::: Application Report

Applications of Silicon Carbide (SiC) Vessels in Microwave Synthesis

The unique silicon carbide vessel can be employed for a variety of applications in microwave-assisted organic synthesis that cannot be performed in usual glass vials.

1 Introduction

Employing silicon carbide as a heating aid for microwave synthesis is not a new technique - microtiter plates made out of SiC for parallel microwave chemistry applications in multimode instruments were already introduced a few years ago.[1]

However, so far there was no SiC reaction container for monomode microwave instrumentation available.

The present report summarizes the most important fields of application for the unique SiC vessel (Fig 2, officially called „Silicon Carbide Vessel C10") which can exclusively be employed in Monowave 100, 200, 400 and 450. This vessel has proven to be an extremely useful accessory.[2-4]

Fig. 1 The C10 vessel and the G10 vial for the monomode reactors Monowave 100, 200, 400 and 450 have completely similar dimensions.

2 Equipment

IR calibration factors for SiC vessels are already available in the software. Just make sure that the correct vessel type („Silicon Carbide Vessel C10") is selected when creating an experiment.
In Monowave 200, 400 and 450 the SiC vessel can also be used with the Ruby Thermometer.

3 Microwave heating of SiC

SiC heats rapidly in the microwave field, since microwave irradiation induces a flow of electrons that heats the material very efficiently through (ohmic) resistance heating mechanisms.[2] The IR picture in Fig. 2 shows that only 2 - 3 minutes of microwave irradiation at 1400 W are sufficient to heat the SiC vessel to almost 600 °C.

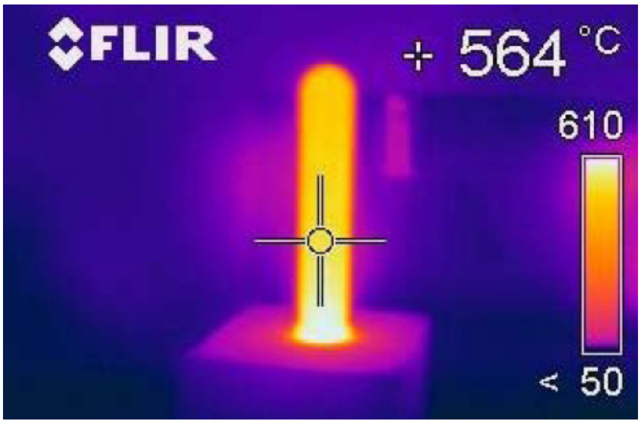


Fig. 2 IR picture of a SiC vessel heated in the cavity of Synthos 3000 (the predecessor of Multiwave PRO).

4 Applications for SiC vessels

4.1 Microwave transparent solvents

Since SiC strongly absorbs microwave energy, also non-absorbing solvents can be heated very efficiently in the microwave field. Fig. 3 shows the heating curves of 5 mL toluene in a standard 10 mL pyrex vial and in a SiC vessel. While in a pyrex vial toluene needs approx. 10 minutes to be heated to 250 °C, the same target temperature can be reached within only 60 seconds in the C10 vessel.

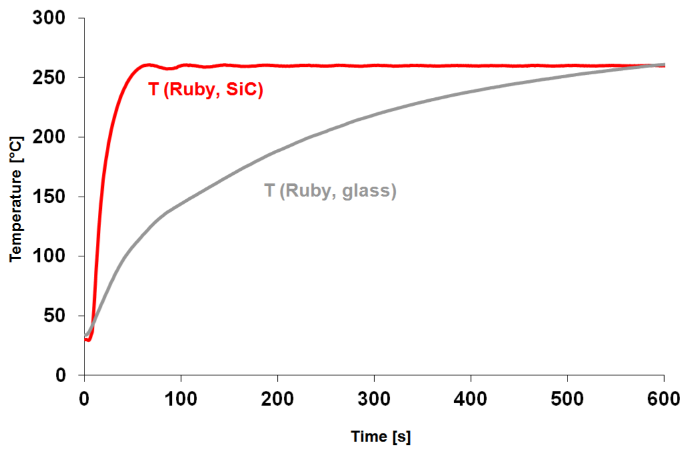
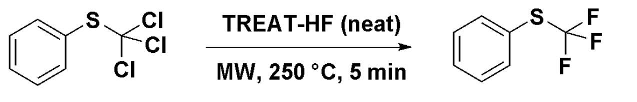


*Fig. 3 Monowave 400 heating curves of 5 mL toluene to 250 °C with Ruby Thermometer control in the G10 vial (gray curve) and in the **C10 vessel** (red curve).*

4.2 Microwave assisted fluorination reactions

It is not only the impressive heating efficiency in the microwave field which makes SiC such a valuable vessel material, but also due to its chemical resistance it is very useful.[2,3] SiC is chemically inert, which means it tolerates not only mineral acids (even aqua regia and hydrofluoric acid) but also alkaline solutions which usually degrade commonly used pyrex reaction vials.

When Kremsner et al. performed the fluorination reaction shown in Scheme 1[3] they noticed significant degradation of the pyrex reaction vessel although HF was not directly applied but generated from TREAT-HF in situ throughout the reaction process (Fig. 4).



Scheme 1: Fluorination of (trichloromethylthio)- benzene

The vessel wall of vial B (Fig. 4) is only 0.35 mm thick and the vial has lost more than 4 grams of its original weight due to corrosion by TREAT-HF.

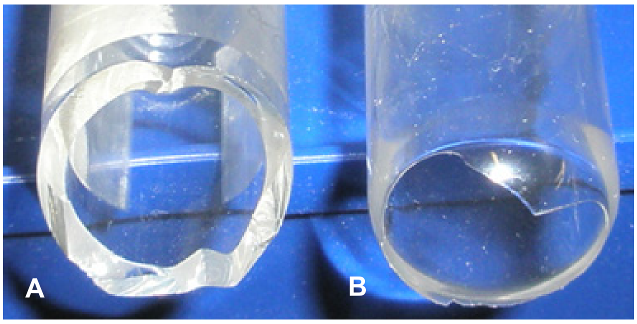


Fig. 4 A: Image of a new broken 10 mL microwave vial. B: Etched microwave vial after several times of reuse under the conditions shown in Scheme 1.

Performing the same reaction in the SiC vessel did not harm the reaction container. The weight of the C10 vessel was similar before and after the reaction and the fluorination resulted in full conversion.[2]

4.3 Investigation of non-thermal microwave effects

Besides its preparative advantages, the SiC vessel can also be used for basic research in the investigation of non-thermal microwave effects.

Since by employing SiC as a vessel material any effects of the electromagnetic field on the reaction mixture can be eliminated, one can rapidly separate thermal from specific (non-thermal) effects.

In 2010, Kappe et al. presented 21 different chemical reaction examples and stated, that in almost every reaction virtually identical results in terms of conversion, purity profiles, and/or isolated product yields were obtained, comparing experiments that involve genuine microwave chemistry in pyrex vials with "microwave heating" in SiC vessels. 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.[2,4]

4.4 Controlling thermal runaways and temperature overshoots

Apart from the possibility to separate thermal from non thermal microwave effects, an additional preparative benefit of SiC vessels involves the control of exothermic reactions. The reaction shown in Scheme 2 usually proceeds in a thermal runaway if performed solvent-free in a pyrex vial under microwave irradiation. Although the magnetron output power was immediately reduced to 0 W as soon as the thermal runaway was initialized, the temperature rose up to ~ 210 °C within 40 seconds. This temperature overshoot was less severe in the SiC experiment. The maximum overshoot is only 26 °C due to the 10 times higher thermal effusivity of SiC compared to Pyrex.[2]

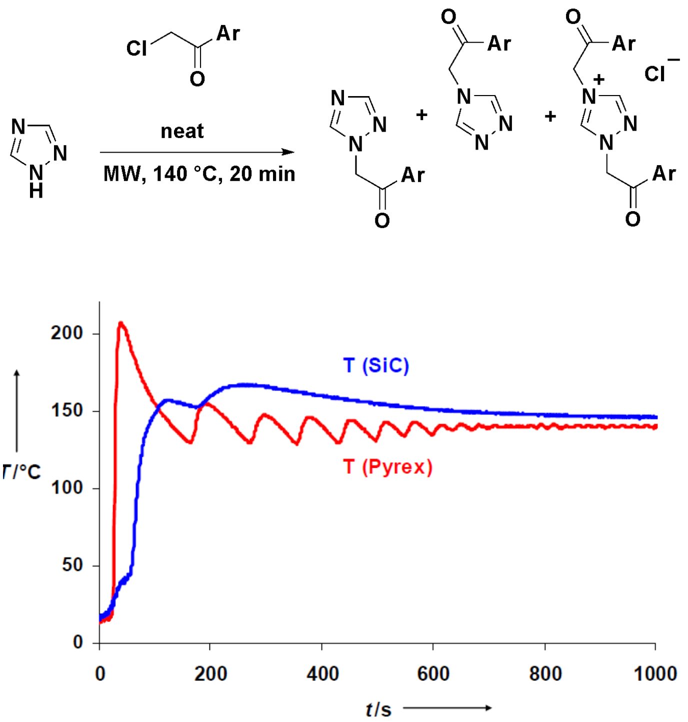


Fig. 5 Scheme and temperature profile for the alkylation of triazole under neat conditions in ***pyrex vials*** *(red curve) and* ***SiC vessels*** *(blue curve). The set temperature in both cases was 140 °C.*

5 Conclusion

Due to its beneficial properties, SiC is a very useful alternative to commonly used pyrex reaction vials for microwave chemistry. 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 use as a vessel material in microwave reactors.

6 References

[1] J. M. Kremsner, A. Stadler, C. O. Kappe, *J. Comb. Chem.* **2007**, *9*, 285; M. Damm, C. O. Kappe, *J. Comb. Chem.* **2009**, *11*, 460; M. Damm, C. O. Kappe, *Mol. Diversity* **2009**, *13*, 529.

[2] B. Gutmann, D. Obermayer, B. Reichart, B. Prekodravac, M. Irfan, J. M. Kremsner, C. O. Kappe, *Chem. Eur. J.* **2010**, 12182.

[3] J. M. Kremsner, M. Rack, C. Pilger, C. O. Kappe, *Tetrahedron Lett.* **2009**, *50*, 3665.

[4] D. Obermayer, B. Gutmann, C. O. Kappe, *Angew. Chem. Int. Ed.* **2009**, *48*, 8321.