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# Gas-Solid Contactors and Catalytic Reactors with Direct Microwave Heating: Current Status and Perspectives

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## ABSTRACT

Microwave heating (MWH) transforms energy from an electromagnetic wave to heat. In contrast to conventional heating (CH) mechanisms that use slower heat transfer processes via conduction, convection or radiation, microwaves (MW) directly interact with MW susceptor materials and induce a rapid conversion of the electromagnetic energy into heat. This rapid heating provides MWH with distinct features that can be leveraged to increase conversion, selectivity and/or energy efficiency of chemical processes. Here we discuss recent significant advances reported in MWH processes involving gas-solid interactions. Special attention is devoted to key aspects such as the methodologies to accurately determine local temperatures under the influence of electromagnetic (EM). Other relevant aspects such as the consideration of the solid catalyst dielectric properties or the design of novel gas-solid contactor configurations will be discussed. Emerging aspects such as the potential of MWH to minimize secondary by-products in high temperature reactions or to efficiently perform in transient processes, e.g. adsorption-desorption cycles, are highlighted. Finally, current challenges and perspectives towards a wide application of MWH in gas solid contactors will be critically discussed.

**KEYWORDS.**

Microwaves; Structured reactors; Heterogeneous Catalysis; Electrification; Cavity; Hot Spots; Selectivity

## 1. Introduction

Most of us are familiar with the use of microwave heating (MWH) in our daily lives, however this instance (heating of polar liquids in a small scale) is just one of the possibilities afforded by MWH, and in fact industrial scale heating is possible using microwaves. Since its discovery in the 1950’s the food industry employs microwaves for drying, thawing, tempering, defrosting, cooking, sterilizing and freeze drying [1]. Vulcanization started in the 1960’s and is also a well-established microwave process [2]. Material processing also leverages the advantages of the fast and efficient heating afforded by MWs, resulting in energy savings and improved properties of the processed materials[3]. These include ceramics, metals and alloys, advanced composites and fiber reinforced plastics [4, 5]. By comparison, chemical processes have been slower to implement microwave-based energy supply. A strong research interest arose during the

1990’s when microwave equipment started to be employed for liquid phase reactions with outstanding results in terms of selectivity and fast kinetics for organic synthesis. The “microwave effect” was often invoked, although in most cases the results could be explained simply as a result of a faster heating or of the generation of hot-spots compared to conventional heating [6, 7]. The mechanisms involved in the heating of solids took longer to be understood and controlled [8], but this subject remains highly interesting because MWH of solids presents the huge advantage of direct energy transfer to the solid material, something of paramount importance in heterogeneous catalysis. On the other hand, MWH of solids presents some important problems of its own, such as the increased probability of hot spots. This problem becomes critical in gas-solid systems, due to the limited heat removal capability of the surrounding gas. In the following sections we discuss some important features of MWH in gas-solid contactors including the main heating mechanisms, scenarios where MWH potential is highest, some guidelines on reactor design and the problems and bottlenecks that must be solved for a widespread application of this technology.

## 2. Heating solids with microwaves

Microwaves comprise the range of wavelengths from 0.01 m to 1 m and the corresponding frequency range of 0.3–300 GHz. MWs have an electric (E-Field) and a magnetic component (H-Field) that propagate perpendicularly in space [8]. The MW field can penetrate suitable materials (those interacting with the electrical or magnetic components) and deposit energy. Thus, heat can be generated throughout the whole volume of the irradiated materials (the so-called volumetric heating), although generally this cannot be achieved in a homogeneous way.

The ability of MWs to heat a solid depends on the specific interaction of the electric and magnetic fields with susceptible elements within the solid. Microwave power absorption (P) and microwave penetration (Dp) are two key parameters directly related with the capability of solids to be heated under MW irradiation. Dp, the penetration depth of the microwave field inside a material, is defined as the depth inside the material when the field intensity has decreased to 36.8% (1/e) of the surface value and can be calculated with the following simplified equation [9]:

$$D_p = \frac{\lambda_o \sqrt{\varepsilon'}}{2\pi\varepsilon''}$$

Where $\lambda_0$ is the wavelength of the incident radiation (12.24 cm for 2.45 GHz and 32.75 cm for 915 MHz), ε´and ε´´ correspond to the real and imaginary parts of permittivity which indicates the polarizability of a material when exposed to an electric field. The real component, also known as dielectric constant (ε´) defines the capability of materials to store electric energy. The imaginary part or loss factor (ε´´) accounts for the loss of electric energy in solids, it represents the ability of the material to dissipate the absorbed electromagnetic energy, converting it into heat. Thus, this is the first value to look at to know if a solid could be easily heated by microwaves. In this sense, and base in our experience materials with a ε´´ below $10^{-2}$ will barely heated by microwaves. The ratio of the imaginary to the real component is the loss tangent (tan δ = ε´´/ε´) a key parameter to evaluate the heating capability of materials under MW field. Different loss processes resulting from the interaction of the electric (E) or magnetic (H) field components of the MW radiation and the material [8] can be used for heating and in fact tan δ must be measured under the specific conditions of use as it depends strongly on the experimental parameters, especially temperature. Table 1 show ε´ and ε´´ values corresponding to some of the most representative supports employed in MW-assisted heterogeneous catalysis. In the case of zeolites, water adsorbed inside the cages plays an important role. Table 1 shows for instance a decrease in loss factor for zeolites after being totally dehydrated. The different zeolitic structure and also the cations, number and type play an important role in the MW heating mechanism [10]. The cations located inside the cages of the structure, move under the electric field of microwaves and are the responsible of the heating. In contrast to zeolites, other materials like carbon nanotubes (CNTs) or SiC typically used as MW absorber show a high loss factor [11-13].

Table 1. Dielectric properties of selected catalytic materials at different temperatures [11-13]

| Material | Temp (K) | Dielectric Constant ε’ | Loss factor ε” |
|---|---|---|---|
| H-ZSM-5<br>(Zeolyst® CBV2314)<br>$SiO_2/Al_2O_3$=23<br>Nominal catión $NH_4$ | 303[a] | 2.76 | $4.26 \bullet 10^{-1}$ |
| | 303 | 2.35 | $9.32 \bullet 10^{-2}$ |
| | 464 | 2.58 | $1.02 \bullet 10^{-1}$ |
| | 565 | 2.58 | $1.01 \bullet 10^{-1}$ |
| ZY<br>(Zeolyst® CBV100)<br>$SiO_2/Al_2O_3$=5.1<br>Nominal cation $Na^+$ | 296[a] | 1.49 | $5.08 \bullet 10^{-2}$ |
| | 311 | 1.33 | $7.89 \bullet 10^{-3}$ |
| | 469 | 1.41 | $2.99 \bullet 10^{-2}$ |
| | 578 | 1.51 | $1.18 \bullet 10^{-1}$ |
| ZY (Zeolyst CBV400)<br>$SiO_2/Al_2O_3$=5.1<br>Nominal cation $H^+$ | 303[a] | 1.54 | $9.01 \bullet 10^{-3}$ |
| | 308 | 1.54 | $7.92 \bullet 10^{-5}$ |
| | 475 | 1.64 | $2.06 \bullet 10^{-2}$ |
| | 582 | 1.72 | $8.21 \bullet 10^{-2}$ |
| ZY (Zeolyst CBV780) | 299[a] | 1.53 | $9.00 \bullet 10^{-3}$ |
| | 307 | 1.42 | $1.41 \bullet 10^{-5}$ |
| | 473 | 1.51 | $1.80 \bullet 10^{-5}$ |
| CNTs<br>(Bayer) | 311 | 17.8 | $2.64 \bullet 10^{+1}$ |
| | 571 | 17.9 | $2.45 \bullet 10^{+1}$ |
| | 1081 | 22.1 | $5.17 \bullet 10^{+1}$ |
| α-SiC | 311 | 17.0 | $7.68 \bullet 10^{-1}$ |
| | 571 | 18.0 | $1.65 \bullet 10^{-1}$ |

| | | | |
|---|---|---|---|
| | 1071 | 26.9 | $6.24 \bullet 10^{0}$ |
| β-SiC | 300 | 6.06 | $1.51 \bullet 10^{-1}$ |
| | 570 | 6.37 | $1.38 \bullet 10^{-1}$ |
| | 1070 | 15.9 | $1.28 \bullet 10^{+1}$ |

[a] Hydrated zeolytes

The average power absorbed P in a specific volume V could be calculated by the following simplified equation [9]:

$$P = \frac{2\pi\varepsilon_0 E_{rms}^2 V}{\lambda_0}$$

where $\varepsilon_0$ is the permittivity of the free space and $E_{rms}^2$ is the root mean square of the electric field E.

There are three mechanisms potentially contributing to MWH: i) Conduction (Joule) loss is the dominant heating mechanism governed by electron movement (i.e. conductivity) induced by the alternating E and H fields in materials with high electrical conductivity, such as metals; ii) Dielectric loss is due to the interaction of dipoles or electric charges present in a material under an alternating E field and includes phenomena such as the polarization of materials, collisions electric charges and interfacial polarization; iii) Magnetic losses arise from the interaction of the magnetic field component of the radiation and the magnetic moment of the material. These losses are caused by Eddy currents, hysteresis, domain wall and electron spin resonance under alternating H fields. This latter mechanism is mostly observed in magnetic iron oxides at high temperatures [14]. Magnetic loss mechanisms were in fact responsible some of the earlier reported MWH processes in gas-solid systems [15]. However, the heating processes in most solids involve the interaction of the E field, and, in this case heating can be dipole or charge carrier based [16]. These mechanisms enable a number of heating possibilities beyond magnetic materials and will be the focus of this section.

The mobile charges in solid conductors also lead to losses under MW irradiation because of Joule heating when electrical conduction is induced by the oscillating E field. In general, there is a correlation between conductivity and microwave heating; as a result, this mechanism is associated to high electrical conductivity materials such as metals. However, in this case it must be considered that Dp can be extremely small. Thus, penetration depth for many important catalytic metals (Pt, Pd and Fe) is in the order of a few microns [14, 17-19]. This skin-level penetration should be enough to heat efficiently micro and nanoparticles, however, achieving meaningful temperature increases in these systems remains challenging due to the small MW absorption cross section and large surface area of micro and nanoparticles, with a rapid heat loss to the surroundings. It has been reported that isolated nanoparticles on a support do not heat up significantly more than the support [20, 21]. In contrast, thin NPs structures consisting of films prepared by sputtering could be heated [22, 23].

Dielectric loss mechanisms are typically associated to interactions with the alternating E-field and include two main processes governed by molecular dipoles or charge recombination. The orientation and relaxation of molecular dipoles governs heating in polar liquids such as water and even some instances of solid heating, as the dipoles may also exist on the surface of the solid. In this case, the interaction of the E field with the solid occurs on the surface at the molecular level. The surface of solids may include MW-sensitive moieties such as hydroxyl groups, amino groups or even oxygen vacancies [24]. In solids with a high specific surface area (e.g. nanoporous solids) the energy deposited through the interaction of the E field with a surface with suitable functional groups can be very considerable [25-27].

The so called “space-charge recombination” is another important mechanism in solids, involving charges carriers [8]. In this case the electric field drives the movement of charges (electrons or ions), resulting in a transient charge-separated state that recombines. This mechanism is one of the most efficient in solids and in some cases could even result in runaway heating processes. In the case of Mott materials exhibiting insulator to metal transition (IMT), the movement of charge carriers (polarons) results in dramatic heating beyond the transition point. In this regard, Gracia et al.[28] observed a heating rate of 660 K/s for a $LaCoO_3$ perovskite. This mechanism was also the driver in the contactless $H_2$ production from water mediated by microwave-triggered redox activation of solid-state ionic materials recently reported by Serra et al. [29].

Zeolites are microporous crystalline aluminosilicates, composed of silica ($SiO_4$) and alumina ($AlO_4$) tetrahedra interconnected with neighboring oxygen atoms. Cations in the framework compensate the charge deficiency to give an electrically neutral material. Ohgushi and co-workers [30-34], Legras et al. [35, 36] and Cherbanski et al. [37] paved the way to understand the influence of the changes of dielectric properties in different zeolites under MW irradiation. They systematically evaluated microwave heating against different hydration levels (i.e. initial water content, that increases heating rate under MW) and how the ionic mobility of smaller monovalent cations ended up with thermal runaways [34] in contrast to zeolites containing bulkier divalent cations [35, 36]. The Si/Al ratio of the zeolite is critical here, as it determines the density of charges to be compensated by cations in the zeolite framework, but also the type of exchange cations, as they have a direct effect on the number of available hopping entities and the activation energy of the jumps (Figure 1a). Apart from the influence of adsorbed water, when zeolites are subjected to MW heating, the ions in the framework jump to different ion-exchange positions and the resulting heating is related to the intensity of the cation hopping process, which in turn is related to the number of mobile cations and the activation energy of each position exchange [10] (Figures 1a-1c). Gracia et al.[10] validated these studies with DFT calculations to carefully identify the influence and key positions of mobile cations. In general, increasing the Al content of the zeolite tend toincrease the MW heating rate by increasing the number of exchange cations. On the other hand, using divalent cations such as $Ca^{2+}$ instead of $Na^+$ will decrease the number of hopping entities and consequently decrease heating (Figure 1a-1c). Also, the use of smaller cations ($Na^+$ instead of $K^+$) tends to decrease the activation energy required for the positional jumps, increasing the frequency of hopping and therefore the intensity of MWH (see Figure 1a-1b).

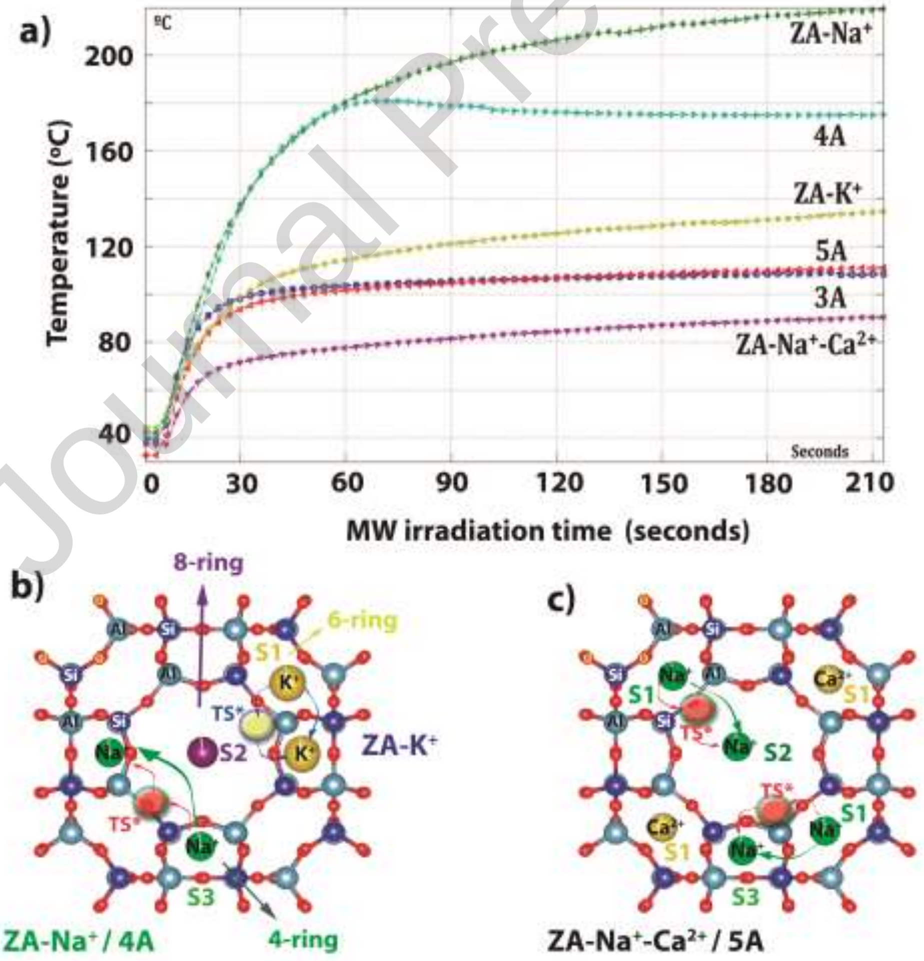

***Figure 1.*** *MWH of zeolite A induced by cation hopping: a) Heating profile of zeolite type A with different cation substitutions; Image reproduced with permission from the American Chemical Society (ref. [10]); b) Projection of Zeolite-A unit cell based on a cubic Pm-3m model describing the main sites for the accommodation of cationic species within the aluminosilicate network and the most probable cation hopping for* $Na^+$ *and* $K^+$ *ions: Sites-1 (S1) correspond to the center of six oxygen rings; Sites-2 (S2) are attributed to in-plane positions within eight-ring cages and Sites-3 (S3) correspond to positions in the vicinity to 4-ring cages; The most favorable transitions for* $Na^+$ *species are restricted from S3 to S3 positions; More voluminous* $K^+$ *jump from S1 to S3 but these transitions are less plausible given its larger size; the more favored transition states (TS) predicted theoretically are also included; c) Description of the most plausible cation hopping in zeolite A containing both* $Na^+$ *and* $Ca^{2+}$ *ions; The presence of divalent cations reduce the number of monovalent cations available thereby reducing the overall MWH effect; the most plausible hopping pathways only involve* $Na^+$ *species shifting from S1 or S2 sites into S3 sites.*

In contrast, for carbon materials the entities responsible for MWH are delocalized π electrons that move on the external surface resulting in an interfacial polarization process [38-40] also leading to intense heating. This has been used for instance to heat carbon materials and achieve the efficient transformation of amorphous carbon to graphitic carbon [38, 39]. Porous carbon structures, such as activated carbon, have increased MW absorption properties, thanks to the enhanced interaction with MWs provided by pore channels [41]. As with zeolites, this has important implications for gas-solid contactors, as a wide variety of carbon materials can be used as catalyst supports or adsorbents while presenting a high dielectric loss (Table 1).

In summary, a plethora of mechanisms enables the heating of solids by microwaves, if susceptible entities such as dipoles or mobile charge carriers are available. However, there are also solids that are not heated by MWs or, more precisely, the heating intensity is not enough to reach high temperatures because the interaction of the field with the solid is weak and heat losses to the surroundings quickly balance the energy deposited by the MW field. In this case it is still possible to benefit from MWH either by functionalization of the solid, to introduce susceptible elements on its surface [24] or by using hybrid fixed bed reactors that include both, the catalyst and a second material that acts as a MW susceptor. Thus, MW energy would be deposited on the susceptor and then transferred by conduction to the catalyst. The use of susceptor materials for MW heating is already well established in the materials processing industry [1, 42-44]. In the case of catalytic reactors the active phase could be mixed with a strong MW susceptor such as carbon or SiC, or supported on particles of these materials [12, 45-50]. Alternatively the catalyst or adsorbent could be deposited in structured reactors made of suitable susceptor materials [50, 51].

## 3. Opportunities enabled by using a microwave field to heat solids

### *3.1. Conventional versus microwave heating of solids*

Conventionally heated gas-solid contactors typically use an external heat source (such as an oil bath, steam, hot gases or electrical resistance) coupled to the reactor wall and heat is then transferred inwards from the wall surface by conduction, convection and radiation, giving a decreasing temperature profile with a minimum at the center of the reactor (see Figure 2a). This conventional heating (CH) mechanism is relatively slow and inefficient, and depends on the thermal conductivity of the material and on convection patterns. In addition, in CH the temperature is highest at the reactor wall, and this may lead to multiple undesired side reactions on this region [50-54].

In contrast, MWH operates on a completely different way.  First, penetration is instantaneous, without time delay, and takes place in the whole volume, according to the material parameters (P, Dp). As illustrated in Figure 2b, the highest temperature is usually at the center of the heated volume unlike CH [48, 55, 56]. More importantly, heating is selective, meaning that in a volume occupied by heterogeneous materials, those susceptible to MWs will heat up first, allowing the design of materials with hot and colder domains under MWH. These intrinsic characteristics of MWH provide unique opportunities in terms of increased conversion, selectivity and energy efficiency, as will be shown below.

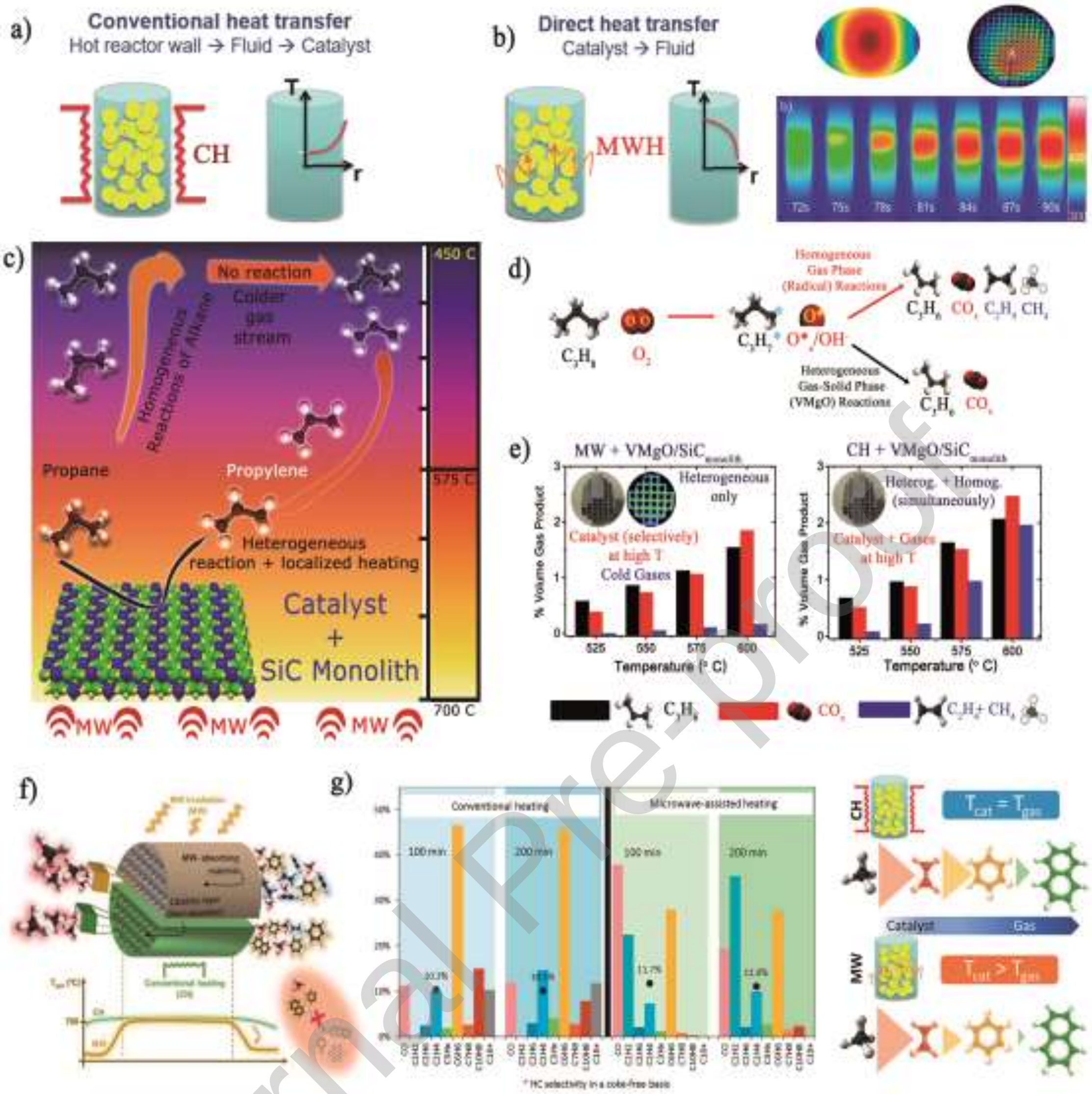

*Figure 2. Conventional versus Microwave Heating: a) Schematic illustration of the a conventional heating mechanism where heat transport occurs via convection/conduction mechanisms from the external heating source into the center of the reactor establishing a temperature gradient until steady conditions are reached; b) Schematic illustration of the MW heating mechanism where the electromagnetic radiation penetrates and specifically heats the MW suscepting materials from inside the reactor; Additional insets display the heating profiles experimentally obtained upon heating a lanthanum cobaltite deployed on structured monoliths or the heating of Pt-Y zeolite on a fixed quartz bed reactor; Images adapted with permission from [28] and*

*[57]; c) Scheme illustrating the mechanism behind the enhanced selectivity observed in the oxidative dehydrogenation (ODH) of propane carried out under MWH conditions of a structured SiC monolith coated with a VMgO catalyst; the selective heating of the catalyst favors a gas to solid gradient that prevents the formation of secondary by-products via homogeneous mechanisms; d) Main ODH propane reaction pathways and by-products formed in the heterogeneous and homogeneous mechanisms; e) Influence of the CH and MWH conditions on the ODH propane product distribution; Images adapted with permission from ref. [53]; f)-g) Influence of CH and MWH on the overall product distribution of the methane non-oxidative coupling (MNOC) reaction; the temperature gap favors the formation of light hydrocarbons and retards the formation of coke deposits; Images adapted with permission from ref. [50].*

### *3.2. A more efficient energy supply*

The direct energy supply afforded by MWH is faster and more efficient than conventional heating procedures as demonstrated for a number of heterogeneous catalytic processes, and extremely high heating rates (> 500 ºC/s) can be achieved using adequate MW susceptors and conditions [28, 55, 58]. These are possible because of the volumetric nature of MWH that allows instantaneous energy deposition to take place throughout the susceptible material volume. Instead, in conventional heat transfer a sequential process takes place from the reactor wall to the fluid, then to the solid catalyst surface and finally to the inside of the catalyst particles. This leads to a highly efficient deposition of energy that is the basis for the improvements observed in a wide variety of processes (as example of comprehensive recent reviews see e.g. [59, 60]). Ondruschka and coworkers [61] carried out a detailed comparison of conventionally heated and microwave-heated reactors for the same process (oxidation of methanol in air) and showed that a conventional system would require 280 ºC, 1 h preheating and a consumption of 393 kWh per working day, compared with 160 ºC, 18 min and 203 kWh for the system under MWH. Bermudez et al. [62] evaluated MW heating for a number of scaled up processes, including torrefaction of wheat straw, heating of water, synthesis of xerogels, calcination of charcoal and treatment of metallurgical coke. The authors found that scaling up the processes from 5 g up to 100-200 g involved a 90-95% decrease in specific energy consumption, regardless of the process.

However, the use of MWH is especially interesting for endothermic gas-solid catalytic processes, as it deposits the energy where it is needed, on the catalyst itself. This provides the same reactant conversion at lower overall temperatures, as reported for instance in several gas phase dehydrogenation reactions [63-66]. It can also be very attractive for exothermic systems when the energy released is not enough to sustain the reaction. For instance, if combustion were used to purify air containing some tens of ppm of an organic pollutant, under CH the whole air stream would have to be heated to the desired temperature, several hundred of degrees. In contrast with MW heating only the solid catalyst needs to be heated to the combustion temperature. Since the solid is directly heated by microwaves and heat loss to the gas phase is limited (gas-solid heat transfer coefficients are typically one to two orders of magnitude smaller than liquid-solid heat transfer coefficients, even under forced convection) the gas temperature can be considerably lower (tens to hundreds of ºC) than that of the solid phase, especially when structured monolith reactors [51, 52, 54] or fluidized bed reactors are used [67, 68]. Summarizing, the largest gradients are produced if energy is deposited in the solid at a high rate (due to microwave heating and/or due to the exothermic reaction itself) while energy is removed from the solid at a lower rate (for instance in gas-solid systems under slower heat transfer conditions). To increase the rate of energy deposition in the solid materials with high dielectric losses are the best candidates. To reduce the heat transfer from the solid to the surroundings, suitable operating modes and reactors (e.g. monolith rather than packed beds) can be selected.

This concept is even more interesting for periodic operation, as it makes use of the main characteristic of MWH, namely the selective and instantaneous energy transfer to the solid. Thus for instance, in VOCs removal from dilute streams using adsorption or adsorption-combustion processes, an efficient capture of the VOC from the air stream is first achieved with the adsorbent at lower temperature, then MWH is applied to achieve an extremely fast desorption [57, 69], leading to a concentrated VOC stream that can then be converted by conventional or MW-assisted combustion processes. The nearly instantaneous nature of MWH could also prove invaluable in other processes where achieving a fast approach to the desired reaction temperature is critical, e.g. reducing the cold start emissions in catalytic converters [66, 70].

### *3.3. A higher reaction selectivity*

Taking into account the previous discussion on the possibility of operating with a substantially lower temperature in the gas phase surrounding the solid, the main scenario for selectivity increase is straightforward: reactions where gas phase processes are detrimental to selectivity. A prototypical case could be methane oxidative coupling, where consecutive gas-phase reactions may reduce the selectivity towards the desired products. In this case, it has been concluded that the lower gas phase temperature afforded by MWH leads to a higher selectivity, at least for low and intermediate conversions [55]. In 2004, Ondruschka and coworkers [56] reviewed different MW-assisted gas phase processes and noted several instances where different product distributions were reported when working under MWH or CH conditions, but concluded that these differences could generally be explained by the formation of undetected hot spots because of MWH. The problem of hot spots and arcing was also discussed recently in the excellent review of MW heating for multiphase reactors by Vlachos and coworkers [46], and again was deemed responsible for many of the gains reported in conversion and selectivity in a variety of chemical processes. In fact, the possibility of hot spots has plagued the field of MW-heated reactors with uncertainty, underlining the need for accurate and extensive real time temperature measurements, as will be discussed below. However, there are some systems where the selectivity improvement gained by depleting gas phase processes has been clearly demonstrated. Recently, in two different works of our laboratory we investigated oxidative dehydrogenation of propane [53] (Figures 2c-2e) and $CO_2$-mediated oxidative dehydrogenation of isobutene [52]. In both cases, the temperature of the gas and solid phases were measured simultaneously and significant selectivity improvements were observed when MWH was used instead of CH thanks to the 50-70 K lower gas phase temperatures. An increased selectivity was also predicted in a simulation study for n-butane oxidation in a fluidized bed reactor [68].

Another case of changes in selectivity because of a lower gas phase temperature under MWH was reported by Julian et al. [50] for methane non-oxidative coupling (MNOC) (Figure 2f-2g). Under MWH the product distribution was shifted towards $C_2$ hydrocarbons with a much lower concentration of aromatic hydrocarbons, that act as precursors of coke, the main responsible for catalyst deactivation in this process. The rate of coke deposition was halved and a much more stable operation could be achieved. In addition, independently of gas phase temperature, the very shape of the temperature profile obtained under MWH (Figure 2f) also helped to decrease the amount of byproducts formed: under CH the hottest point is often at the metallic wall of the reactor, that acts as a focus for molecule decomposition and coke formation, while this is the coldest spot when operating under MWH.

### *3.4. Transient operation*

The fast, selective and volumetric action that constitutes the trademark of microwave heating has for a long time been used in drying processes [71-74], but is also extremely attractive for processes where a rapid temperature cycling is needed. In gas-solid systems the list includes primarily adsorption and adsorption-reaction processes, where MWH is used to achieve a rapid and efficient regeneration of the solid adsorbent, with less energy wasted in the form of heat losses to the surroundings and less sensible enthalpy in the exit gas stream [37, 75]. This requires of course that the adsorbent itself is MW-sensitive (e.g. carbon, zeolites) or, alternatively, that it can be made MW-sensitive through functionalization (e.g. amino-functionalized silica) (Figures 3a-3c) or by putting it in close contact with MW-sensitive elements (such as SiC).

The advantages of MWH for the regeneration of MW-sensitive adsorbents are obvious, since the solid undergoes fast heating thanks to the energy directly deposited by MWs. This is not only more energy efficient (no energy is wasted heating the gas stream and the reactor itself), but also gives rise to a swift desorption of the adsorbate, producing a concentrated stream that can then be subjected to downstream processing, e.g. by condensation or combustion. It is also interesting to exploit the selective heating of MWs in systems with more than one adsorbate. Legras et al.[76] conducted competitive adsorption experiments using different zeolites (NaX, NaY, DAY, NaA) and adsorbate pairs of different polarity (i.e. $H_2O/CO_2$ and $H_2O$/Toluene). As could be expected, they found no significant differences in the selectivity of the co-adsorption equilibria regardless of the heating mechanism or the packing of the catalyst bed (fixed vs. fluidized), the adsorption process was only controlled by temperature. Interestingly, they explored the combination of different zeolites with different MW response within the same bed and were able to use the preferential heating of the more hydrophilic zeolite (higher Al content) to transfer heat to a dealuminated zeolite with low dielectric loss where less polar compounds were preferentially adsorbed. In another example of competitive adsorption, Nigar et al.[69] also explored the selective adsorption and removal of low amounts of n-hexane from humid air and MW-powered desorption in a Microwave Swing Adsorption (MWSA) process. In this case, dealuminated zeolite Y (DAY) was identified as a proper target: a zeolite with sufficient MW response in spite of its reduced Al content, and still organophilic enough to adsorb VOCs in the presence of water moisture excess (that will be always present in real scenarios). The efficiency of MWH was patent in the sharp, fast desorption peaks obtained in comparison with CH, even under high heating rates.

The concept of coupled adsorption and desorption/combustion was explored by the same authors using hybrid zeolite beds [57] (Figure 3d). In this case two zeolites with different MW susceptibility and hydrophobicity (thanks to their different Si/Al ratios, NaY (Si/Al=2.5) and DAY (Si/Al=40)) were packed separately in a two-stage fixed bed (Figures 3e-3f). DAY adsorbed hexane from moist polluted air and quickly released it when MWH was activated. On the other hand, the NaY zeolite was been doped with 1.5 wt% Pt [77] to enable combustion of the desorbed hexane. Upon activation of MWH both sections heat simultaneously (Figure 3f). Hexane was released from the DAY bed, then entered the Pt/NaY bed, that was already hot enough to fully convert it to $CO_2$

(Figures 3g-3h). Thanks to the very rapid heating provided by MWH (the combustion temperature of ca 500 K was reached in little over one minute) continuous removal of 400 ppm of hexane in air was possible by periodic operation in which MWH was active less than 40% of the time (Figures 3g-3h). Other recent examples in the literature have explored the modification of conventional NaY zeolites to diminish their hydrophilicity as alternative to maximize the absorption of VOCs while maintaining a sufficiently active MW response [78].

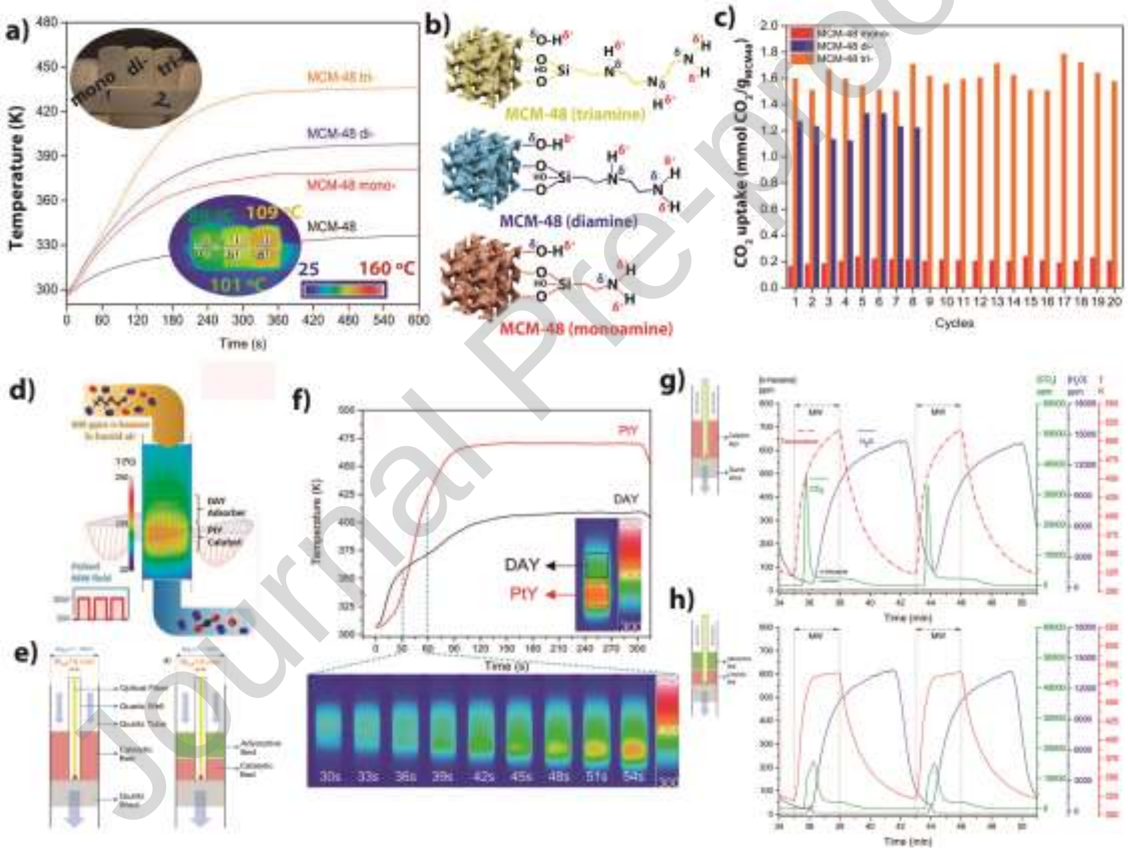

*__Figure 3.__ Adsorption, desorption and reaction under MWH conditions: a) Heating profiles obtained with MCM-48 catalysts functionalized with different amine groups that enhance their interaction with $CO_2$ and their affinity towards MWH; insets correspond to the digital images of different MCM-48 slabs and the corresponding temperatures detected on their surface under MWH by an IR camera (Images adapted with permission from [24]); b) Scheme of the MCM-48 supports and the corresponding*

*amine groups grafted; the main dipoles responsible for the MW induced response are also depicted; c) Cyclic* $CO_2$ *adsorption cycles after MW induced regeneration with* $N_2$ *purge gas; Adapted with permission from ref. [24]; d) Schematic display of the two-bed reactor for adsorption-desorption-reaction of n-hexane; e) Schemes illustrating the differences between the single bed containing the DAY zeolite (preferentially adsorbent) and the double bed concept including a DAY bed accompanied by a second reactive bed containing Pt Y zeolite; f) Heating profiles induced by MWH for a DAY and a Pt-Y zeolites and the corresponding thermal images acquired during the heating; g)-h) Influence of MWH on the time course evolution of the n-hexane,* $CO_2$*,* $H_2O$ *concentrations and reactor wall temperatures in the single bed and double bed configurations, respectively; Images from f)-g)-h) reproduced with permission of the American Chemical Society from ref. [57].*

As already mentioned, carbon materials in general and especially microporous carbons (MCs) represent another appealing alternative for rapid adsorption-regeneration processes using MWH. MCs exhibit a high affinity towards VOCs in comparison with the zeolitic family and they also present a strong susceptibility to MW [41, 79] that can increase considerably, depending on the nature of the C bonding and/or the presence of different surface functionalities. In contrast, there are some drawbacks such as flammability [79-81] instability in oxygen-containing atmospheres and sometimes challenging heating control due to generation of hot spots and electric arcs under MW irradiation [82]. However, porous carbon presents exciting possibilities in its dual capacity as both MW susceptor and catalyst support or adsorbent and will undoubtedly be a strong candidate for processes that can operate in the absence of oxygen. Also, even thin carbon layers offer the possibility of turning a MW-inert system into a strong MW susceptor, as demonstrated by Chaouki et al. [67] using a submicron C coating on silica beads. Furthermore, the extremely fast heating rates that can be obtained with both, carbon supports and some zeolites offer the possibility of using these particles as a confined environment in which pre-adsorbed reactants can be converted. This has been shown with contaminants such as $SO_x$ or $NO_x$ in carbon-based adsorbants under MWH [60]. The pre-adsorption of $CO_2$ or light alcohols [83-85] can be also of great interest for the production of fuels after rapid activation with MW. In this regard, multifunctional catalytic beds involving materials with different chemical selectivity (and possibly different susceptibility to MWH) could offer interesting possibilities in cascade reactions (e.g. $CO_2$ to aromatics) [86, 87].

## 4. Microwave reactor designs and scale-up feasibility

The design of contactors for processes under MWH is a subject that is often overlooked, in spite of its central role in the performance of microwave-heated reactors. A microwave-heated reactor consists mainly on three components, i) a microwave source that can be either a magnetron or a solid-state generator; ii) a waveguide where the microwaves are directed to the target to be heated and iii) the microwave cavity itself, where the reactor is located. The design of microwave system determines the distribution of the electric and magnetic fields in the solid and thus the heating patterns and the resulting temperature distribution. There are three basic reactor types regarding the way microwaves are supplied to the catalyst: multimode, monomode and travelling wave microwave reactors. They are schematically presented in Figure 4.

In a multimode cavity, the type commonly found in domestic applications, a generator (typically a magnetron) drives microwaves inside a metallic container and the waves get reflected in all directions, resulting in multiple resonance modes in the cavity. The heating is highly inhomogeneous, even with the application of the so-called mode stirrers (typically rotating metallic structures), and results in intense hot spots unless the load (material to be heated) is rotated, which may present significant challenges for high temperature gas phase processes. In spite of this, multimode contactors are the most frequently employed at the industrial scale [1, 4, 5], mainly in low temperature applications, such as heating of aqueous liquids and drying of solids. However, it is interesting to note that, for gas-solid reactions, there is already an example of a scaled up configuration using multimode MW heating. Ondruschka and coworkers modified a multimode MW with the addition of a second magnetron and the fine-tuning of the heating mode, adjusting the intensity of the MW field from a few watts to kilowatts (Figures 4a-4b). They were able to attain a uniform heating during propane combustion [56, 61] or methanol combustion. Another interesting system was developed by Kanno and coworkers [88] and instead of rotating the solid load, a circulating fluidized bed was used. A multimode MWH was applied to the riser part of a circulating fluid bed reactor for the decomposition of trichloroethylene. Only a limited throughput and conversion were achieved, but the authors stated that the system was amenable to a scaled up version (10 kg/h) with a higher applied MW power.

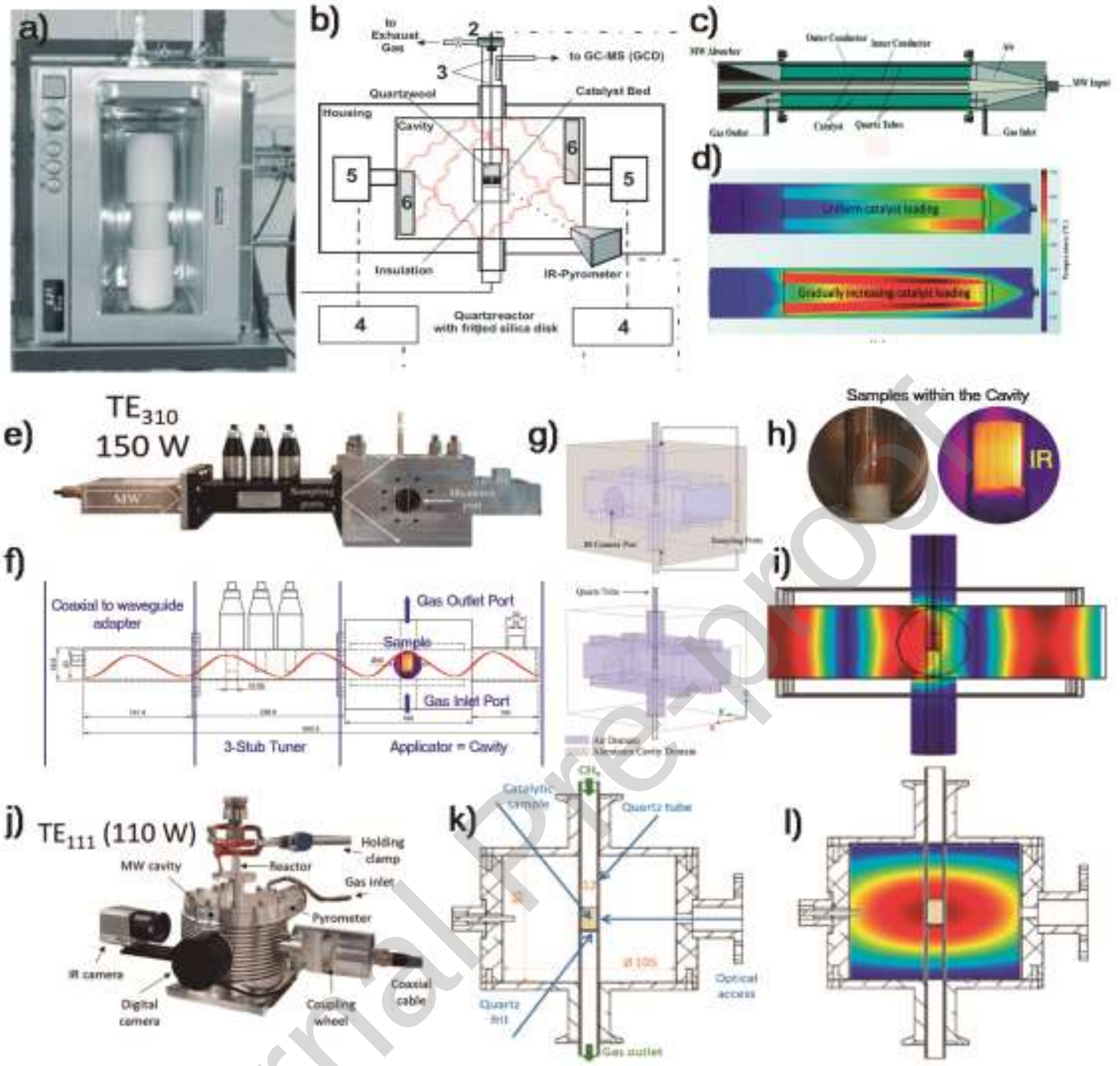

*Figure 4. Microwave reactor setups: a) Digital picture of the modified multimode MW cavity used for heterogeneous catalysis (reprinted with permission from ref. [56]; Scheme of the multimode MW cavity including the main components: 4: switched mode power supply; 5: magnetrons; 6: turning antennas; Adapted with permission from ref. [56]; c)-d) Schematic overview of a travelling MW reactor and the corresponding heating profiles upon different loading patterns: uniform and gradually increasing; Images reproduced with permission of the Royal Society of Chemistry from ref. [58]; e)-f) Digital image and schematic fixed-angle projection of the 3D modeled empty microwave heating cavity corresponding to a 3-Stub Tuner monomode MW cavity able*

*to operate at a maximum power of 150 W (manufacturer: Saica Iberica) in a* $TE_{310}$ *resonant mode; g) Perspective views of the cavities (assuming aluminum or air domains); Images reproduced with permission from ref. [89]; h) Digital images and IR images corresponding to a monolith placed at the center of the MW cavity and subjected to MW irradiation; Images reproduced with permission from ref. [52]; i) Simulated electric field distribution inside the loaded cavity; Reproduced with permission from ref. [89]; j)-k)-l) Stainless-steel cylindrically-shaped resonator working in a* $TE_{111}$ *resonant mode, in which the maximum electric field is found at the cavity center with a substantially constant field area; This microwave resonator prototype was designed and fabricated by the DIMAS group (Polytechnical University of Valencia, Spain).*

Monomode cavities, on the other hand offer a much more homogeneous MW field thanks to a standing wave design with only one mode present inside the waveguide (Figures 4e-4l). Their main limitation is that a high and homogeneous field can only achieved near the nodes of the standing field, meaning that the effective dimensions for heating are about one third of the wavelength, a few cm in the case of a 2.45 GHz microwave. In addition, the location of the maximum intensity nodes in the standing wave changes depending on the volume and dielectric properties of the load introduced. To make the position of the maximum intensity coincident with the location of the load, the position of the maximum has to be shifted using moving devices such as stub tuners or sliding short circuit, another feature that represents a significant obstacle for scaled up applications (Figures 4e-4f). It is also possible to adjust the position by changing the frequency of the MW, though only when solid state generator are used as the MW source [89] (Figures 4j-4l). Another important requirement of both monomode and multimode MW-heated reactors is that the wall of the chemical reactor itself (i.e. the vessel where the catalyst and the reactants are contained) must allow the pass of MWs, meaning that metals cannot be used as wall materials and the reactors have to be constructed of suitable materials such as silica, quartz or Teflon®, another important drawback especially for gas-solid systems.

Finally, the third type of MW-heated contactors corresponds to the so-called travelling microwave reactors (TMWR) (Figures 4c-4d). In principle, TMWR avoid both the multiple reflection problems of multimode systems and the maximum node location problems caused by the resonant requirements of monomode cavities, as explained by Stankiewicz and co-workers [90, 91]. In addition, the TMWR is able to circumvent the non-metallic wall problem, as the waveguide itself can act as the reactor wall and be filled with catalysts and contain the gas flow in gas-solid processes. As drawbacks, the design of the TMWR can be considerably more complex, with MW input and output port design issues and strong temperature non-uniformities [92], or the requirements of conical sections to improve MW field homogeneity along the reactor length [93]. The most frequent arrangement in the catalytic TMWR involves a coaxial configuration with the catalyst packed in the annular space between both walls, although other modified traveling wave reactor designs have been proposed, e.g. a reverse traveling wave [94] and rectangular traveling wave [95].

In spite of its size limitations, the monomode configuration can provide high field intensity and relatively homogeneous temperature profiles in the catalytic samples, so it is preferred for high temperature conditions (T > 450 ºC) (Figures 4i and 4l). Therefore, the question of scaling up reactor throughput in this cavity arises. Recently, Julian et al. [12, 49] performed a 150-fold scale up for a monomodal reactor used for methane aromatization (MDA). Furthermore, the operability of the system was demonstrated working remotely under unmanned conditions using a TE10x microwave cavity and a solid-state generator operating at frequencies 902-928 MHz, maximum power 600 W. The system processed 150 times higher reactant flows (at the same spatial velocity) just using a six-fold higher microwave power input with respect to the lab-scale cavity [12, 49]. However, a rotary design was required in this case to obtain homogeneous heating profiles. Among the scarce examples of scaled-up MW commercial reactors operating at industrial scale for gas-solid processes are those of Bionic Laboratories and Microwave Chemical Co, in Germany and Japan, respectively [43]. These companies take advantage of MWH for the gasification and pyrolysis of biomass, wastes and other feedstocks [96-102]. It is foreseeable that the evolution of solid-state MW generators will further extend the MW irradiation ranges, allowing greater flexibility of operation.

In addition to the way MWs are supplied to the reactor, the type of reactor itself is of great importance for MW-heated reactors. Thus, while fixed bed reactors are often used on account of their simple operation and high catalyst density, they are prone to the development of hot spots and arcing at particle to particle contact points [103]. It is noteworthy that fixed bed reactors as such are only usable when the catalyst itself or the catalyst support are able to absorb microwaves. Otherwise, as noted above, the catalyst needs to be deposited on a suitable MW susceptor or mixed with a susceptor solid in a hybrid packed bed configuration.

When structured reactors are used, the material that forms the structure is often the MW susceptor itself. SiC is widely used in this role, on account of its high MW absorption (tan $\delta = 0.2$) and good thermal conductivity, that helps to dissipate hot spots. In this respect, the probability of hot spot formation in a monolith with straight channels is smaller than in a foam of the same material, due to the fact that the electromagnetic field is intensified at sharp edges (see Figures 5a and 5d). However, the amount of catalyst supported on straight channel structured reactors is limited, giving a low overall catalyst density in the reactor. Vlachos et al.[45] alleviated this problem by packing their catalyst inside the channels of a SiC monolith (Figures 5b to 5d). The high MW susceptibility of SiC and its good thermal conductivity allowed the operation of the hybrid structured-packed bed reactor with a high catalyst loading, allowing to process higher gas flow rates (Figures 5b to 5d). Computational Fluid Dynamic (CFD) showed the influence of flow rate (residence time) and heat transport between wall and gas phase on the gas-solid temperature gaps inside the MW irradiated monolith. Under certain conditions (not necessarily for endothermal processes), simulation studies suggest that a rapid quenching of the gas immediately after the MW heated structured reactor could strongly contribute to the suppression of secondary gas-phase reactions [45].

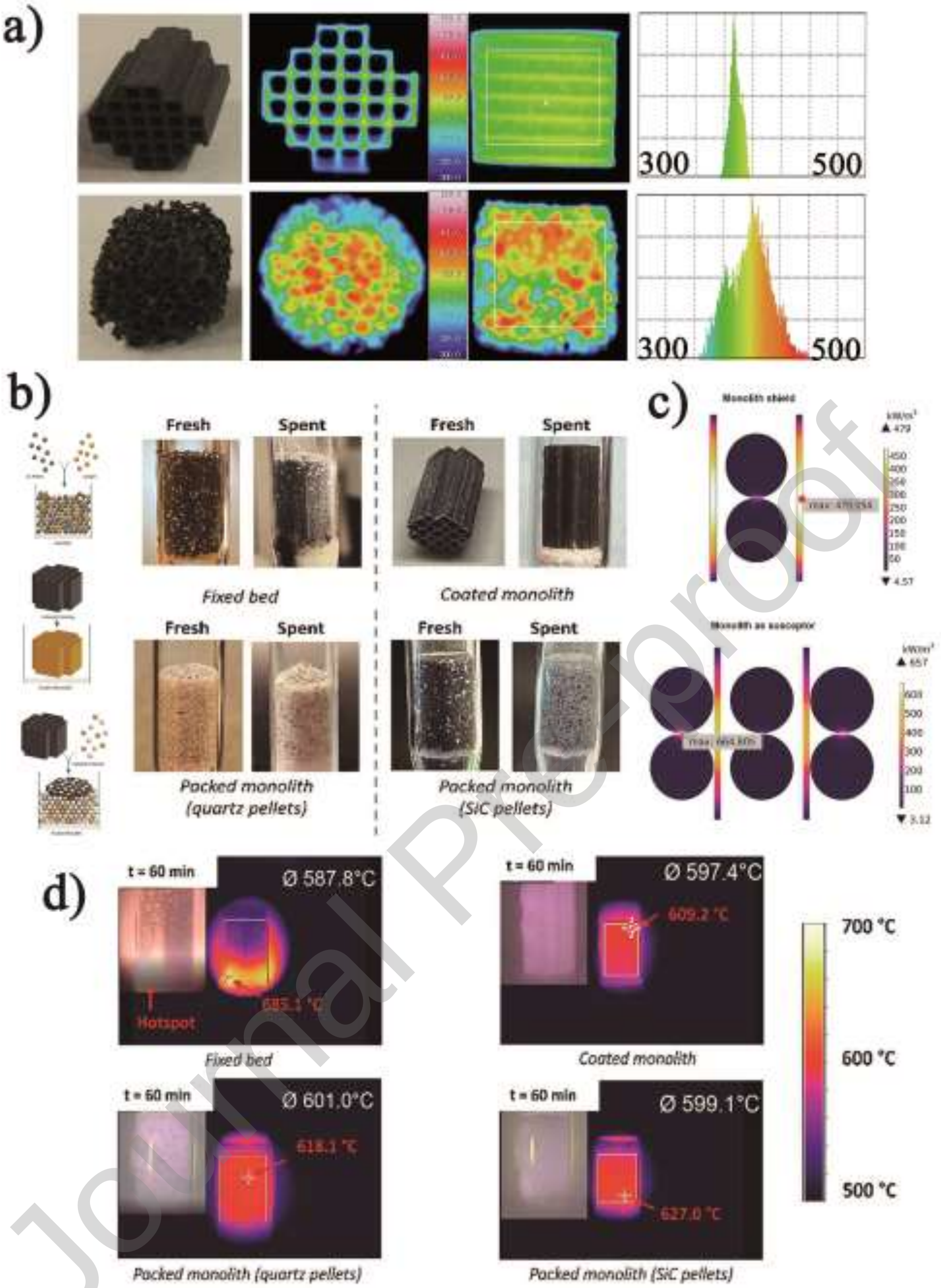

***Figure 5.*** *Structured and packed catalytic beds under MWH conditions: a) Influence of the morphology of SiC supports and how foam render a major number of hot spots during MW irradiation in comparison with straight-channel monoliths; Images reproduced with permission from ref. [53]; b) Schematic display of different packing configurations of catalysts for MW induced gas phase reactions: fixed bed, coated monolith, and packed monolith. In the packed monolith, a microwave absorbing*

*material, such as SiC, can be used as a heating scaffold and filled with pellets of other active (catalyst) or inactive (quartz) materials; c) Scheme of particles inside the monolith channels; Cross sections of electromagnetic power dissipation density in particles shielded by a monolith and particles placed inside and outside a monolith; Images adapted with permission from ref. [45]; d) IR and digital (insets) images of the reactors under different packing configurations during the MW induced ethane dehydrogenation reaction; Images reprinted with permission from ref. [45].*

Other opportunities to develop new reactor configurations beyond conventional fixed bed reactors rely on the use of fluidized or moving beds. These alternative designs could help to overcome the drawbacks of non-uniform heating. Thus, the inherent temperature uniformity in bubbling fluidized bed reactors thanks to the solid mixing can be leveraged to avoid hot-spots common under MWH. A circulating fluidized bed irradiated by MWs was employed for coating powders by CVD-plasma [104]. Other examples of MW-heated fluidized bed catalytic reactors have been cited above (*vide supra*), including decomposition of trichloroethylene, dry reforming of methane and oxidation of hydrocarbons.

## 5. Problems and bottlenecks in the development of MW-heated contactors

Significant problems in the use of MW reactors at industrial scale have already been mentioned. The difficulties in scaling up monomode reactors are real and are related to intrinsic MW characteristics such as the wavelength used, that determines the region where a more homogeneous field can be achieved. Also, the need to have a MW-transparent wall may represent a serious problem in high pressure or high temperature gas-solid processes, where materials and gas tightness requirements become more complex. However, the main problem in the development of larger scale MW reactors remains that of a reliable temperature measurement and control. Although this is a key feature (e.g. as shown above solid-gas temperature differences hold the key for the selectivity found in some systems and undetected hot spots on the other hand are thought to be responsible for the apparent enhancement of yields reported in some reactors under MWH), the methods for temperature measurement at still lacking and a strong effort in this direction is urgently needed.

Conventional temperature measurements (e.g. contact thermometers and thermocouples) are strongly restricted under an electromagnetic field, as pointed out by Stankiewicz and co-workers [91, 105]. Optical fibers may be used and do not interfere with microwaves, but standard optical fibers can only work at temperatures up to 300 ºC. There are other optical fibers, e.g. those based on doped silica, that can accurately measure temperatures in excess of 1000 ºC [106], or the metal-coating free optical fiber able to measure temperatures up to 1550 ºC, developed by Lin et al. [107]. All of these special fibers are very expensive and in any case give only a point measurement, i.e. undetected hot spots are still likely to happen given the strong temperature gradients that can be encountered in gas-solid systems. In liquid-solid systems temperature gradient are likely to be lower, thanks to the higher heat removal capability of liquids. For instance, temperature distributions have been assessed by means of fluorescent molecules located on the surface of the solid [108], and a temperature gradient of 12 ºC was measured while the liquid phase was at 48ºC [109]. In the case of higher temperatures, the organic probes will be degraded. Contactless systems such as thermal cameras or pyrometers use infrared radiation to estimate the temperature of the target objects. Their main limitation is that their accuracy depends on the correct estimation of the emissivity of the heated material at a given temperature and surrounding atmosphere

[51, 54]. The changes of emissivity with temperature is characteristic for each material [110]. In addition, some gases absorb infrared radiation in the spectral range of the contactless devices (typically 8 – 14 µm wavelength) and some others not. Moreover, these contactless thermometers only provide an estimation of temperatures at the surface exposed to the infrared readings. However, due to the microwave volumetric heating mechanism the core of the heated material is hotter than the external surface, adding uncertainty to the temperature measurement in microwave-assisted catalytic systems.

For specific systems, some alternative protocols may provide a more accurate estimation of inner temperatures. Thus, Garcia-Banos et al.[111] developed a method to estimate the temperature of the inner core of fixed beds based on the measurement of the outer bed layer coupled with in-situ Raman spectroscopy. Using materials with well-known phase transitions they correlated Raman spectra with the phase-change temperature and, thus, sample core temperature. For thin packed beds (1 cm diameter) they found that the inner temperature was roughly 20% higher than that measured at the external surface. Ramirez et al. [51, 52, 54] also used specific properties (in this case infrared-absorbing reaction atmosphere) to be able to estimate solid-gas temperature differences in straight-channel monoliths under MWH, using top view monolith readings with an infrared camera (Figures 6a to 6j). They were able to estimate the apparent emissivity of the reactive gas mixture at different temperatures and used IR transparent windows that for the first time allowed simultaneous monitoring of gas and solid temperatures under microwave heating (Figures 6a-6f). With a careful calibration they estimated the temperature gap at 50–60 K for the conditions used in that work [54] (Figures 6a-6j). Similar combinations of IR techniques with IR transparent windows have already been used in the literature to measure temperatures in heterogeneous catalytic systems and to determine the enthalpy of fast exothermic reactions. Ramirez et al. [52] also used gas-phase kinetic models to indirectly obtain the gas phase temperature based on the product distribution coming from homogeneous gas-phase reactions, and used this value to estimate the stable gas-solid temperature gap in the reactor [52].

The key factor for unmanned operation of catalytic system is based on achieving homogeneous temperature in the system and appropriate measurement combined with a control loop [49]. This was successfully achieved in the SiC coated monolith scale-up system for MDA, heated with a solid state generator in a monomode cavity. The temperature was measured with a thermographic camera, focusing the central part of the monolith through a lateral window of the cavity (Figures 6k-6n). A continuous rotation of the system at 6 rpm ensured homogeneous temperature profile with a maximum temperature difference between the hottest spot and the average sample temperature along the observation area below 15 ºC. The implemented control loop enabled to switch from reaction cycles at 680 ºC to regeneration at 580 ºC, thanks to the interconnection between automatic valves, thermal camera and MW generator. The system was successfully operated for almost 300 uninterrupted hours (Figures 6k-6n).

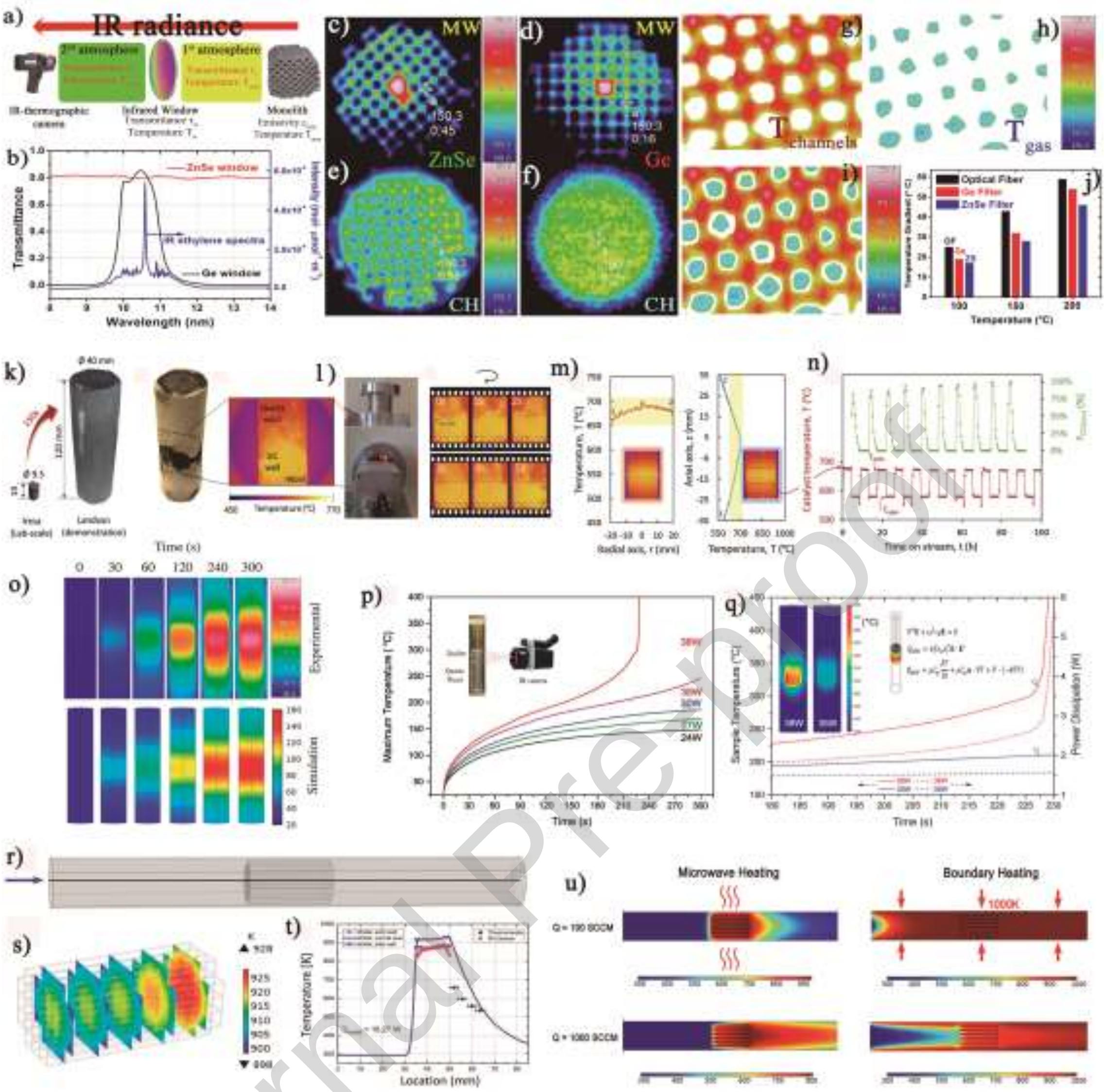

*Figure 6. Temperature measurements: Experimental acquisition and numerical simulations: a) Experimental determination of reaction temperatures using an IR thermographic camera; different parameters must be carefully taken into account (i.e. transmittance, IR spectra of the reactants, composition of windows and their specific absorption parameters); b) Schematic representation of the different factors under evaluation that can influence the readings of the thermographic camera. Left axis: IR transmittance of the employed Ge and ZnSe windows; Right axis: Infrared spectra of ethylene; c) to f) Thermal images of monolith inside the reaction vessel, under conventional and MW heating and using different windows compositions (Ge or ZnSe);*

*g) to i) Close-up thermal image reconstruction of the monolith surface, the gas phase along the monolith channel and the merging reconstruction; j) Average temperature gradients between the surface of the catalyst and the gas determined by different methods; Images from a) to j) reproduced with permission from ref. [54]; k) Scaled-up SiC monoliths coated with Mo-ZSM-5 before and after the MDA reaction; l) thermal images and snapshots at different time on stream (TOS) to illustrate sample rotation and temperature homogeneity; m) radial and axial sample temperature profiles during a MDA reaction stage; n) Average catalyst temperature cycles during MDA-regeneration cycles and corresponding* $CO_2$ *volume fractions; Images from k) to n) are adapted with permission from ref. [49]; o) Surface temperature of the quartz wall measured by an IR camera at different time periods and the corresponding simulated data using a 3D finite element model and fluid dynamics; p) Experimental temperature evolution of NaY zeolite heating at different MW power until reaching thermal run away; q) Computational simulation of the transient temperature profiles and power dissipation at different incident power; Images from o) to q) adapted with permission from ref. [89]; r) Computational simulation of a monolith placed within a quartz tube for MWH experiments; s) Cross-sectional color mapping of the temperature distribution at different positions of the monolith; t) Comparison of experimental and calculated temperatures using calculations; u) Prediction of temperature gradients under MWH and CH including the influence of gas flow rates (chemical reactions excluded); Images from r) to u) adapted with permission from ref. [48].*

Rigorous numerical simulations are also becoming an interesting alternative to indirectly estimate temperature distributions under MWH, and may be the only tool available for certain systems. Indeed, a sufficiently accurate knowledge of dielectric properties of solids at different temperatures will be necessary as well as a detailed description of the system geometry, but the simulations can provide a global picture of reactor temperatures that is beyond the reach of experimental measurement techniques. For this purpose, Multiphysics simulation allows coupling electromagnetic field Maxwell Stefan equations together with fluid dynamics and heat transfer. Nigar et al. [89] developed such a model for a zeolite bed heated in a monomode cavity validating temperature evolution under non-steady conditions (see Figures 6o-6q). Figure 6o shows the simulated temperature map distribution and recorded thermograms. The model was able to predict thermal runaway in the zeolitic system. Another good recent example is the work of Malhotra et al.[48], that showed that even a relatively simple lumped model can give good estimations of temperature variations in a structured flow reactor (Figures 6r to 6u).

Finally, another important issue with MW reactors refers to their operating stability. There are several aspects to be considered here, the first one is related to the conventional concept of thermal stability in a chemical reactor. Achieving this in MW reactors may be more difficult than in conventionally heated systems, given the strong dependency of dielectric properties with temperature [89]. Thus, in many cases the mobility of charge carriers responsible for MWH increases with temperature, this causes an instability loop where an increase in temperature increases mobility and microwave absorption leading to further increase in temperature and finally a runaway reaction [32]. In principle, under MWH this runaway could take place even for non-exothermic reactors, something that would not be possible in conventionally heated systems. The second issue concerns the influence of coking. Being a carbon-rich material, coke deposits are strong MW absorbers. Again, an instability cycle is possible here: coke deposits are preferentially heated, their temperature increase and even more coke is formed, giving rise to further temperature rises and multiple hot spots. To face coke-related instabilities, a structured reactor that is both a good MW absorber and has high thermal conductivity seems the best choice. Thus, Julian et al. [50] used a SiC monolith whose high MW absorption capability was able to balance the field perturbations due to coking during methane aromatization for up to 4 hours of reaction, until regeneration becomes necessary.  Finally, the last instability refers to the catalyst itself. When the catalyst material itself has a high tangent loss, the volumetric MWH can lead to high temperatures inside the catalyst pellets, leading to deactivation by sintering. Even if the catalyst does not have a high MW susceptibility, it may become a high MW absorber after being coked in the reaction. In this case, as explained above, coke deposits increase the temperature leading to accelerated coking and further temperature rise, producing a fast catalyst deactivation due to combined coking and sintering.

## 6. Outlook and Conclusions

The supply of energy using microwaves has a huge potential for gas-solid processes, driven by the intrinsic characteristics of MWH (selective, rapid, volumetric) and the limited heat removal capabilities of gas environments. The MW field leads to different heating patterns ("reverse" temperature profiles with fast heating and hot spot generation) compared to conventional heating mechanisms, something that can be a challenge but also a source of opportunities. Thus, the role of MW technology is bound to increase in a scenario of green electricity supplied from renewable sources. MWH can sustain a much more energy-efficient operation with reduced operation costs, and provide a higher conversion and selectivity. The prospects are especially good for strongly endothermic processes where direct energy supply to the catalyst can be leveraged and in high temperature processes where gas phase reactions harm reaction selectivity.

However, to achieve these goals, reliable ways to monitor and control temperatures must be implemented, in particular in this case a control loop enabling the interconnection between automatic valves, thermal camera readings and MW solid state generator system output had to be developed to enable prolonged unmanned operation [49]. New experimental systems for extensive temperature monitoring are still needed, as well as rigorous simulation models that can adequately predict temperature distributions beyond the reach of experimental measurements and enable realistic reactor scale up. The chemical industry is among the highest energy consumers, representing 46% of the total consumption in US in 2018. Rethinking energy supply to chemical reactors with new powered heating mechanisms (not only MW based) broadens the field of chemical reaction engineering and allows the exploration of new routes to increase energy efficiency and sustainability [29, 112-114]. Still, thorough economical and energy cost thorough analyses are also necessary and must progress in parallel to the development and implantation of these technologies. This represents a formidable challenge and remains beyond the scope of this work.

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## CREDIT AUTHOR STATEMENT

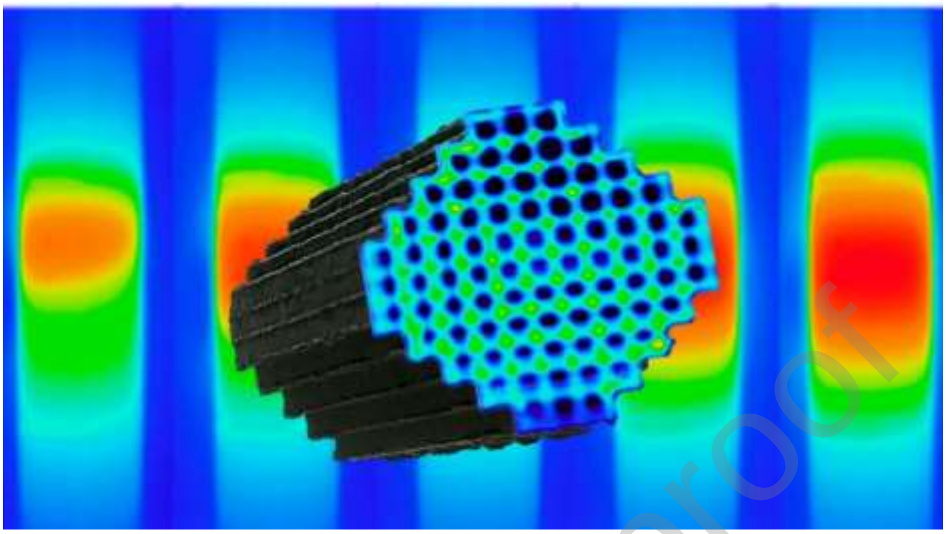
All authors contributed to the Writing and Review of the original draft and the subsequent revised versions.

**Declaration of interests**

☒The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

# GRAPHICAL ABSTRACT



**A critical overview on the current status of MW-assisted heterogeneous catalysis**

## Highlights

- Critical overview of the current state of MW heterogeneous catalysis
- Evaluation of the types of MW reactors
- Advantages of gas-solid temperature gradients induced by MW
- Enhanced adsorption-desorption-reaction mechanisms
- Examples of enhanced selectivity induced by MW