Novel solid-supported catalysts derived from palladium supported on silicon carbide were prepared. The resulting catalysts produced high methyl cinnamate yields (>80%) for more than 20 cycles of the Heck reaction of iodobenzene and methyl acrylate. The use of microwave heating during catalyst preparation was found to significantly improve the catalytic activity compared with conventional heating. This result is interpreted as being due to an accelerated decomposition of the palladium species resulting in improved palladium-nanoparticle dispersion under microwave heating.

### Graphical Abstract

Novel SiC-supported palladium catalysts were prepared, which can be used repeatedly for the Heck reaction over 20 times. The microwave heating during catalyst preparation significantly improved the catalytic activity.



**Keywords:**

C-C Bond Formation

Heck Reaction

Iodobenzene

Nanodispersion

Nanoparticle

Palladium

Reusable Catalyst

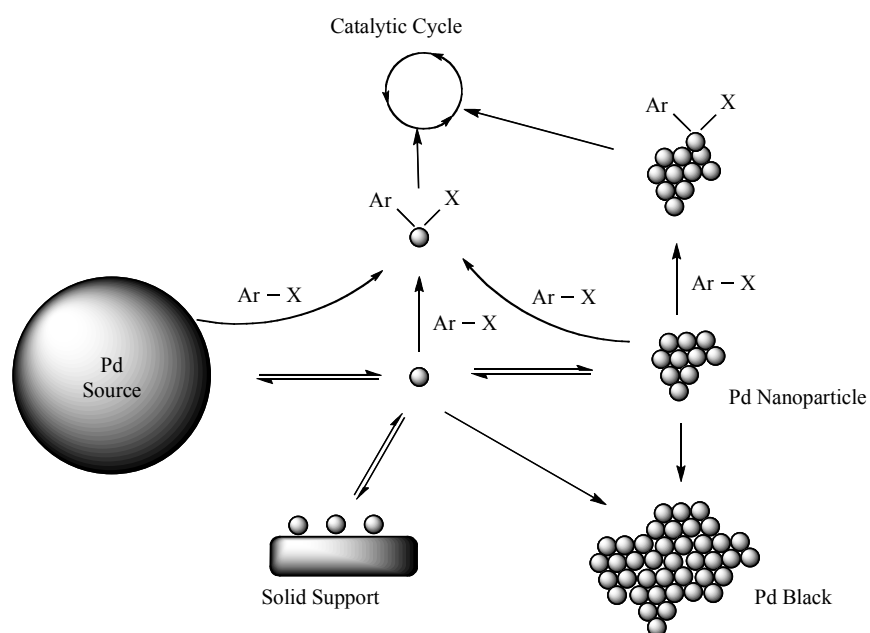
Silicon Carbide

Solid-Supported Catalyst

Suzuki Reaction

## **Introduction**

Solid-supported catalysts play an important role in industrial chemistry because they facilitate the separation of catalysts and products in a reaction mixture [1–4]. Solid-supported palladium catalysts are mainly used for hydrogenation and C-C bond coupling reactions such as the Heck reaction of aryl halides. In the latter case, they do not, however, serve as heterogeneous catalysts as illustrated in Scheme 1 [5–13]. Instead, the aryl halide undergoes oxidative addition to palladium nanoparticles forming a solution-soluble organopalladium particle, which is the actual active species. This particle serves as a homogeneous catalyst until the aryl halide is fully consumed. After which, the particle becomes unstable and aggregates to form catalytically inactive palladium black. Another path in which the floating particles redeposit either on the reaction vessel wall or on the solid-support allows the catalyst to be reused in the subsequent catalytic reaction cycles. In other words, the solid-support should not only adsorb metal species onto its surface but also release them gradually into the reaction solution. In this context, development of a new solid-support satisfying these conflicting properties remains challenging.



**Scheme 1.** Behavior of the palladium species in the catalytic reaction using aryl halide.

From an environmental viewpoint, increasing the reusability of the catalyst, and, therefore, considerably decreasing noble metal consumption, is important. Because commonly used solid-supported catalysts are usually in the powder form, filtration is necessary for their recovery from the reaction mixture. Using a bulk solid-support would omit this process, and be advantageous with regard to their practical use.

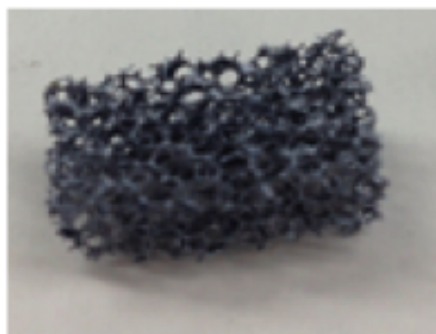
In the present work, we studied the development of a palladium catalyst supported on silicon carbide (SiC). Because of its high rigidity and thermal stability, SiC is a widely used structural material and abrasive [14–16]. Recently, SiC has been used for manufacturing semiconductors [17, 18], light emitting diodes [19, 20], engineering ceramic [21], jewelry [22], and so on. In addition, SiC is chemically inert, has high thermal conductivity, and strongly absorbs microwave energy [23], which is of

particular interest to this study. Indeed, a SiC microwave heating vessel is commercially available [24]. Our study on Pd/SiC catalysts, showed that catalyst reusability was significantly increased when microwave heating was used for catalyst preparation. This is described in detail in the following sections.

## **Materials and Methods**

### **General**

The  $^1\text{H}$  NMR spectra were measured on a Bruker Ascend-400 at 400 MHz with TMS as an internal standard. Scanning Electron Microscope observation was performed using Hitachi SEM S-3000N. Microwave heating was performed using Anton-Paar Microwave 300 (850 W, 2455 MHz) using a 10 mL glass vessel. All the reagents and solvents were commercially available and were used as received. SiC was provided and cut to a small piece (15 mm  $\times$  10 mm  $\times$  5 mm, Figure 1) by NIPPON PILLAR PACKING CO., LTD.



**Figure 1.** Silicon carbide used as a solid-support.

### **Preparation of the Pd/SiC Catalyst (Catalyst OB) Using Conventional Heating**

In a screw-capped test tube, SiC was put in a solution of palladium acetate (1 mg, 4  $\mu$ mol) in acetonitrile (3 mL). After sealing, the resultant mixture was heated at 100 °C for 10 h on an oil bath. The SiC was taken out from the solution, and washed with acetonitrile (3 mL  $\times$  5) to afford catalyst **OB10**. Catalyst **OB3** was also prepared in the same way.

### **Preparation of the Pd/SiC Catalyst (Catalyst MW)**

In a screw-capped test tube, SiC was put in a solution of palladium acetate (1 mg, 4  $\mu$ mol) in acetonitrile (3 mL). After sealing, the resultant mixture was heated at 100 °C for 3 h by microwave heating. The SiC was taken out from the solution, and washed with acetonitrile (3 mL  $\times$  5) to afford catalyst **MW3**. Catalyst **MW1** was also prepared in the same way.

### **Heck Reaction**

In a screw-capped test tube, to a solution of iodobenzene (23  $\mu$ L, 0.2 mmol), methyl acrylate (23  $\mu$ L, 0.25 mmol) and triethylamine (35  $\mu$ L, 0.25 mmol) in acetonitrile (3 mL), catalyst **OB** (or **MW**) was added. After sealing, the resultant mixture was heated at 120 °C for 6 h using an oil bath (or microwave). After evaporation, the residue was dissolved in deuterated chloroform, and the yield of methyl cinnamate was estimated by  $^1\text{H}$  NMR, in which the integral value was compared with that of an internal standard, 1,1,2,2-tetrachloroethane. The recovered Pd/SiC catalyst was used for the next reaction

without any special treatment.

When other substrate was used, the experiment was conducted in a same way.

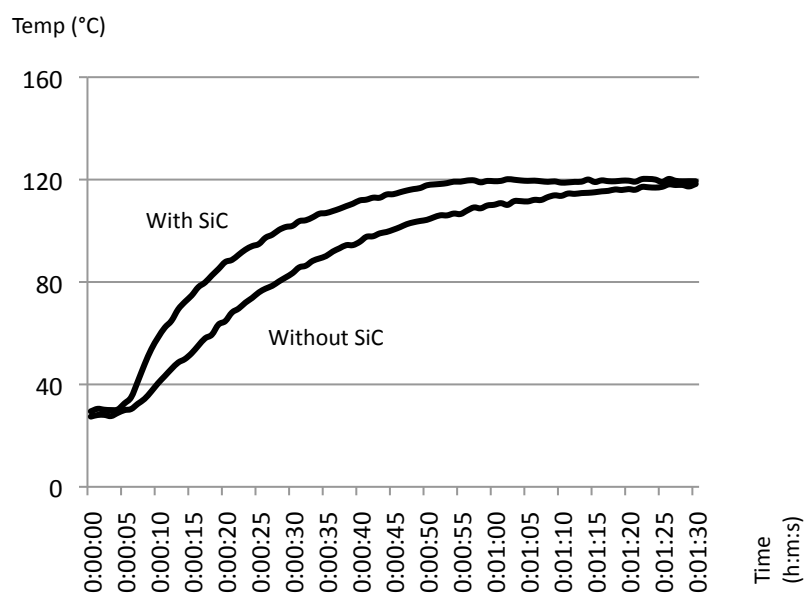
### **Suzuki Reaction**

In a screw-capped test tube, potassium carbonate (70 mg, 0.5 mmol) and 4-methylphenylboronic acid (60 mg, 0.44 mmol) were dissolved in a mixed solvent of acetonitrile (3 mL) and water (1 mL). To the solution, catalyst **MW3** was added. After addition of iodobenzene (46  $\mu$ L, 0.4 mmol) and sealing, the resultant mixture was heated at 80 °C for 2 h using an oil bath. The reaction mixture was poured into water (50 mL), and extracted with dichloromethane (20 mL  $\times$  3). The organic layer was dried over magnesium sulfate. After evaporation, the residue was dissolved in deuterated chloroform, and the yield of methyl cinnamate was estimated by  $^1\text{H}$  NMR, in which the integral value was compared with that of an internal standard, 1,1,2,2-tetrachloroethane.



## Results and Discussion

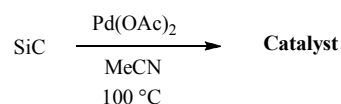
At first, the assisting effect of SiC for microwave heating was studied. When only acetonitrile was heated by microwave in the absence of SiC, 1.5 minutes were necessary until the temperature inside the vessel reached to 120 °C. To the contrary, the temperature reached to the same value within 1 minute in the case of heating with SiC (Figure 2). These results indicated that SiC assisted to elevate the temperature enough even though it had a meshwork structure as shown in Figure 1.



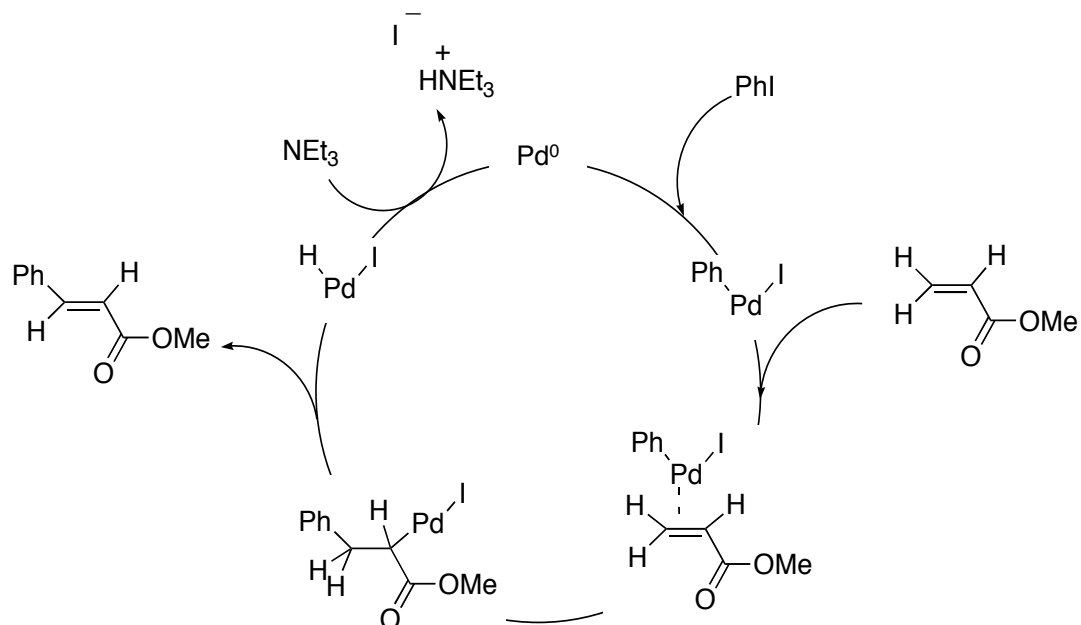
**Figure 2.** Temperature ramp for microwave heating acetonitrile with/without a SiC piece.

Palladium species were adsorbed onto SiC by two different heating methods (conventional heating and microwave heating) from a solution of palladium acetate in acetonitrile, affording four different catalysts (catalyst **OB3** and **OB10**, catalyst **MW1** and **MW3**) that use different heating methods (Table 1). Catalysts prepared using conventional heating on an oil bath and microwave heating were labeled **OB** and **MW**, respectively. The resulting catalysts were subjected to the Heck reaction of iodobenzene and methyl acrylate affording methyl cinnamate (Scheme 2). As shown in Scheme 1, since the palladium particles redeposit not only on the support but also on the reaction vessel wall, the amounts of palladium species on the support gradually decreases during the repeated use of the catalyst, which results in the loss of the catalytic activity. Thus, the catalytic activity was evaluated by determining the number of the catalytic reaction cycles, affording over 80% methyl cinnamate yields. The results for the commercially available catalysts are shown in Table 2, and those for catalysts **OB** and **MW** are shown in Table 3.

**Table 1.** Preparation of catalysts **OB** and **MW** series.

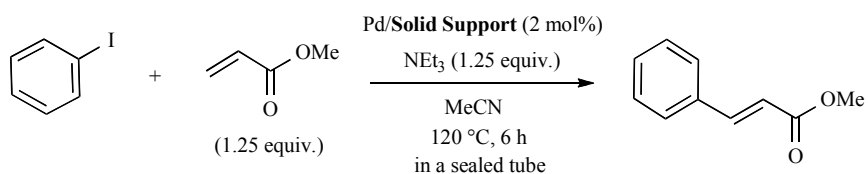


Heating Method	Time / h	Catalyst
Oil Bath	3	<b>OB3</b>
Oil Bath	10	<b>OB10</b>
Microwave	1	<b>MW1</b>
Microwave	3	<b>MW3</b>

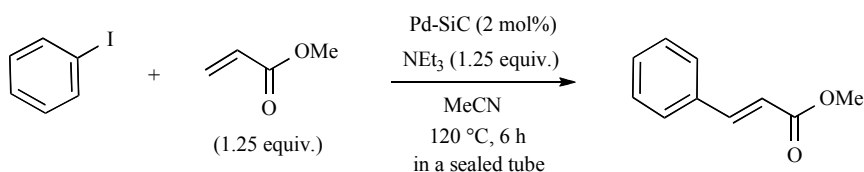


**Scheme 2.** A mechanism of the Heck reaction using iodobenzene with methyl acrylate.

**Table 2.** Reusability of the commercially available Pd/Solid support catalysts for the Heck reaction.



Solid-Support	Yield/%							Average
	1	2	3	4	5	6	7	
Carbon	96	54	33					61
Alumina	99	96	85	95	47	27		75
Barium Sulfate	94	79	76					83
Hydrotalcite	67	13						40
Urea Resin	100	81	82	64	33			72
Fibroin	89	89	80	93	81	78	70	83

**Table 3.** Reusability of the Pd/SiC catalysts for the Heck reaction.

Run	Catalyst	Method <sup>a</sup>	Yield/%										Average
			1	2	3	4	5	6	7	8	9	10	
			11	12	13	14	15	16	17	18	19	20	
1	<b>OB3</b>	A	100	75	67								81
2	<b>OB10</b>	A	100	100	97	88	88	68	44				84
3	<b>MW1</b>	A	100	99	97	100	75	67					90
4	<b>MW3</b>	A	95	91	86	99	100	100	96	80	98	100	
			88	93	92	90	100	80	95	89	90	98	93
5	<b>MW3</b>	B	100	99	89	65	72						85

<sup>a</sup> The reaction mixture was heated by two methods: Method A; by oil bath, Method B; by microwave.

The most commonly used catalyst, Pd/carbon, was only usable for one Heck reaction cycle under the employed conditions. Pd/alumina exhibited higher catalytic activity, affording methyl cinnamate yields in over 80% yields over four reaction cycles. On the other hand, barium sulfate and hydrotalcite were found to be unsuitable solid-supports for the present Heck reaction. In the case of polymer supports, urea resin and fibroin, it was possible to reuse the catalysts three or five times; however, damage to the support was observed after the reaction.

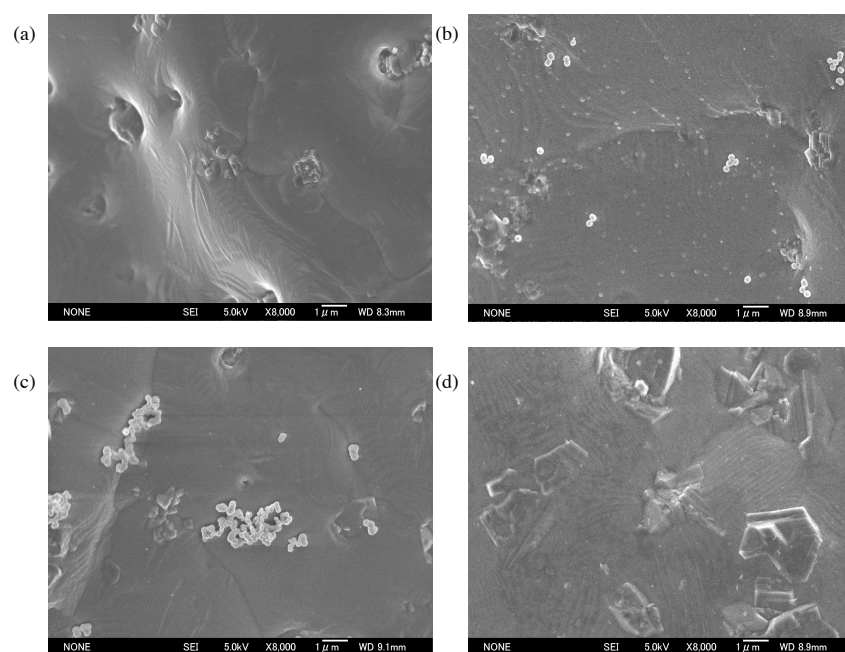
To the contrary, Pd/SiC catalysts exhibited a higher catalytic activity than the commercially available catalysts. Regarding the catalysts prepared by conventional heating methods, although a high methyl cinnamate yield was only obtained during the

first cycle on catalyst **OB3** (Table 3, run 1), increasing the heating time during catalyst preparation affected the catalytic activity and catalyst **OB10** was reusable five times affording methyl cinnamate in an average yield of 84% (Table 3, run 2). Microwave heating was found to be considerably effective in further improving the catalytic activity. Catalyst **MW1** was reusable four times with a 90% average yield (Table 3, run 3). To our great surprise, catalyst **MW3** exhibited a high catalytic activity even after 20 reaction cycles (Table 3, run 4). However, the use of microwave heating, as opposed to conventional oil bath heating, during the Heck reaction decreased the catalyst reusability (Table 3, run 5).

The significant difference in the catalytic activity of catalysts **OB10** and **MW3** was probably caused by differences in the surfaces of these catalysts, as observed by SEM (Figure 3). Figure **3a** shows the SiC-support surface. After the adsorption of the palladium species, palladium nanoparticles were observed on SiC surfaces heated by both the methods, as shown in Figures **3b** and **3c**. Compared with conventional heating (catalyst **OB10**, Figure **3b**), microwave heating assisted the adsorption of larger amounts of palladium nanoparticles (catalyst **MW3**, Figure **3c**). This is proposed to be the reason for the longer-life catalytic activity of the microwave-heated catalysts. On the other hand, nanoparticles were no longer observed on the SiC surface of catalyst **OB10** after the Heck reaction. This implies that the solid-support serves as a releaser of palladium species.

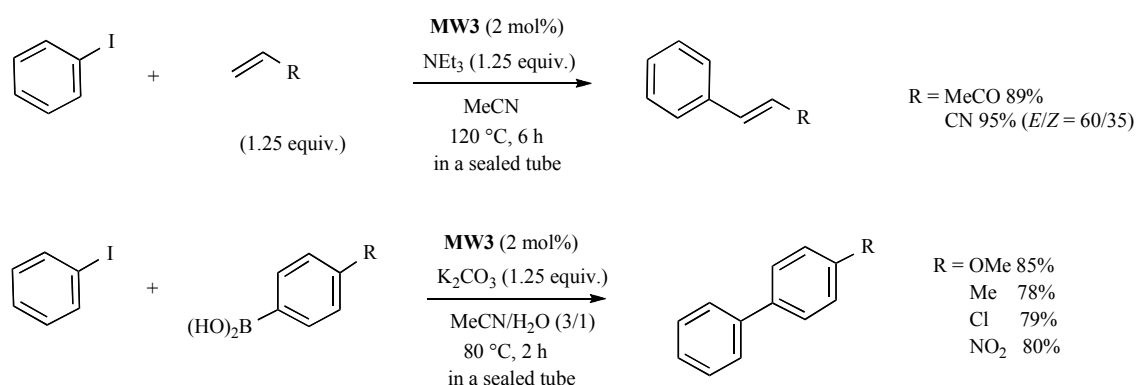
Catalyst preparation begins with the adsorption of palladium acetate onto the SiC surface. Upon heating, thermal decomposition of palladium acetate proceeds to form

palladium nanoparticles, during which the acetate ion presumably serves as a reductant [25]. When microwave heating was used, the surface temperature increased quickly causing rapid decomposition of palladium acetate. As a result, nanoparticles formed are well dispersed on the SiC surface. On the other hand, heating on an oil bath increased the surface temperature gradually, resulting in a competitive aggregation. This difference is considered to result in quite different catalytic activities of the catalysts prepared using the two different heating methods. However, the use of microwave heating during the Heck reaction, accelerated the release of catalytically active palladium species, resulting in an accelerated loss of catalytic activity.



**Figure 3.** SEM Images of the surface of SiCs. (a) SiC before adsorption of palladium species (b) Pd/SiC catalyst prepared using oil bath heating (**OB10**) (c) Pd/SiC catalyst prepared using microwave heating (**MW3**) (d) Used catalyst **OB10** for the catalytic reactions.

The SiC-supported palladium catalyst was applicable to other reactions as shown in Scheme 3. The catalyst **MW3** underwent the Heck reaction of iodobenzene with methyl vinyl ketone to afford unsaturated ketone in 89% yield. In the case of acrylonitrile, *E* and *Z* isomers were formed in 60% and 35% yields, respectively. The catalyst was also applicable to the Suzuki reactions. Phenylboronic acid having both an electron-donating and withdrawing group reacted with iodobenzene to afford corresponding biphenyl derivatives efficiently.



**Scheme 3.** Heck reactions using other substrates and Suzuki reactions.

As discussed so far, we have developed a SiC-supported palladium catalyst. The catalytic activity was found to be considerably improved when the catalyst was prepared under microwave irradiation, which improved the dispersion of the palladium nanoparticles. The chemical and thermal stability of SiC enables its use as a catalyst support [26, 27]. Several reports were found that use microwave heating in either

catalyst preparation or catalytic reactions [28–31]. However, to the best of our knowledge, there is no report on the effect of microwave heating on the dispersion of the nanoparticles of metal catalysts. Hence, this study will provide useful insights for researchers studying catalytic and microwave chemistry. Further application of this method is currently under investigation and will be presented in due course.

### **Acknowledgements**

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### **Conflict of Interest**

We have not obtained any funding for this study.

### **Abbreviation List**

SiC: silicon carbide

SEM: scanning electron microscope



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