

## Sintered Silicon Carbide: A New Ceramic Vessel Material for Microwave Chemistry in Single-Mode Reactors

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**Abstract:** Silicon carbide (SiC) is a strongly microwave absorbing chemically inert ceramic material that can be utilized at extremely high temperatures due to its high melting point and very low thermal expansion coefficient. Microwave irradiation induces a flow of electrons in the semiconducting ceramic that heats the material very efficiently through resistance heating mechanisms. The use of SiC carbide reaction vessels in combination with a single-mode microwave reactor provides an almost complete shielding of the contents inside from the electromagnetic field. Therefore, such experiments do not involve electromagnetic field effects on the chemistry, since the semiconducting ceramic vial effectively pre-

vents microwave irradiation from penetrating the reaction mixture. The involvement of electromagnetic field effects (specific/nonthermal microwave effects) on 21 selected chemical transformations was evaluated by comparing the results obtained in microwave-transparent Pyrex vials with experiments performed in SiC vials at the same reaction temperature. For most of the 21 reactions, the outcome in terms of conversion/purity/product yields using the two different vial types was virtually identical, indicating that

the electromagnetic field had no direct influence on the reaction pathway. Due to the high chemical resistance of SiC, reactions involving corrosive reagents can be performed without degradation of the vessel material. Examples include high-temperature fluorine–chlorine exchange reactions using triethylamine trihydrofluoride, and the hydrolysis of nitriles with aqueous potassium hydroxide. The unique combination of high microwave absorptivity, thermal conductivity, and effusivity on the one hand, and excellent temperature, pressure and corrosion resistance on the other hand, makes this material ideal for the fabrication of reaction vessels for use in microwave reactors.

**Keywords:** ceramics • dielectric properties • microwave chemistry • silicon carbide • thermal effusivity

### Introduction

Microwave chemistry generally relies on the ability of the reaction mixture to efficiently absorb microwave energy, taking advantage of microwave dielectric heating phenomena such as dipolar polarization or ionic conduction mechanisms.<sup>[1]</sup> This produces efficient and rapid internal heating (in-core volumetric heating) by direct interaction of electromagnetic irradiation with the molecules (solvents, reagents, catalysts) that are present in the reaction mixture.<sup>[1]</sup> For mi-

crowave irradiation to be able to penetrate to the reaction mixture, reaction vessels employed in microwave chemistry are typically made out of low microwave absorbing or microwave transparent materials, such as borosilicate glass (Pyrex), quartz, or suitable polymers like PTFE (Teflon).<sup>[2]</sup> These materials exhibit many distinct and valuable advantages when used in microwave chemistry, but also face some limitations in high-end applications under extreme reaction conditions as far as temperature/pressure resistance, or chemical stability to aggressive media is concerned. Problems also exist when attempting to heat microwave transparent or low-absorbing reaction media in these types of reaction vessels.

In recent years, the use of sintered silicon carbide (SiC) has become increasingly popular for a variety of applications in microwave chemistry. SiC is a strongly microwave absorbing chemically inert ceramic material that can be utilized at extremely high temperatures due to its high melting point ( $\approx 2700^\circ\text{C}$ ) and very low thermal expansion coeffi-

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cient.<sup>[3]</sup> Microwave irradiation induces a flow of electrons in the semiconducting SiC that heats the material very efficiently through resistance (ohmic) heating mechanisms.<sup>[3]</sup> A variety of SiC materials in the form of powders, granules, and vessels (crucibles) have been used for some time in high-temperature microwave processing applications taking advantage of the extremely good microwave absorption properties, chemical resistance, and high thermal conductivity.<sup>[4–9]</sup> Several studies have described the use of SiC as so-called microwave susceptor or sensitizer in material sciences,<sup>[4,5]</sup> aiding for example in the rapid microwave-assisted synthesis of superconducting MgB<sub>2</sub> at temperatures close to 800 °C,<sup>[6]</sup> or in the microwave sintering of ZrO<sub>2</sub> ceramics.<sup>[7]</sup> In fact, because of its high melting point and chemical resistance, SiC crucibles have been used for the microwave melting of aluminum, copper, and nuclear waste glass.<sup>[8]</sup> SiC has also been exploited as a support material for metal catalysts in the microwave-assisted thermochemical (800–1000 °C) conversion of glycerol to syngas.<sup>[9]</sup>

More related to the field of synthetic chemistry, our group has recently developed so-called passive heating elements (PHEs) made out of sintered SiC that aid in the microwave heating of weakly absorbing or transparent reaction mixtures.<sup>[10]</sup> The cylindrical shape of the PHEs allows the use of these materials in reaction vials designed for both single-mode<sup>[11,12]</sup> and multimode microwave reactors.<sup>[13]</sup> In addition, microtiter plates made out of SiC for parallel microwave chemistry applications in multimode instruments were introduced in the past few years.<sup>[14,15]</sup> For these applications, the high thermal conductivity of SiC is of particular importance, avoiding the formation of temperature gradients within the plate.<sup>[15]</sup>

Herein, we describe the development and utilization of reaction vials designed for single-mode microwave chemistry made entirely out of sintered SiC ceramic. Although the concept of using a strongly microwave absorbing reaction vessel for microwave chemistry may seem counterintuitive or even irrational at first sight, the use of this technique provides several unique opportunities in microwave chemistry, such as the investigation of specific/nonthermal microwave effects, or the utilization of aggressive reaction media in a high-temperature regime. The full details of this technology are described in this publication.<sup>[16]</sup>

## Results and Discussion

**Design and vessel construction:** For the experiments described in this work a 10 mL reaction vial made out of sintered SiC of the exact same geometry as a standard microwave-transparent Pyrex process vial was used (Figure 1). The SiC vessel was fabricated by pressureless solid-phase sintering of a green compact of silicon carbide in the presence of various sintering aids (such as carbon) at  $\approx 2000$  °C in an inert atmosphere. As the sintering activity of SiC is comparatively low, fine-grained powders with a grain size of less than one micrometer were used for densification. Using



Figure 1. Reaction vial made out of sintered silicon carbide (SiC) for performing microwave chemistry under single-mode conditions. For comparison purposes a standard 10 mL Pyrex vial with a snap cap, internal FO probe sensor and a magnetic stir bar is also shown (see Experimental Section for details).

this procedure, the high strength of the obtained SiC remains almost unchanged up to about 1600 °C (ROCAR<sup>®</sup>S, Table 1). As a suitable microwave platform we have selected

Table 1. Comparison of material data for sintered silicon carbide (ROCAR<sup>®</sup>S) and borosilicate (Pyrex) glass.<sup>[a]</sup>

		ROCAR <sup>®</sup> S	Pyrex
melting point	m.p. [°C]	$\approx 2700$	$\approx 800$
thermal conductivity	$\lambda$ [W m <sup>-1</sup> K <sup>-1</sup> ]	115	1.2
thermal coeff. of expansion	$\alpha$ [K <sup>-1</sup> ]	$3.0 \times 10^{-6}$	$3.3 \times 10^{-6}$
specific heat capacity	$C_p$ [J g <sup>-1</sup> K <sup>-1</sup> ]	0.6	0.7
density	$\rho$ [g mL <sup>-1</sup> ]	3.15	2.23
thermal effusivity <sup>[b]</sup>	$e$ [J s <sup>-1/2</sup> m <sup>-2</sup> K <sup>-1</sup> ]	15000	1400
porosity (closed)	$P$ [%]	2	–
vickers hardness	HV 0.5	2300	–

[a] Data from reference [20]. [b] The thermal effusivity  $e$  of a material is defined as the square root of the product of its thermal conductivity and volumetric heat capacity [ $e = (\lambda \rho c_p)^{0.5}$ ].

a Monowave 300 single-mode reactor (Anton Paar GmbH) as this instrument allows simultaneous temperature measurement and control by both an external infrared (IR) and internal fiber-optic (FO) sensor.<sup>[17]</sup> Recent evidence has demonstrated that in several instances the use of an external IR sensor, recording the surface temperature of the vessel, does not accurately reflect the genuine reaction temperature inside the reaction vial and therefore may lead to erroneous results.<sup>[18,19]</sup> As with the standard Pyrex vial, the SiC vessel can be fitted with a thermoplastic snap cap and PTFE-coated silicone septa to allow microwave processing up to 300 °C and 30 bar pressure (Figure 1). For internal temperature measurements, punched seals to insert an immersing tube were employed. For both vial types stirring is ensured by magnetic stir bars.

One of the important original design features of the SiC vessel technology was the concept of shielding the reaction mixture contained inside from the electromagnetic field in order to investigate specific/nonthermal microwave effects (see below).<sup>[16]</sup> Due to the high microwave absorptivity of

SiC (see Figure S1 in the Supporting Information) we have assumed that the semiconducting ceramic will effectively prevent microwave irradiation from penetrating to the reaction mixture. Based on the results obtained with our previously used SiC vial prototype (1.8 mm wall thickness)<sup>[16]</sup> and more recently performed electromagnetic field simulations,<sup>[21]</sup> we have now moved to a 2.85 mm wall SiC vial. This ensures that for most reaction mixtures, heating will occur mainly by conventional heat-transfer mechanisms and not by dielectric heating effects (see below).

The 10 mL SiC reaction vial (Figure 1) is mechanically extremely robust. While standard Pyrex microwave process vials for single-mode microwave reactors have an approved pressure rating of 20–30 bar and may effectively resist internal pressures of > 50 bar before vessel failure,<sup>[2]</sup> the SiC tube has a pressure rating of >200 bar and in fact destruction of the vial could not be induced by standard pressure resistance tests. Intense microwave heating of SiC vessels in a multimode reactor leads to vial temperatures >600 °C within 2–3 min, confirming the excellent microwave absorptivity of this material (Figure S2 in the Supporting Information).

**Temperature measurement:** In a first set of experiments we evaluated the heating characteristics of four common solvents with vastly different loss tangents ( $\tan\delta$ )<sup>[22]</sup> in SiC vials at constant microwave power using internal FO temperature monitoring (Figure 2, top). The fact that nearly microwave transparent hexane ( $\tan\delta = 0.02$ ) is heated at the same rate as the strongly absorbing EtOH ( $\tan\delta = 0.941$ ) clearly indicates that the microwave field intensity inside the SiC vial must be extremely low, and that heating occurs in essence via conventional heat-transfer mechanisms and not by dielectric heating effects (see below). Because of its high thermal conductivity ( $\approx 100$  times higher than for Pyrex glass, Table 1) the heat flow through the 2.85 mm wall of the SiC reaction vessel is exceptionally fast. In addition, due to its extremely high thermal effusivity (a measure for the ability to exchange thermal energy with its surroundings) being  $\approx 10$  times higher than for Pyrex glass (Table 1), the contents inside the SiC reaction vial are also heated in a very efficient manner. A direct comparison of the heating profiles attained in Pyrex and SiC vials for each of the four individual solvents discussed above (Figure 2) demonstrates that solvents are generally heated at an equal rate if not faster in the SiC vial compared to the Pyrex vial, in particular in the high-temperature range (Figure S3).

Similar to standard microwave heating experiments involving microwave transparent Pyrex vials, the use of higher power levels in SiC vials, as expected, also leads to a more rapid heating of the solvent as exemplified for *N*-methyl-2-pyrrolidone (NMP;  $\tan\delta = 0.275$ ) in Figure S4 in the Supporting Information.

Importantly, heating experiments using SiC vials in combination with single-mode microwave reactors cannot only be performed in power control mode (Figure 2), but also in temperature control mode by using either the internal FO

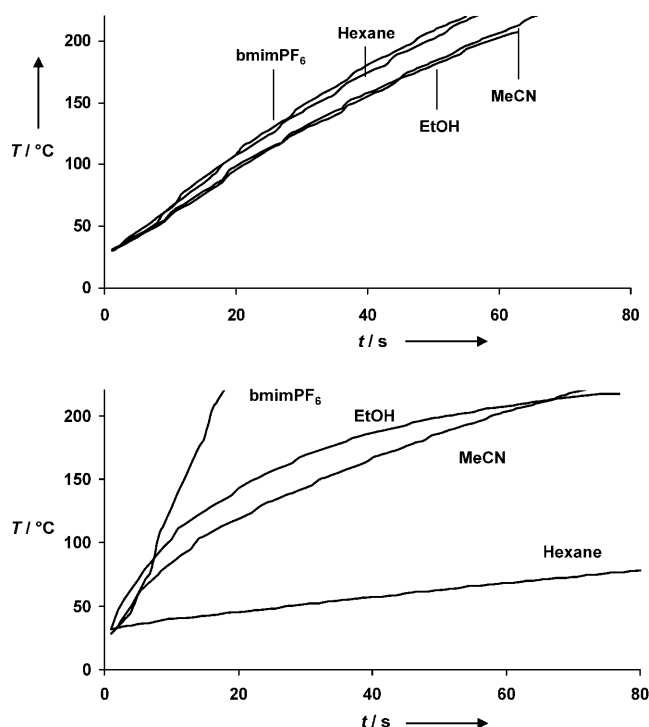


Figure 2. Heating rates for 3 mL samples of hexane ( $\tan\delta = 0.02$ ),<sup>[2]</sup> MeCN ( $\tan\delta = 0.062$ ),<sup>[2]</sup> EtOH ( $\tan\delta = 0.941$ ),<sup>[2]</sup> and bmimPF<sub>6</sub> ( $\tan\delta = 0.185$ )<sup>[21a]</sup> at 130 W constant magnetron power in a 10 mL SiC vial (2.85 mm wall thickness; top), and in a 10 mL Pyrex vial (2.85 mm wall thickness; bottom). Single-mode microwave irradiation, magnetic stirring, internal fiber-optic temperature measurement.

probe, or the external IR sensor as a lead sensor to control the magnetron output power. Successful heating experiments under temperature control in the Monowave 300 instrument were conducted either in the “as-fast-as-possible” or a ramp mode.<sup>[17]</sup> In most instances, the temperatures recorded by the IR and FO probes were very similar, although small differences were sometimes seen, mainly depending on IR sensor calibration (Figure 3). Whereas temperature control through the internal FO probe (IR as slave) is generally a beneficial choice for Pyrex vessel experiments in

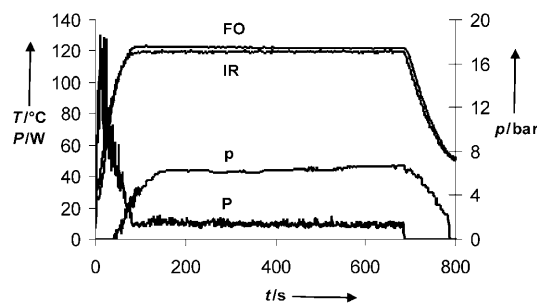


Figure 3. Temperature (internal FO and external IR), pressure (*p*) and microwave power profiles (*P*) for the heating of 3 mL of water to 120 °C in a SiC vial performed with IR temperature control (FO probe as slave). The corresponding profiles using FO temperature control are shown in Figure S5 in the Supporting Information.

which the selected target temperature is attained by dielectric heating of the solvent, the IR sensor turned out to be superior to the FO probe when SiC vessels were used.<sup>[23]</sup>

**Heating and cooling characteristics:** Figure 2 displays the heating profiles of solvents with different  $\tan\delta$  values in SiC and Pyrex vessels using constant microwave power. While the heating profiles using the Pyrex vials followed the expected trend and were correlated to the  $\tan\delta$  value of the solvent (Figure 2, bottom),<sup>[22]</sup> the heating of solvents in the SiC vessel was apparently not related to their microwave absorptivity, but rather dependent on other parameters such as specific heat capacity, viscosity and heat-transfer coefficients (Figure 2, top). Comparing the profiles obtained in the 2.85 mm SiC vial shown in Figure 2 (top) with our previously published data of essentially the same experiment, but employing a 1.8 mm wall thickness vessel (see also Figure S6 in the Supporting Information),<sup>[16]</sup> the stronger shielding using the thicker SiC vial is clearly evident, in particular for the strongly microwave absorbing 1-butyl-3-methylimidazolium hexafluorophosphate (bmimPF<sub>6</sub>). These experimental data are in good agreement with electromagnetic field simulations of the heating behavior of the same solvents comparing 2 with 3 mm SiC vials.<sup>[21]</sup> It should be emphasized that the microwave absorptivity of organic solvents and of the SiC ceramic is strongly dependent on the temperature, which must be considered in these experiments and simulations.<sup>[1,2]</sup> At room temperature the strongest microwave absorber of the five materials is EtOH, as it exhibits the highest  $\tan\delta$  value. At this frequency EtOH and MeCN are heated primarily by means of a dipolar polarization mechanism, hence their ability to absorb microwaves decreases with increasing temperature as the reduced bulk viscosity leads to reduced molecular friction.<sup>[1,21]</sup> The ionic liquid bmimPF<sub>6</sub> is heated by an ionic conduction mechanism, so its ability to absorb microwaves increases with increasing temperature.<sup>[1,21]</sup> At room temperature the loss tangent of SiC is lower than both EtOH and bmimPF<sub>6</sub>, however, its  $\tan\delta$  increases strongly with temperature and exhibits a peak at 200 °C (Figure S1 in the Supporting Information). Both the experimental data (heating profiles, Figure 2, top) and the electromagnetic field simulations<sup>[21]</sup> suggest that for strongly absorbing reaction mixtures at ambient temperature there is still some contribution from dielectric heating phenomena, while at temperatures >100 °C most of the heating will result from conductive heat-transfer mechanisms through the hot vessel surface. The SiC vials can therefore be viewed as “self-sealing” autoclaves, as with increasing temperature less microwave energy will be able to penetrate inside, and at the range of typical microwave-assisted transformations (100–300 °C) virtually all heating will occur by conventional heat-transfer mechanisms.

An apparent practical advantage of using SiC vials in microwave chemistry is that even completely microwave transparent solvents or reaction mixtures can be efficiently heated to high temperatures, which would be impossible utilizing standard (nearly microwave transparent) Pyrex vials

(Figure S7 in the Supporting Information). The effect is similar to the use of passive heating elements (PHEs) made out of the same ceramic material.<sup>[10]</sup> Weakly microwave absorbing solvents,<sup>[22]</sup> for example toluene ( $\tan\delta=0.040$ ) can be heated much more rapidly to the desired target temperature compared to an experiment in a Pyrex vessel (Figure S8 in the Supporting Information). Importantly, the heating rate using the SiC vial is largely independent on the  $\tan\delta$  of the solvent or reaction mixture (Figure 2, top). As the  $\tan\delta$  for most organic solvents (and water) generally decreases with increasing temperature,<sup>[1,2,21]</sup> this effect is particularly valuable for accessing a high-temperature regime in which genuine dielectric heating phenomena are often difficult to sustain.

An additional beneficial aspect of the use of SiC vials is the fact that for low-absorbing reaction mixtures considerably less magnetron power is used (Figure S8 in the Supporting Information). It is generally not advised to heat non- or low-absorbing reaction mixtures for prolonged periods of time in microwave reactors. This leads to the magnetron continuously operating at the maximum power level trying to reach the selected set temperature and ultimately can result in overheating and damage of the magnetron or destructive coupling of microwave irradiation with sensitive instrument and/or vessel parts. Similar energy-saving effects have been noticed using SiC passive heating elements.<sup>[10,11]</sup>

Because of the high thermal effusivity of the SiC material (Table 1) the heat flow through the 2.85 mm wall of the SiC vessel is exceptionally fast in both directions. This means that the cooling efficiency by compressed air at the end of a reaction is at least as high as when using a Pyrex vial. More importantly, we have recently demonstrated that the use of a SiC reaction vessel can aid in the prevention of exotherms, as the heat generated during a microwave-assisted chemical reaction can be efficiently exchanged with the comparatively cool air in the microwave cavity via the SiC ceramic.<sup>[16,18]</sup> Perhaps not surprisingly in this context, SiC ceramics have also been employed in the construction of microreactors for continuous-flow processing of strongly exothermic reactions, since the thermal effusivity of SiC is even higher than that of stainless steel.<sup>[24,25]</sup>

**Microwave field strength inside the SiC vials:** A prime motivation for the development of the SiC vial was the attempt to shield the contents inside the vial from microwave irradiation, and therefore to be able to separate thermal from specific/nonthermal microwave effects (see below).<sup>[16]</sup> The fact that the electric field strength and the power density inside the SiC vial must be comparatively low can be derived from the following set of experiments. First of all, the heating profiles obtained for solvents with different microwave absorptivity at constant power (Figure 2, top) provide clear evidence that the SiC vial provides efficient shielding of its contents from the microwave field. The heating profiles for all four solvents almost run in parallel, in particular at higher temperatures. As discussed already above, these experiments clearly indicate that “microwave” heating in a

single-mode reactor using SiC vials essentially involves conventional conductive heat-transfer mechanisms. These data are in good qualitative agreement with the results obtained from heating different solvents in parallel using SiC micro-titer plates utilizing a multimode microwave instrument.<sup>[15]</sup>

In a complimentary set of experiments the four solvents used in the experiment shown in Figure 2 were heated in temperature control mode to a target temperature of 180 °C. Importantly, the used magnetron microwave power for all four solvents—in sharp contrast to experiments in Pyrex vessels—was virtually identical (Table 2 and Figure S9 in the

Table 2. Required average microwave power ( $P$  [in W]) comparing the heating of solvents to 180 °C for 20 min in SiC and Pyrex vials.<sup>[a]</sup>

	tan $\delta$	SiC		Pyrex	
		$P$ overall <sup>[b]</sup>	$P$ hold time <sup>[c]</sup>	$P$ overall <sup>[b]</sup>	$P$ hold time <sup>[c]</sup>
hexane	0.020	20.4	14.7	155.9	107.5
MeCN	0.062	21.3	15.5	23.4	17.9
EtOH	0.941	21.0	14.8	24.7	19.9
bmimPF <sub>6</sub>	0.185	20.3	15.0	6.0	5.0
empty	–	22.4	17.9	–	–

[a] Conditions: solvent (3 mL), 180 °C set temperature (FO temperature control), hold time 20 min, 10 mL SiC/Pyrex vials (2.85 mm wall thickness), magnetic stirring. For a graphical representation of the required energy see Figure S9 in the Supporting Information. [b] Overall average power required during the entire heating process (20 min hold time and 2–3 min ramp time). [c] Average power required during the 20 min hold time.

Supporting Information). Even for a completely empty vial, the same magnetron power was used. These results strongly suggest that the heating of the SiC vial in the temperature-control mode is largely independent on its contents, which again points to the strong shielding effect of the SiC vessel.

Additional support for the shielding concept of SiC vials is derived from recently conducted electromagnetic field simulations on heating effects comparing Pyrex and SiC vials in a single-mode cavity by using the same solvent systems as used in our experimental work described herein.<sup>[21]</sup> In short, the simulations suggest that the electric field and power density distribution within a SiC tube is dependent upon the dielectric properties of the solvent within it and on the temperature. For low-absorbing solvents, such as hexane, the power dissipated within the liquid due to dielectric heating is negligible, as the tan  $\delta$  value for hexane is very low. For stronger absorbing solvents (MeCN, EtOH) a significant contribution from dielectric heating effects can be seen at room temperature in a 2 mm SiC vessel. However, at higher temperatures (>100 °C) these contributions are significantly reduced (<10% dielectric heating) and most of the heating will occur by conductive heat transfer from the vessel. As expected, the simulations for 3 mm SiC vials demonstrate an even stronger shielding effect.<sup>[21]</sup> Therefore, the electromagnetic field simulations are in good overall agreement with the experimental results described herein.

As an additional method for estimating the shielding effect of SiC vials, we performed a number of experiments

with electrodeless discharge lamps (EDLs) and filament lamps. In the presence of a microwave field these devices will illuminate and emit UV/Visual light.<sup>[26]</sup> Even by applying a 300 W magnetron output power in a single-mode instrument it was not possible to induce a gas discharge in the SiC vial.<sup>[16]</sup> In contrast, in a standard Pyrex vial 1–5 W of microwave power was sufficient to trigger gas discharge, causing the emission of UV/Vis irradiation in these EDLs (Figure S10 in the Supporting Information).<sup>[16]</sup> Since filament lamps do light at lower field strengths, similar experiments were performed with these devices in order to detect the presence of the electric field inside the SiC vessel. Indeed, a weak lighting was observed with a 0.24 W filament lamp (6 V, 40 mA, socketless LED-design with shortcut connectors to prevent arcing) inside a SiC vessel (Figure S11 in the Supporting Information). The calculated induced power of 0.04 W matches approximately with the observation of weak lighting of the bulb at 15 W applied constant microwave power in a single-mode instrument, indicating a very similar field strength for both simulation and experiment.<sup>[21]</sup>

Based on the evidence presented herein, it can be concluded that for most practical purposes in relation to microwave chemistry, the use of SiC vials in a single-mode reactor will provide an almost complete shielding of the contents inside from the electromagnetic field. In essence, this technology allows to use a standard single-mode microwave reactor platform to perform a noncontact heating autoclave experiment under very carefully controlled and monitored conditions (heating and cooling ramp, final set temperature, pressure, stirring speed). Importantly, this experiment—although performed in a microwave reactor—does not involve electromagnetic field effects on the chemistry, since the SiC vial effectively prevents the penetration of microwave irradiation to the reaction mixture.

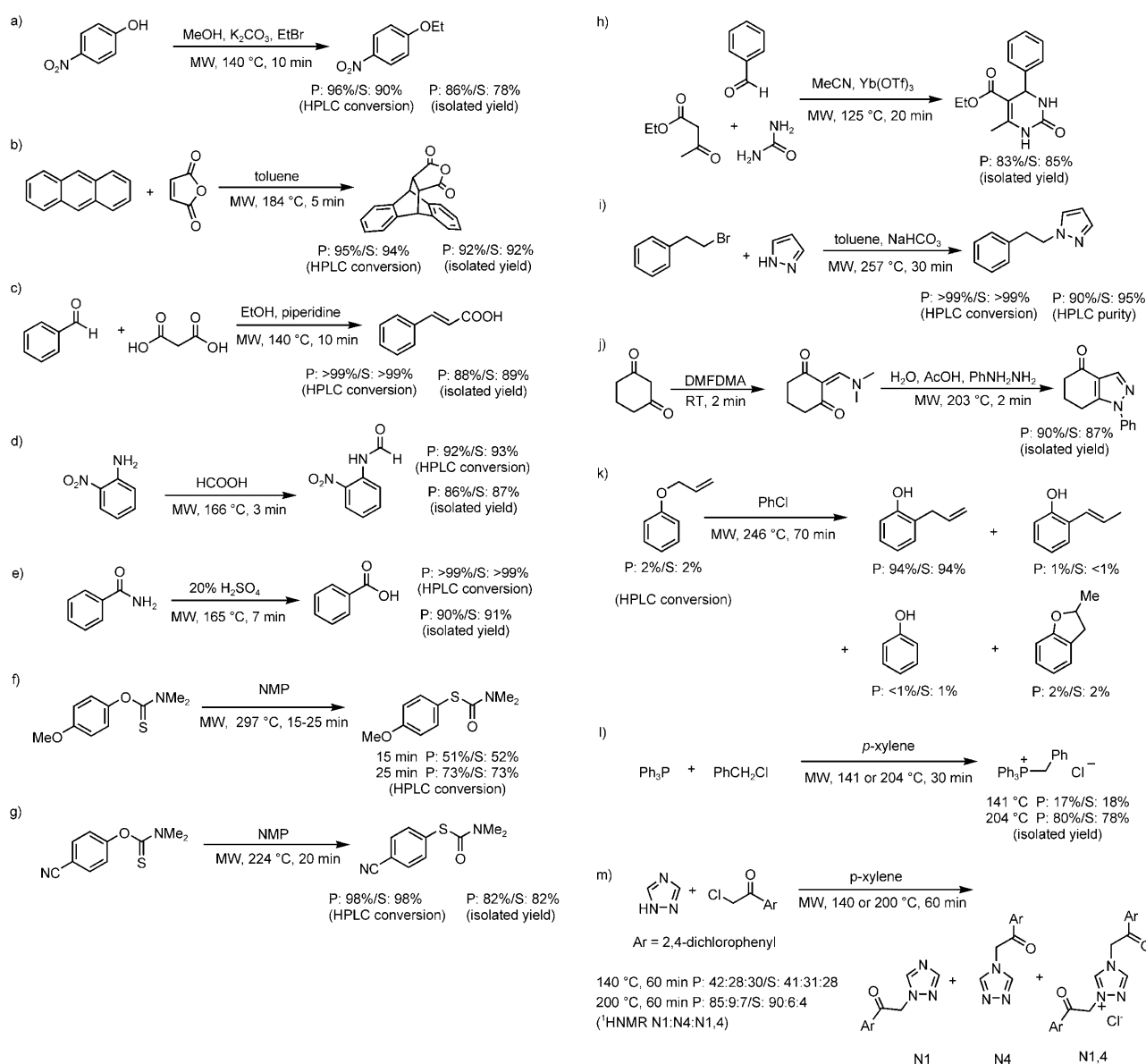
**Investigating microwave effects:** Regardless of the relatively large body of published work in the field of microwave chemistry, there is still considerable controversy on the exact reasons why microwave irradiation is able to enhance chemical processes. In particular, there is an ongoing debate in the scientific community if the observed enhancements are the result of purely thermal/kinetic effects as a consequence of the rapid heating and high bulk reaction temperatures that can be attained using microwave dielectric heating,<sup>[1,2]</sup> or are related to selective interactions of the electromagnetic field with specific substrate molecules, reagents, or catalysts not connected to a macroscopic bulk temperature effect (so-called “specific” or “nonthermal” microwave effects).<sup>[27,28]</sup> Indeed, there is experimental evidence that certain chemical transformations when carried out at the same measured reaction temperature, by using either microwave or conventional heating, lead to different results in terms of product distribution (selectivity) and/or yield.<sup>[28]</sup>

The SiC vessel technology described herein therefore appears ideally suited to investigate the significance of specific and nonthermal microwave effects, since by simply switching from a microwave transparent Pyrex to a strongly micro-

wave absorbing SiC vial any effects of the electromagnetic field on the reaction mixture (i.e., on the chemistry) can be eliminated, while retaining the sealed vessel capabilities, rapid heating/cooling and excellent process control features inherent to modern microwave reactors.<sup>[2]</sup> To some degree, this concept has been emulated previously by using passive heating elements (PHEs) made out of SiC in conjunction with standard Pyrex vials.<sup>[12]</sup> The addition of the SiC PHEs can lead to a significant reduction (30–70%) in the required microwave power as compared to experiments without heating element at the same temperature, and therefore in the case of specific/nonthermal microwave effects should lead to some measurable effects on conversion or yield.<sup>[12]</sup> Clearly, the use of a vessel completely made out of SiC allows a

much more efficient investigation of the effects of electromagnetic fields on chemical transformations.

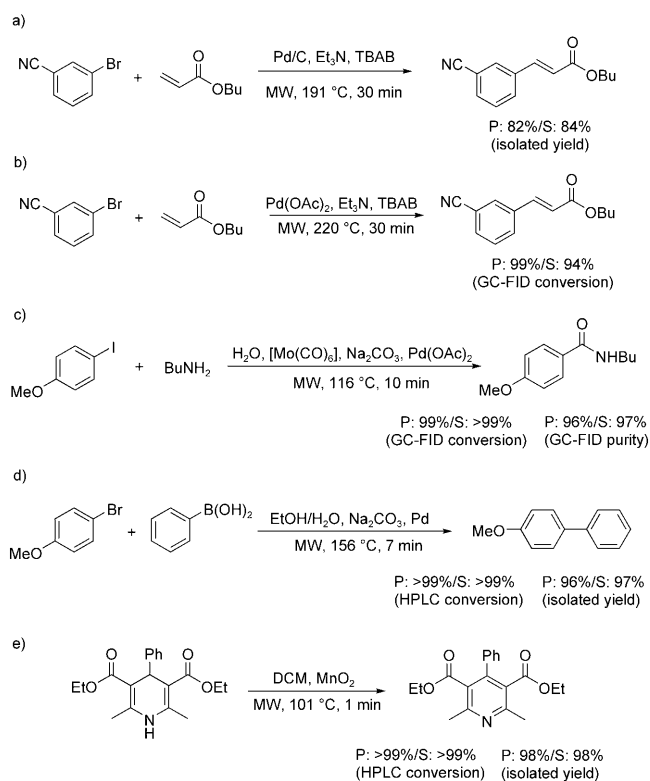
In the initial phase of our studies we have applied this concept to a variety of microwave-assisted transformations that had been previously investigated in our group,<sup>[2,10–12,19,29,30]</sup> in which enhancements compared to standard oil bath reflux conditions had been published (Schemes 1 and 2). The chosen reactions involved both strongly and weakly microwave absorbing solvents in a temperature range of 100–300 °C using reaction times of 1–70 min. Experiments were carried out on a 2–5 mL scale in both low- and high-boiling solvents, and included reactions that were either fully homogeneous, or involved heterogeneous starting materials, reagents, or catalysts. Gratifyingly, for



Scheme 1. Conversions/yields obtained for sealed vessel microwave experiments performed in Pyrex (P) or silicon carbide (S) reaction vials. Single-mode microwave irradiation, magnetic stirring, internal fiber-optic temperature measurement. For further details, see the Supporting Information.

all chemistry examples, it was possible to achieve similar internal FO temperature profiles switching from Pyrex to SiC vials, with other process parameters like pressure and stirring speed also being identical (Figure S12 in the Supporting Information).

For the eighteen chemistry examples presented in Schemes 1 and 2, virtually identical results in terms of conversion, purity profile, and/or isolated product yields were

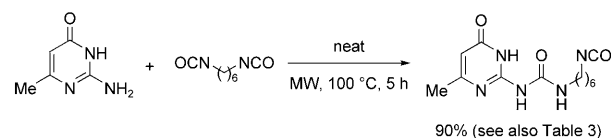


Scheme 2. Conversions/yields obtained for sealed vessel microwave experiments performed in Pyrex (P) or silicon carbide (S) reaction vials. Single-mode microwave irradiation, magnetic stirring, internal fiber-optic temperature measurement. For further details, see the Supporting Information.

obtained, comparing experiments that involve genuine microwave chemistry in Pyrex vials with “microwave heating” in SiC vials. This confirms that for these specific cases only bulk temperature effects are responsible for the observed enhancements and that the electromagnetic field has no direct influence on the reaction pathway (specific or non-thermal microwave effects).<sup>[27,28]</sup> Since the time of our original publication of this technology,<sup>[16]</sup> an additional four examples have been investigated in our laboratories, again not exhibiting any difference between Pyrex and SiC processing (Scheme S25 in the Supporting Information).<sup>[29]</sup>

After these successful proof-of-concept studies we wanted to explore the use of the SiC vial concept for the investigation of more challenging chemical transformations for which specific or nonthermal microwave effects had been explicitly documented in the literature. Our first example involved the

addition of 6-methylisocytosine to hexamethylenediisocyanate (HDI) leading to selective monourea formation (Scheme 3).<sup>[31]</sup> This transformation is carried out in suspen-



Scheme 3. Nucleophilic addition of 6-methylisocytosine to hexamethylenediisocyanate.

sion using an excess of HDI (7.5 equiv) as a solvent. Importantly, the reaction mixture remains heterogeneous during the addition process as the solid starting material is transformed to the even less soluble urea product. Hulshof and co-workers have recently studied this addition process and have found that reactions performed under multimode microwave irradiation conditions were significantly faster compared to experiments conducted by conventional heating, applying the same reaction vessel, internal reaction temperature, and stirring rate.<sup>[31]</sup> For example, at a reaction temperature of 100 °C, the isocyanate addition required  $\approx 3$  h to go to full conversion using conventional heating, whereas the microwave run was completed within  $\approx 20$  min.<sup>[31]</sup> The authors have rationalized this apparent microwave effect by selective heating of the solid/liquid interface, leading to an enhanced solubility of 6-methylcytosine in the diffusion layer and an increased reaction rate due to local overheating.<sup>[31]</sup>

A careful reinvestigation of this reaction revealed the following facts: in agreement with the studies by Hulshof and co-workers<sup>[31]</sup> we found the isocyanate addition to be rather sensitive to temperature (Figure S13 in the Supporting Information) and to the quality of the HDI reagent. Therefore, the same bottle of HDI was used for all comparison experiments and extreme care was taken to exclude moisture during reagent removal. In addition, we noticed from conventional oil bath experiments using round-bottomed flasks with magnetic stir bars that the stirring speed had a notable effect on the conversion, with higher stirring rates leading to increased conversions (Figure S14 in the Supporting Information). By visually observing the progress of the heterogeneous addition process we noticed that within the range of 30–60% of conversion it was difficult to keep all solid materials properly suspended in the flask. At this stage, a solid mass accumulated at the edges of the round-bottom flask, thus not being effectively mixed with the HDI reagent. Interestingly, when the exact same reaction mixture was processed at the identical nominal stirring speed (600 rpm) in a 10 mL Pyrex microwave process vial instead of a 10 mL round-bottomed flask, different reaction rates were observed, with the flask experiment being significantly faster than the vial experiment (Figure S15 in the Supporting Information). This result clearly demonstrates that stirring/agi-

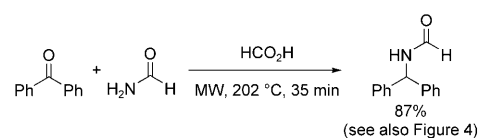
tation is a critical factor in this heterogeneous transformation (Scheme 3), and once again highlights the fact that the commonly used 10 mL cylindrical microwave vials do not provide a high stirring efficiency, in particular when heterogeneous mixtures or highly viscous reaction media are involved.<sup>[32]</sup>

With this background information in hand we next performed comparison experiments for the addition of 6-methylisocytosine with HDI (Scheme 3) under microwave conditions at 100 °C using SiC and Pyrex vials (Ar atmosphere). To ensure efficient agitation we employed two 10 × 3 mm stir bars for both vial types. Control experiments have shown that the use of two stir bars instead of only one significantly enhances the agitation efficiency/reliability for this heterogeneous reaction mixture. This is of particular importance for the SiC ceramic vials, in which stirring with Teflon-coated magnetic stir bars may be compromised due to the different surface morphology compared to glass. In our hands, when performed at the same internal reaction temperature of 100 °C (see Figure S16 in the Supporting Information for temperature profiles), using the same heating and cooling ramps, and applying the same stirring speed (600 rpm), the conversion in both sets of addition experiments was identical within experimental error (Table 3 and Figure S17 in the Supporting Information). These data suggest that no specific/nonthermal microwave effects are involved in this transformation. To confirm this result we have additionally per-

formed an experiment using the 10 mL Pyrex vial applying conventional oil bath heating (Table 3, CONV Pyrex). Again, the data obtained from this experiment closely matched the microwave runs confirming the absence of any specific/nonthermal microwave effect.

As the work of the Hulshof group<sup>[31]</sup> was originally performed in a multimode microwave instrument (as opposed to the single-mode reactor used herein), we have furthermore reproduced the chemistry shown in Scheme 3 in an identical multimode system to exclude any influence of varying electromagnetic field strength between single- and multimode microwave instruments. However, also under these conditions the conversions were similar to the conventionally heated runs (Figure S18 in the Supporting Information), and not the previously published microwave experiments.<sup>[31]</sup>

As a second example, we have chosen the Leuckart reductive amination of benzophenone with formamide in the presence of formic acid as reducing agent (Scheme 4). This



Scheme 4. Leuckart reductive amination of benzophenone.

Table 3. Comparison of microwave heating in Pyrex and SiC vials for the addition of 6-methylisocytosine to hexamethylenediisocyanate at 100 °C (Scheme 3).<sup>[a,b]</sup>

<i>t</i> [min]	Heating method	Conv. <sup>[c]</sup> [%]	<i>t</i> [min]	Heating method	Conv. <sup>[c]</sup> [%]
15	MW Pyrex	3.6 ± 1.5	180	MW Pyrex	68.1 ± 3.7
15	MW SiC	3.9 ± 0.9	180	MW SiC	63.9 ± 3.3
15	CONV Pyrex	4.1 ± 0.7	180	CONV Pyrex	69.7 ± 4.6
30	MW Pyrex	9.4 ± 0.6	210	MW Pyrex	77.4 ± 3.5
30	MW SiC	9.1 ± 0.9	210	MW SiC	73.5 ± 2.5
30	CONV Pyrex	12.5 ± 2.9	210	CONV Pyrex	77.9 ± 5.2
60	MW Pyrex	20.9 ± 2.2	240	MW Pyrex	83.7 ± 5.0
60	MW SiC	19.6 ± 2.8	240	MW SiC	80.9 ± 2.3
60	CONV Pyrex	24.4 ± 2.1	240	CONV Pyrex	84.3 ± 4.9
90	MW Pyrex	30.4 ± 3.7	270	MW Pyrex	89.7 ± 2.6
90	MW SiC	30.8 ± 3.5	270	MW SiC	86.6 ± 1.8
90	CONV Pyrex	37.2 ± 3.2	270	CONV Pyrex	89.1 ± 5.9
120	MW Pyrex	45.7 ± 4.4	300	MW Pyrex	93.0 ± 1.6
120	MW SiC	43.3 ± 3.6	300	MW SiC	91.1 ± 1.5
120	CONV Pyrex	48.6 ± 3.9	300	CONV Pyrex	93.0 ± 4.5
150	MW Pyrex	57.3 ± 4.4			
150	MW SiC	54.2 ± 2.7			
150	CONV Pyrex	60.6 ± 4.4			

[a] 6-Methylisocytosine (2.00 mmol) and hexamethylenediisocyanate (15.0 mmol) were reacted neat at 100 °C in 10 mL Pyrex or SiC vials employing either microwave (MW) or conventional oil bath heating (CONV). Magnetic stirring, 600 rpm, two stir bars. For further details, see the Experimental Section. [b] Internal reaction temperature measured by fiber-optic probe sensor. The heating profiles and a graphical representation of conversion are reproduced in the Supporting Information (Figure S16 and 17 in the Supporting Information). [c] Determined by HPLC-UV analysis at 254 nm. All experiments were performed in triplicate.

transformation was demonstrated by Loupy and co-workers to exhibit a dramatic nonthermal microwave effect when performed in a single-mode reactor at 202 °C (IR temperature measurement): while the conventionally heated experiment resulted in only 2% conversion within 30 min, the microwave heated run provided 99% conversion toward the desired amide product during the same time period (97% isolated yield).<sup>[33]</sup> This striking difference in conversion was rationalized in terms of a nonthermal microwave effect, for which the dipolar transition state in the Leuckart reductive amination is stabilized by the electromagnetic field, thereby leading to a lowering of activation energy and thus an enhancement of reactivity.<sup>[33,34]</sup>

Comparison studies between Pyrex and SiC vial single-mode microwave experiments using the identical reaction mixture composition but employing internal FO temperature monitoring quickly demonstrated that microwave effects are probably not involved in this chemistry. For both types of experiments, high conversions could be realized within 30–40 min (Figure 4). However, careful analysis of the results indeed indicated that experiments performed applying dielectric heating in Pyrex vials provided somewhat higher conversions compared to the identical experiments using wall heating in SiC vials. We speculate that this phenomenon may be related to an enhanced thermal decomposition of the reducing agent formic acid on the hot SiC vessel surface. It can be argued that the higher surface area provided by the SiC ceramic (of higher porosity) will lead to more rapid thermal decomposition of formic acid than in a



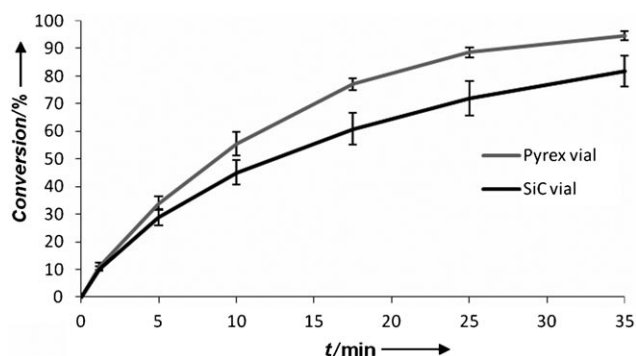
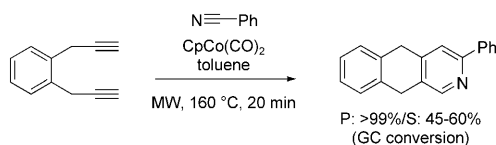


Figure 4. Conversion over time for the Leuckart reductive amination of benzophenone with formamide in the presence of formic acid (Scheme 4). Experiments were performed at 202 °C in triplicate using Pyrex and SiC reaction vessels. Conversions were monitored by GC-FID analysis. The heating profiles are reproduced in the Supporting Information (Figure S19). For further details, see the Experimental Section.

Pyrex glass vessel. Evidence for this hypothesis was derived by heating of pure formic acid to 202 °C in SiC vials. The decomposition of formic acid was notably faster than in Pyrex vials as seen by the more rapid rise in pressure (Figure S20 in the Supporting Information).

An additional example in which the use of Pyrex and SiC vials does not lead to identical results involves the Co-catalyzed [2+2+2] cyclotrimerization of 1,2-dipropargylbenzene with benzonitrile leading to a 9,10-dihydro-2-azaanthracene derivative (Scheme 5). Studies published by Dei-



Scheme 5. Co-catalyzed [2+2+2] cyclotrimerization reactions. P = Pyrex vial; S = SiC vial.

ters and co-workers in 2008 comparing microwave and conventional heating at the same monitored reaction temperature have suggested the existence of a nonthermal microwave effect for this transformation.<sup>[35]</sup> A more recent investigation using accurate internal reaction temperature control and matching heating and cooling profiles for both types of heating modes as close as possible has demonstrated that no microwave effects exist for this [2+2+2] cyclotrimerization reactions.<sup>[36]</sup> The Co-catalyzed [2+2+2] cyclotrimerization required 160 °C to lead to complete conversion within 20 min under microwave conditions and furnished a 78% isolated product yield. Performing an oil bath experiment with a similar temperature profile as in the microwave run also gave full conversion and a similar isolated product yield (75%).<sup>[36]</sup> However, using the SiC vial under identical conditions consistently provided conversion in the range of only 45–60%. As in the case of the Leuckart reductive amination described above, we ascribe this phenomenon to an

enhanced thermal decomposition of the Co catalyst on the hot SiC vessel surface of higher porosity.

#### Controlling thermal runaways and temperature overshoots:

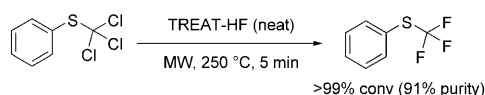
The data presented so far have demonstrated that the use of SiC vials in a single-mode microwave instrument essentially mimics a conventionally heated autoclave experiment under carefully controlled reaction conditions (internal temperature, pressure). Apart from the possibility to separate thermal from specific/nonthermal microwave effects, an additional benefit of this technology involves controlling strongly microwave absorbing and/or exothermic reaction mixtures, in particular under solvent-free conditions. A case in point is the synthesis of ionic liquids via alkylation of nitrogen-containing heterocycles, which is notoriously difficult to control under microwave conditions.<sup>[18]</sup> Not only are these alkylations generally exothermic, but in addition the microwave absorptivity during the process changes significantly from moderate (starting materials) to high (ionic liquids). To further complicate matters, the  $\tan \delta$  of ionic liquids increases with increasing temperature (for bmimPF<sub>6</sub> the  $\tan \delta$  is 0.184 at 25 °C and 3.592 at 200 °C),<sup>[21]</sup> therefore setting the stage for thermal runaways under microwave conditions. Using SiC reaction vials, the fact that the microwave absorptivity of the components is changing during the formation of the ionic liquid is largely irrelevant, as the SiC vial efficiently prevents microwave irradiation from penetrating to the reaction mixture and heating will occur by conventional heat-transfer mechanisms. Coupled with the  $\approx 10$  times higher effusivity of SiC compared to Pyrex (see Table 1) the generation of temperature overshoots or exotherms can often be avoided, as the heat generated during ionic liquid formation is efficiently exchanged with the comparatively cool air in the microwave cavity through the SiC ceramic.<sup>[18]</sup>

Additional examples in which thermal runaways using microwave dielectric heating have been experienced are the alkylation of 1,2,4-triazole with 2,2,4'-trichloroacetophenone (Scheme 1 m), and the alkylation of triphenylphosphine with benzyl chloride (Scheme 11). While in the presence of *p*-xylene as solvent both alkylations can be reasonably controlled using microwave dielectric heating principles (Scheme 11 and 1 m), under solvent-free conditions both transformations lead to strong exotherms, temperature overshoots and inhomogeneities, and ultimately to thermal runaways.<sup>[19]</sup> In particular in the case of triazole alkylation severe thermal runaways were previously observed making this chemistry unsuitable for microwave processing.<sup>[19]</sup> In contrast, the use of SiC vials alleviates these problems to a significant extent and even under solvent-free conditions, reproducible results in a more controllable temperature regime can now be obtained (Figures S21 and S22 in the Supporting Information).

It should be emphasized that the significant advantage of performing these reactions in SiC vials inside a microwave instrument—as opposed to a classical oil bath experiment—lies in the noncontact-heating nature and the dynamic temperature control of this method. Using a conventional oil bath, exothermic reactions are often not noticed and remain

undetected unless the internal reaction temperature is carefully monitored. Even if a thermal overshoot is recognized by internal temperature monitoring, there is no easy way of reducing the thermal energy going into the system unless the reaction vessel is physically removed from the bath (contact heating). In contrast, a thermal overshoot in the SiC microwave system is easily recognized by the internal FO probe, which leads to an immediate adjustment of the magnetron output power, or even to an active cooling step by compressed air.

**Corrosion stability and thermal resistance:** Sintered SiC is a universally corrosion-resistant material that exhibits excellent heat stability and owing to its high hardness additionally reduces wear and erosion.<sup>[3]</sup> This is the reason why SiC is used for many key components in chemical plants and has recently also been employed for the fabrication of gas-tight microreactors operating at high temperatures (700 °C) and harsh environments.<sup>[24]</sup> The corrosion resistance of sintered SiC is, like most ceramics, far better than of metals and even aggressive media such as concentrated acids or bases, HF, or chlorine gas have a negligible impact in terms of corrosion.<sup>[24]</sup> Based on these facts we have employed SiC vials for conducting microwave-assisted, aliphatic fluorine–chlorine exchange reactions using triethylamine trihydrofluoride (TREAT-HF, Et<sub>3</sub>N·3HF) as a reagent.<sup>[36]</sup> TREAT-HF is a commercially available, colorless, hygroscopic liquid with a shelf life of at least one year and has been reported not to corrode borosilicate glassware at ambient conditions.<sup>[37]</sup> Not unlike ionic liquids, the distinctly polar properties of TREAT-HF make it very suitable as a reagent (and/or solvent) in microwave-heated transformations. In fluorine–chlorine exchange reactions involving (trichloromethylthio)benzene at 250 °C (Scheme 6)<sup>[36]</sup> we did, however, notice a



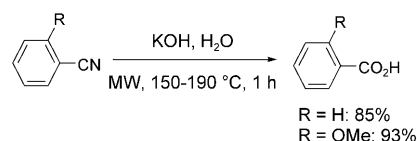
Scheme 6. Fluorination reactions using triethylamine trihydrofluoride (TREAT-HF).

significant corrosion of standard Pyrex microwave reaction vials in the vapor space above the liquid's surface. Although generally considered noncorrosive,<sup>[37]</sup> TREAT-HF can release hydrogen fluoride at elevated temperatures and will therefore attack borosilicate glass to some extent. In a control study measuring the weight loss of unused fresh Pyrex microwave reaction vessels after exposure to TREAT-HF under microwave conditions, we discovered that corrosion occurs even at comparatively low temperatures (100 °C) and is highly dependent on reaction temperature and time. While at 100 °C the weight loss after 5 min is already measurable but comparatively small, a very significant loss of glass was encountered after a 30 min exposure at 250 °C (Figure S23 in the Supporting Information). Importantly, the

corrosion of microwave vials during usage represents a serious safety risk as the pressure rating of the heavy-walled Pyrex vials (20–30 bar) cannot be maintained. Prolonged exposure of Pyrex vials to TREAT-HF at high temperatures and pressures or repeated vial usage must therefore be strictly avoided. In addition, hydrogen fluoride mediated vessel corrosion at these temperatures leads to the formation of gel-type materials, making an extractive workup of the reaction mixture troublesome.

In contrast, the SiC vial proved to be completely resistant to TREAT-HF even at 250 °C for prolonged periods of time (no measurable weight loss). Furthermore, workup of the reaction mixture was simplified due to the absence of glass corrosion products.

Similar investigations on the corrosion stability of SiC versus Pyrex reaction vials under microwave conditions were performed in the context of the high-temperature hydrolysis of aromatic nitriles using strong aqueous bases. The hydrolysis of a nitrile function in alkaline medium to obtain a carboxylic acid is a commonly used transformation in organic synthesis. The described conditions for hydrolysis, in particular for aromatic nitriles, are in most cases rather harsh, involving long reaction times and/or high temperatures.<sup>[38]</sup> For our model studies, the hydrolysis of benzonitrile and 2-methoxybenzonitrile using 20 % aqueous KOH in a temperature range of 100–190 °C was evaluated (Scheme 7).



Scheme 7. Hydrolysis of aromatic nitriles using 20 % aqueous KOH.

While for benzonitrile complete hydrolysis to benzoic acid could be achieved after 1 h at 150 °C (2 equiv KOH, 20 % aqueous solution), the sterically hindered 2-methoxybenzonitrile required exposure at either 170 °C for 2 h or at 190 °C for 1 h (5 equiv KOH, 20 % aqueous solution). The results in terms of HPLC conversion for experiments performed in Pyrex and SiC vials were essentially the same; however, isolated product yields in the SiC vial were significantly higher (>85 %), since hydrolysis experiments performed in Pyrex vials resulted in large amounts of glass degradation products (silicates), making product isolation troublesome.

A more detailed evaluation of the corrosion of standard Pyrex microwave process vials with aqueous KOH demonstrated that severe degradation is typically obtained at temperatures > 150 °C, largely independent on the concentration of KOH (20–60 %) (Figure S24 and Table S1 in the Supporting Information). In several of these experiments vessel failures resulting in severe explosions were observed, in particular in the high-temperature/pressure range, or when the filling volume was too low. In the latter case we assume that evaporation of solvent (large headspace) leads to deposition of solid KOH at the liquid boundary that will strongly inter-

act with the microwave field and can lead to a localized melting of Pyrex glass. Experiments under microwave conditions involving strong bases in combination with Pyrex vials should therefore be avoided. In particular in the high-temperature range, significant internal pressures will develop (10–20 bar) that can lead to catastrophic vessel failures.

Control experiments with SiC vials demonstrated that the ceramic material is completely corrosion resistant to KOH as no weight loss of the vial was detected, even after exposure to 20% KOH at 210°C for 1 h.

An additional feature of using a reaction vial made out of a strongly microwave-absorbing and high-temperature resistant material in microwave chemistry is that vessel failures due to the deposition of strongly absorbing materials on the inside such as metals can be eliminated. In particular in the field of homogeneous transition-metal catalysis using microwave conditions<sup>[39]</sup> a common phenomenon is that the metal catalyst (for example Pd) ultimately is being deposited on the inner vessel wall due to catalyst decomposition initiated by the high reaction temperatures.<sup>[2,40]</sup> The inadvertently formed and strongly microwave absorbing solid zero-valent metal deposits can cause melting of the Pyrex glass or will lead to arcing phenomena.<sup>[40,41]</sup> Both effects ultimately may result in catastrophic vessel failures and to severe instrument damage. As the electromagnetic field strength inside the SiC vial is dramatically reduced, the possibility for arcing phenomena is minimized. In addition, the significantly higher melting point of SiC compared to Pyrex glass (see Table 1) will prevent melting of the reaction vial and therefore should allow safe microwave processing even in the presence of metals or other strongly microwave absorbing materials. In all the experiments performed with SiC vials in our group so far vessel failure or vial damage has never been observed.

## Conclusion

In summary, we have demonstrated that the use of reaction vials made out of sintered silicon carbide (SiC) ceramic in microwave chemistry provides an interesting alternative to the more commonly used standard Pyrex glass vessels. The high melting point and pressure stability of SiC combined with its excellent chemical resistance allows the safe use of corrosive reagents in a high-temperature/pressure regime not suitable for processing in standard glass vials. The virtually indestructible reaction vials have been used up to 300°C and 30 bar pressure, and potentially could be used at even higher temperatures and pressures due the specific properties of this ceramic material.

Importantly, as shown by electromagnetic field simulations and heating experiments of solvents with different microwave absorptivity, performing a microwave chemistry experiment in a SiC vessel mimics a conventionally heated autoclave experiment, while retaining the rapid heating (flash heating) and excellent process control features inherent to microwave chemistry. The combination of high microwave

absorptivity, thermal conductivity, and effusivity of SiC allows a very rapid heat exchange with its surroundings, which is not only important for achieving fast heating rates of the reaction mixtures, but can also prevent exotherms due to the noncontact heating nature of this technology. The method described herein therefore makes it possible to rapidly separate thermal from specific/nonthermal effects, since by employing the SiC vial any effects of the electromagnetic field on the reaction mixture can be eliminated. Future work using this technology will be aimed at studying the use of SiC vials in other areas ranging from organic and polymer synthesis to nanomaterials research, and investigating the scale-up potential.

## Experimental Section

**General remarks:** <sup>1</sup>H NMR spectra were recorded on a Bruker 300 MHz instrument. <sup>13</sup>C NMR spectra were recorded on the same instrument at 75 MHz. Chemical shifts ( $\delta$ ) are expressed in ppm downfield from TMS as internal standard. The letters s, d, t, q, and m are used to indicate singlet, doublet, triplet, quadruplet, and multiplet, respectively. Low-resolution mass spectra were obtained on an Agilent 1100 LC/MS instrument using atmospheric pressure chemical ionization (APCI) in positive or negative mode. GC-FID analysis was performed on a Trace-GC (ThermoFisher) with a flame ionization detector using a HP5 column (30 m  $\times$  0.250 mm  $\times$  0.025  $\mu$ m). After 1 min at 50°C the temperature was increased in 25°C min<sup>-1</sup> steps up to 300°C and kept at 300°C for 4 min. The detector gas for the flame ionization is H<sub>2</sub> and compressed air (5.0 quality). GC-MS spectra were recorded using a Thermo Focus GC coupled with a Thermo DSQ II (EI, 70 eV). A HP5-MS column (30 m  $\times$  0.250 mm  $\times$  0.025  $\mu$ m) was used with Helium as carrier gas (1 mL min<sup>-1</sup> constant flow). The injector temperature was set to 280°C. After 1 min at 50°C the temperature was increased in 25°C min<sup>-1</sup> steps up to 300°C and kept at 300°C for 4 min. Analytical HPLC (Shimadzu LC20) analysis was carried out on a C18 reversed-phase (RP) analytical column (150  $\times$  4.6 mm, particle size 5  $\mu$ m) at 25°C using a mobile phase A (water/acetonitrile 90:10 (v/v) + 0.1% TFA) and B (MeCN + 0.1% TFA) at a flow rate of 1.0 mL min<sup>-1</sup>. The following gradient was applied: linear increase from solution 30% B to 100% B in 8 min, hold at 100% solution B for 2 min. TLC analyses were performed on pre-coated (silica gel 60 HF<sub>254</sub>) plates. Flash chromatography separations were performed on a Biotage SP1 instrument using petroleum ether/ethyl acetate mixtures as eluent. Melting points were determined on a Stuart<sup>TM</sup> SMP3 melting point apparatus. All anhydrous solvents (stored over molecular sieves), and chemicals were obtained from standard commercial vendors and were used without any further purification.

**Microwave irradiation experiments:** Microwave irradiation experiments were performed using a Monowave 300 single-mode microwave reactor from Anton Paar GmbH (Graz, Austria).<sup>[17]</sup> The instrument uses a maximum of 850 W magnetron output power (2.45 GHz) and can be operated at 300°C reaction temperature and 30 bar pressure. The reaction temperature was monitored by an external infrared sensor (IR) housed in the side-walls of the microwave cavity measuring the surface temperature of the reaction vessel, and/or by an internal fiber-optic (FO) temperature probe (ruby thermometer)<sup>[42]</sup> protected by a borosilicate immersion well inserted directly to the reaction mixture. The magnetron output power can either be controlled by the FO probe (IR as slave) or by the IR sensor (FO as slave). Heating experiments can be performed in temperature control mode (“as-fast-as-possible”, ramp mode), or using a constant power option. Pressure sensing was achieved by a hydraulic sensor integrated in the swiveling cover of the instrument. The reusable Pyrex vials (10 mL and 30 mL) were sealed with PEEK snap caps and standard PTFE coated silicone septa. In case of FO temperature measurement, punched seals to insert the immersing tube were employed. Seals and

caps can be used for both Pyrex and the 10 mL SiC vials. Precision of internal temperature measurement was provided by efficient stirring at a fixed rate of 600 rpm. Reaction cooling was performed by compressed air automatically after the heating period has elapsed. The required pressure of 6–8 bar was also used to pneumatically seal the vials tightly at the beginning to withstand 30 bar, and to ensure smooth release of potentially remaining pressure before opening the cover.

**Sintered silicon carbide (SiC) vials:** For the experiments described herein either a standard 10 mL Pyrex tube (average weight: 25.4 g) or a vessel made out of sintered silicon carbide (ROCAR<sup>®</sup>S; average weight: 39.0 g) of the exact same geometry was used (Figure 1). Both vials are commercially available from Anton Paar GmbH,<sup>[17]</sup> have a wall thickness of 2.85 mm and are fabricated for use with the Monowave 300 instrument. As the SiC vial is opaque, any residues remaining inside from a particular microwave experiment are difficult to identify. A thorough cleaning regime is recommended after each experiment (acetone, water, KOH/isopropanol, aqua regia) to ensure that traces of materials attached to the inner surface will not interfere in subsequent reactions. For strongly corrosive reaction mixtures, the use of the FO temperature probe housed in a borosilicate immersion well should be avoided. As the surface morphology of the SiC is different from Pyrex glass, for strongly heterogeneous reaction mixtures the use of two 10×3 mm stir bars is recommended for SiC vials.

**Comparison of SiC and Pyrex vessel experiments:** All chemical transformations studied in this work (Scheme 1–7) are known in the literature and for the most part (Schemes 1, 2, 5, and 6) have been previously investigated and optimized in our laboratories using standard single-mode microwave technology. For the comparison experiments involving SiC and Pyrex vials, the FO probe was chosen as lead sensor for all Pyrex vial experiments, whereas regulation with the IR sensor as lead sensor generally proved to be superior in combination with SiC vials (especially in combination with reaction mixtures with high thermal inertia, for example, high filling volumes). The corresponding SiC and Pyrex experiments were conducted at the same internal FO temperature and hold-time (see Figure S12 in the Supporting Information). Care was taken to ensure efficient stirring in all experiments. The procedure for conducting oil bath heating experiments with 10 mL Pyrex microwave process vials and internal FO temperature monitoring (Scheme 3) has been described previously.<sup>[19]</sup> Conversions and purities of the crude, homogenized reaction mixtures were determined (where possible) by HPLC (215 or 254 nm), GC-FID and/or GC-MS, or <sup>1</sup>H NMR spectroscopy. The purities of the isolated products were confirmed by HPLC at 215 nm/254 nm and the products were identified by <sup>1</sup>H NMR and by their melting points. The exact methods of preparation including work-up, spectral and analytical data for the obtained products can be found in the Supporting Information.

## Acknowledgements

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