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Microwave-assisted Organic Synthesis in Microstructured Reactors

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Abstract—The coupling of microwave heating with microprocessing in continuous-flow reactors has been reviewed in various organic synthesis reactions. The fast growing field of microwave and microreactor technology has a significant impact on the development of fine chemicals industry. Both technologies offer not only the possibility of realizing many of the individual advantages integrated into one combined system, but also the potential of eliminating the major hurdle of a limited microwave penetration depth for large-scale chemical synthesis. Metal film-coated capillary microreactors allow creation of local hot spots to achieve temperatures far in excess of the solvent temperature, which accelerates chemical reactions under MW heating.

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Microwave (MW) irradiation holds much promise for the development of resource- and energy-saving and environmentally friendly technologies. Microwave heating is fast and efficient method for heating of a reaction medium. The use of MW energy instead of heating medium presently employed in most commercial plants allows considerable simplification of the engineering design due to the exclusion from it of all processes and apparatuses associated with processing of heat carrier, as well as considerable reduction of hazardous atmospheric emissions [1, 2]. The use of microwave radiation as an energy source makes it possible to accelerate most processes, enhance their efficiency and selectivity, and reduce operational costs. Wide use of microwaves in industry has still been prevented by a high cost of MW generators. This limitation could be overcome due to considerable recent advances in construction of MW generators.

The first research on the application of MW irradiation in organic synthesis dates back to 1986 [3, 4]. The authors of these works obtained evidence for high efficiency of the MW-assisted synthesis of organic compounds in sealed reaction vessels. They have shown, the MW heating decreases the reaction time up to 200 times at comparable yields of target products. At the same time, the main disadvantage of the batch reactors used in the cited works is related to a small penetration depth of MW irradiation (as little as a few centimeters, depending on the dielectric properties of the solvent). Therefore, MW irradiation is not used for heating reactors larger than 1 l in volume [5]. This problem was suggested to be approached by placing several smaller reactors into a MW cavity. In 1994 Cablewski et al. [6] made use of a continuous-flow reactor heated with MW irradiation. Over the past 15 years the methods of MW-assisted synthesis in continuous-flow reactors have substantially progressed [7–10].

Note that the experimental methods depend depends on the MW system (multimode or single-mode), as well as on the reactor type (batch or continuous-flow). The first MW installations for chemical synthesis, specifically CMR (continuous microwave reactor) and MBR (microwave batch reactor), were developed in 1988 by CEM (USA).

Most laboratory MW systems are multimode ones [7] (Fig. 1). Multimode MW systems offer the advantage of a fairly large cavity volume (up to 10 l). Entering a multimode cavity, microwaves are reflected by its walls to produce standing waves (modes) in three directions. Therefore, the field intensity in a multimode cavity is uneven, which can lead to hot and cold spots. A sample, especially if it is relatively large in size, may be heated to much different degrees. Generally, up to 6−8 modes arise in a cavity, which

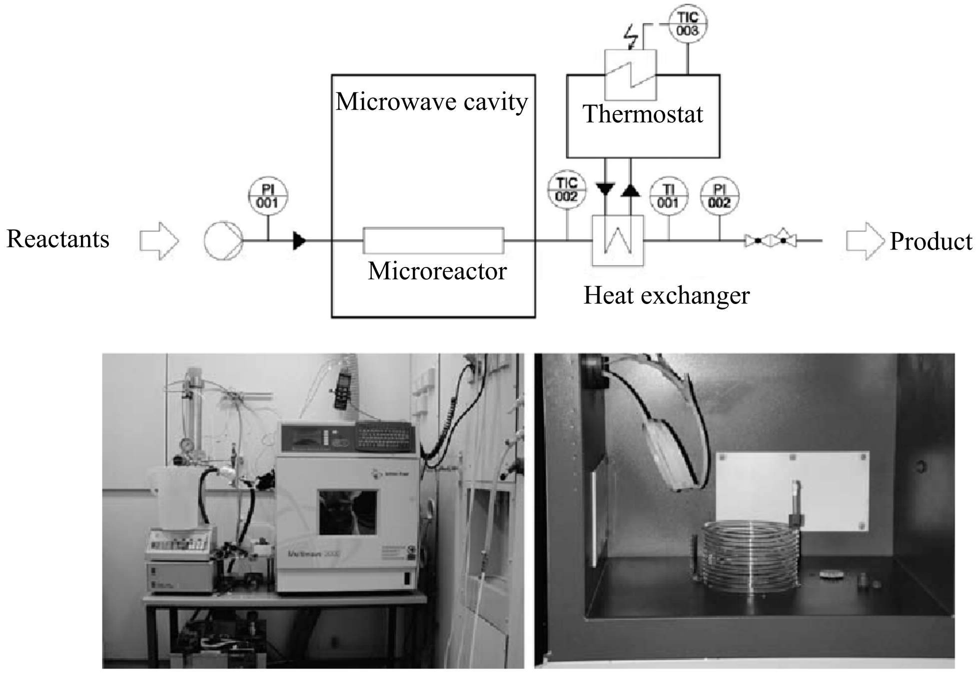


Fig. 1. Scheme of a continuous-flow microreactor for organic synthesis in a single-mode cavity. The image is adapted from [25] upon the authorization of the American Chemical Society.

results in an inefficient use of the energy generated by magnetron: The sample absorbs the energy of a few modes, whereas the residual energy is dissipated as heat in the environment. To equalize the energy density over the entire volume, the cavity is equipped with dissectors and spinning units.

In single-mode reactors, the energy is supplied via a waveguide directly to the load to be heated. Single-mode mocrowave systems have an enhanced performance. At a lower MW power, the yields of products in single-mode systems are higher than in multimode systems. In single-mode systems, radiation is supplied to the chemical reactor as a focused beam. Energy losses in such systems are minimal, and, therefore, they consume less energy than multimode systems.

It should be noted that any object placed into a single- or multimode MW cavity can considerable change the geometry of the electromagnetic field, which results in different MW heating rates in different parts of the cavity [11–13]. Experimental data on MW heating [11] provide evidence for theoretical calculations. In a multimode system, the field energy density can also be redistributed by reflectors. Correct location of reflectors is found by numerical simulation. If dissectors are located in a multimode cavity at an angle of 28.5° to the horizontal plane of the cavity, the field homogeneity parameter S can be increased from 0.33 to 0.63 [14]:

$$S = \frac{1}{n^2\bar{P}} \sum_{i=1}^{n}\sum_{j=1}^{n} |p_{ij} - \bar{P}|, \qquad (1)$$

where p_{ij} and $\bar{P}$ are the local and average field intensities, respectively.

The electric component of the electromagnetic field is responsible for heating of fluids by two mechanisms: polarization and/or ionic conduction [15]. The field–substance interaction is defined by the complex dielectric constant $\varepsilon = \varepsilon' - j\varepsilon''$, where ε' and ε'' are the real and imaginary components of the dielectric constant. The real component relates to the ability of dielec-trics to be polarized in the electric field. The imaginary component characterizeare quantitatively measured by the dielectric loss tangents dielectric losses which:

$$\tan\delta = \varepsilon''/\varepsilon'. \qquad (2)$$

Both components of the complex dielectric constant depend on the field frequency and the temperature. According to the international treaty governing the use of the radio frequency spectrum, MW devices use two frequencies: 915 and 2450 MHz.

The rate of MW heating is proportional to the imaginary component of the dielectric constant and squared field intensity E:

$$Q = 2\pi f_0 \varepsilon_0 \varepsilon'' |E|^2, \quad (3)$$

where f_0 is the EM field frequency; $\varepsilon_0 = 8.85\times10^{-12}$ F/m.

At our laboratory we studied the influence of the inner diameter of a continuous-flow reactor on the efficiency of MW heating in a single-mode cavity [16]. The efficiency of heating was measured by the ratio of the energy absorbed by the liquid (including heat losses to environment) to the energy of electromagnetic field. Several liquids were used in the experiments, such as acetone, water, ethanol, ethylene glycol, having different dielectric loss tangent and temperature dependences $\varepsilon'(T)$ and $\varepsilon''(T)$. Note that the ε'' values of most solvents decrease with temperature, and, therewith, heat losses to the environment tend to increase. As a result, the rate of MW heating decreases with temperature, since the relative change of ε' with temperature is not so essential. A reactor placed in a single-mode cavity affects the local geometry of the electromagnetic field, and, consequently, when $\tan\delta < 0.1$, the electromagnetic field can efficiently interact with the substance only at several specific diameters corresponding to a maximum field intensity inside the reactor. In this case, a high efficiency of MW heating (> 95%) can be reached, when the diameter of the reactor is equal to the electromagnetic wave length in the corresponding medium:

$$\lambda = \lambda_0/\sqrt{\varepsilon'}, \quad (4)$$

where $\lambda_0 = 1.224\times10^{-1}$ m is the wave length in a vacuum.

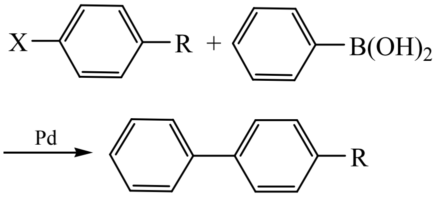
If the reactor diameter is larger or smaller, the efficiency of heating decreases several times [16]. With strongly absorbing liquids ($\tan\delta > 0.1$), the efficiency of heating is independent on reactor diameter and it depends solely on the $\tan\delta(T)$ dependence.

Application of Continuous-Flow Reactors in Microwave-Assisted Organic Synthesis

Stopped-Flow Technique

Application of MW irradiation to carry out chemical reactions in microreactors is an important way for process intensification at the laboratory and industrial scales [17, 18]. The transition from a batch reactor to a continuous-flow microreactor is often carried out by using a stopped-flow reaction technique [19].

Arvela et al. [19] studied the Suzuki reaction in a CEM Voyager single-mode microwave. The reaction occurs on a homogeneous palladium-containing catalyst in aqueous solutions:

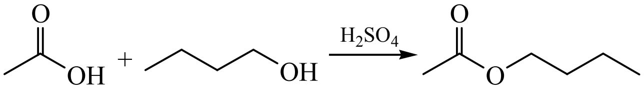


The Suzuki reaction is widely applied in preparative organic chemistry for the synthesis of popyolefins, substituted styrenes, as well as substituted biphenyls, and it most commonly catalyzed by palladium complexes.

One of the key problems associated with reactions in aqueous solutions is that catalysts (in particular, palladium acetate) tend to decompose under MW irradiation, leading to deposition of a metallic palladium film on the reactor walls. The homogeneous catalyst was stabilized by using an aqueous HCl solution. The reaction mixture was pumped into a tubular reactor (80 ml) located in a MW cavity, then the flow was stopped and heated up to 150°C. In 5 min the temperature was lowered by means of forced air cooling, the reaction product was flushed with a flow of ethyl acetate into a receiver. This sequence was repeated until the required quantity of the reaction product was obtained.

The same technique and apparatus were applied to study C–N bond coupling reactions catalyzed by palladium acetate [20]. The target product yields under stopped-flow conditions were comparable with those in batch reactors.

The conversion in the stopped-flow reaction was traced by Raman spectroscopy [21]. The concept of the technique was developed with esterification of acetic acid with butanol as a test reaction:



The conversion was traced by the characteristic absorption band of acetic acid at 800 cm^{-1}. The spectra were recorded at 6-s intervals.

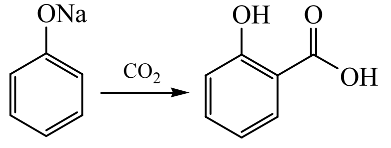
To optimize reaction conditions, experiments in 10-ml and 80-ml glass reactors placed into a single-mode MW cavity were performed. In the10-ml reactor, the quantitative yield of the product (0.013 mol) was reached within 18 s at 130°C with a 2.5-fold excess of acetic acid. As the concentrations of the reagents taken in a 1:1 molar ratio were increased, the yield of the product decreased to 71%, and the reaction time increased to 42 s. In the 80-ml reactor, the reaction was completed in 74 s with a yield of 72%. After the reaction conditions were optimized, the reaction was performed in a stopped-flow regime. To obtain 5.7 mol of the product, 22 cycles each 6 min long were performed. The product yield virtually did not vary from cycle to cycle, providing evidence for a high performance of the technique. This technique can be used for monitoring the Suzuki reaction in aqueous alcohol solutions.

Continuous-Flow Technique

One of the first applications of continuous-flow reactors in organic synthesis can be exemplified by the esterification of benzoic acid with ethanol [22]. The reaction was performed in a glass tubular reactor (diameter 10.7 mm, length 42 cm) packed with an Amberlyst-15 ion-exchange resin. It was found that the reaction kinetics on a heterogeneous catalyst is similar to that with sulfuric acid as catalyst.

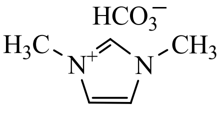
Bremner et al. [23] performed the Suzuki reaction in a continuous-flow microreactor (capillary, diameter 800 μm, length 138 mm) under MW heating. The microreactor contained a layer of supported catalysts (Pd/Al_2O_3, Pd/SiO_2, particle size 355–420 μm). The outer surface of the capillary was coated with a film of gold which efficiently absorbs the MW energy. The reactant contact time in the reactor was 60 s. The conversion varied from 58 to 91%, depending on the substituent in the benzene ring. Catalytic activity was retained for a relatively long time (35 h). The authors suggested that the higher activity of the Pd/SiO_2 catalyst is associated with a stronger MW absorption of SiO_2, which creates a higher temperature on its surface. Baxendale et al. [24] carried out the Suzuki reaction on a heterogeneous palladium catalyst (Pd EnCat) as a model for the synthesis of various compounds in a few-milliliter volume.

Carboxylated phenols are most commonly produced by the Kolbe−Schmitt reaction which involves carboxylation of sodium phenolate with carbon dioxide:

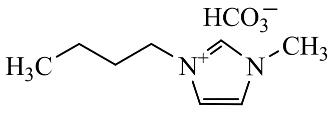


The reaction occurs at the temperature of 140–160°C and pressure of 10–50 bar in a strongly alkaline solution. Benaskar et al. [25] by accomplishing this reaction under MW`heating in a continuous-flow microreactor with channels of 700 μm width, 200 μm depth, and 12 mm length, succeeded to decrease considerably the operating pressure, not sacrificing the high degree of conversion of the reactants [25]. The contact time in the microreactor was rather precisely controlled due to fast cooling of the reaction mixture at the outlet of the MW cavity to room temperature. The surface area of the microreactor is large enough to allow cooling within a few seconds. Whereas the reaction yield in a continuous-flow reactor under thermal heating was 47%, the reaction under MW heating resulted in a yield of 52% at 160°C, pressure 8 bar, and flow rate 1 l/h.

Benaskar et al. [25] have also studied the Kolbe−Schmitt reaction under MW heating in two ionic liquids uded as CO_2 donors: 1-ethyl-3-methylimida-zolium hydrocarbonate (**I**) and 1-butyl-3-methyl-imidazolium hydrocarbonate (**II**)



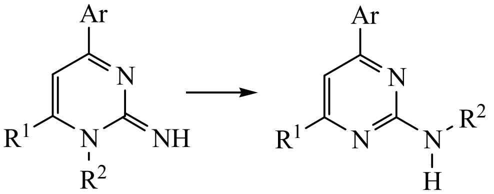
I



II

In the reaction with imidazole **I** the yield decreased to 44%, whereas with imidazole **II** it increased to 59%. The experiments with ionic liquids were performed at a higher temperature (180°C), which was reached due to a higher pressure in the microreactor (35 bar).

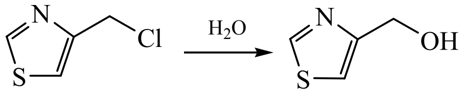
Glasnov et al. [26] studied the Dimroth rearrangement (isomerization of 1-substituted 1,2-dihydro-2-iminopyrimidines into 2-substituted aminopyrimidines):



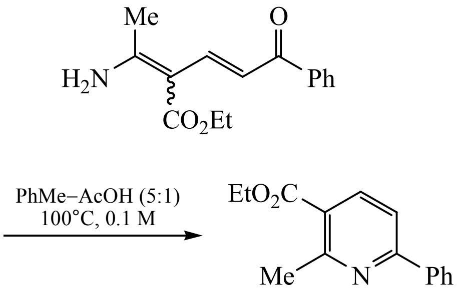
The reaction was performed under MW irradiation in a batch reactor and a continuous-flow microreactor. Since the reaction is accompanied by a strong heat release, its maximum rate in batch reactors depends on the rate of heat removal, rather than the intrinsic reaction rate.

A glass 10-ml microreactor was placed into a single-mode MW cavity. For better reactant mixing the reactor was filled with glass microgranules. The experimental results obtained by scanning differential calorimetry argee well with the predictions of the density functional theory, according to which iminopyrimidines with a 5-ester group reacts at higher temperatures. It was thus shown that the combination MW heating−microreactor is suitable for kinetic studies of fast reactions.

If the temperature of the reaction mixture considerably changes during heating, the EM field intensity maximum is shifted due to changing dielectric constant of the solvent. Therefore, to transfer the energy from magnetron to load without any losses, field correction is required. To this end, mechanical shifting of one of the walls of the single-mode cavity can be applied. Design of all elements of an MW system includes several steps: theoretical calculations, computer simulation, fabrication of the system, and individual tuning. As a rule, all modern MW devices are equipped by a sensor for measuring absorbed and reflected energy, a load for a maximum absorption of supplied energy, as well as temperature sensors and pressure gauges. Bagley et al. [27] used a continuous-flow single-mode 10-ml glass microreactor partially filled with quartz microgranules. The hydrolysis of 4-(chloromethyl)thiazole at 150°C gave the 85% yield of the corresponding alcohol:

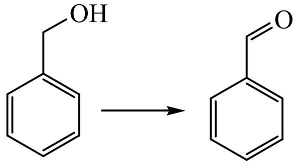


This prototype MW device was also successfully tested in the Bohlmann–Rahtz reaction:



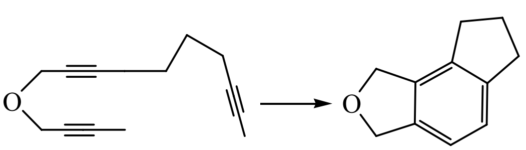
Wilson et al. [28] performed aromatic nucleophilic substitution reactions in a glass helical continuous-flow microreactor (diameter 3 mm) with a back pressure controller. The reactor was placed into a single-mode MW cavity. It was found that the reaction time of 4-fluoro-3-nitroaniline with phenylethylamine under MW heating in this device decreased to 5 h compared to 18 h under conventional heating. The yield of 85% in the Suzuki reaction could be reached within 6 min in a batch reactor and within 8 min in a continuous-flow reactor at 140°C.

The catalytic oxidation of benzyl alcohol



is one of the commercial processes for manufacturing benzaldehyde which serves as a raw material for the synthesis of pharmaceuticals, dyes, and perfumes [29]. To obtain high selectivity in benzaldehyde the reaction should be performed in an isothermal regime. Jachuck et al. [30] developed a continuous-flow isothermal MW microreactor integrated with a heat exchanger. The device is made of two parts: a reaction channel located in a polymer holder and a cooling microchannel (Fig. 2). The cooling channel was encased in an aluminum jacket for protection from MW irradiation. The catalyst was Fe(III) nitrate. Owing to the small distance between the micro-channels, the device provided a rather high heat-transfer coefficient (2.5 kW m^{-2} K^{-1}). Therewith, the reaction mixture heated up by no more than 3 K. When the reactor was operated in an adiabatic regime, the conversion of benzyl alcohol increased, but the authors of [30] reported no selectivity data.

The isomerization of alkynes to form aromatic rings



usually occurs at rather high temperatures, generally above 150°C. The reaction is usually performed at elevated pressures. The reaction temperature could be much decreased by the use of metal catalysts, but the yield was found to depend on the type of the catalyst [31]. As found in [31], complete alkyne cyclo-isomerization under MW heating occurs with a yield of 80% at a temperature as low as 200°C and requires no catalysts, whereas under conventional heating the conversion does not exceed 60%.

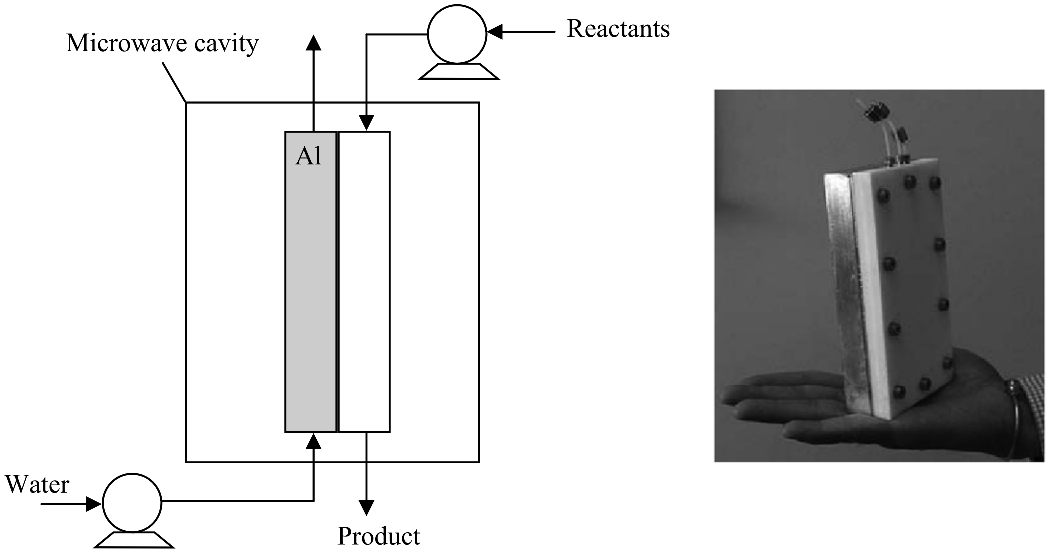
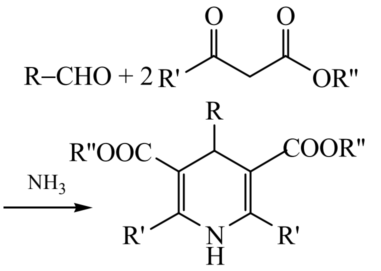


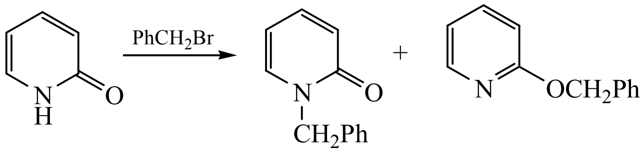
Fig. 2. Scheme of a continuous-flow microreactor integrated with a heat exchanger. The image was adapted from [30] upon the authorization of the Royal Society of Chemistry.

The interest in the Hantzsch synthesis of pyridines is associated with their broad-spectrum biologic activity. Substituted 3(5)-nitro-1,4-dihydropyridines are applied for treatment of circulatory diseases, hypertension, atherosclerosis, stenocardia, and diabetes. Just this circumstance stimulates the synthesis of new representatives of 1,4-dihydropyridines. Khadlikar and Madyar [32] synthesized substituted 2,6-dimethyl-4-phenyl-1,4-dihydropyridines by the Hantzsch reaction in a 65-ml continuous-flow reactor in a multimode cavity. The mixture was cooled down at the reactor outlet. Under MW heating substituted pyridines are formed in quantitative yields.



Owing to fast mixing, continuous-flow microreactors allow simultaneous feeding of three starting compounds [33]. Provided the reactants have been vigorously mixed in the microchanel before they are fed to the MW cavity, quantitative product yields can be reached.

The efficiency of absorption of MW energy was studied in a prototype microreactor with electrodes integrated at the inlet and outlet of the microchannel for fine temperature control by measuring of thermal conductivity [34]. The model reaction was alkylation of pyridin-2-one with benzyl bromide:



Analysis of the temperature field in the microreactor led the authors to conclude that the efficiency of MW energy absorption in a channel of 800 μm in diameter is not higher than 1%, even if strongly absorbing solvents are used. Therefore, MW absorbing films should be deposited onto microchannels. For example, a 10−15-nm gold film applied on the outer surface of a glass capillary favors a much more efficient process [35].

Deposition of Thin Metal Films Inside Microchannels

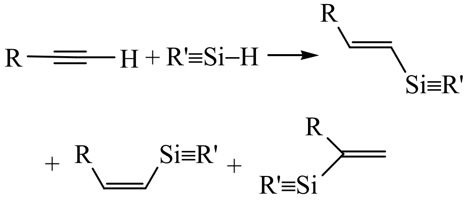
Palladium Films

Shore et al. [36] suggested that the efficiency of reactions can be enhanced by thin metal films deposited on the inner surface of capillary microreactors 1–2 mm in diameter. The Suzuki reaction was performed in a continuous-flow microreactor 1.18 mm in diameter, with a 10-μm palladium film deposited on the inner wall. The procedure for film deposition was adapted from the work of Stadler and Kappe [37] who formed palladium films of the surface of glass capillaries by C–P bond coupling. The Pd film functioned both as a receiver of MW irradiation and as a catalyst. In a continuous-flow regime (10 μl min^{-1}), the yields of target products under MW heating were double those obtained under conventional heating.

A catalytic microreactor with a deposited Pd film was also used to study the Diels–Alder reaction [38]. A-12-cm-long microreactor was heated under single-mode radiation to 205°C at total pressures of 1 and 5 bar. The temperature was measured at the outer wall of the microreactor with an IR thermometer. Therewith, the length of the section exposed to MW irradiation was 2.5 cm. The reactants were fed to the reactor at a rate of 10 μl min^{-1}. The reaction rate was higher than in the reaction under conventional heating, conversin was increased from 75 to 93% at atmospheric pressure. Increased pressure allowed the temperature for a maximum product yield to be decreased from 205 to 180°C. It was suggested that the acceleration of solid-phase reactions under MW heating can be associated with local overheating of the solid catalyst because of its surface nonuniformities [39].

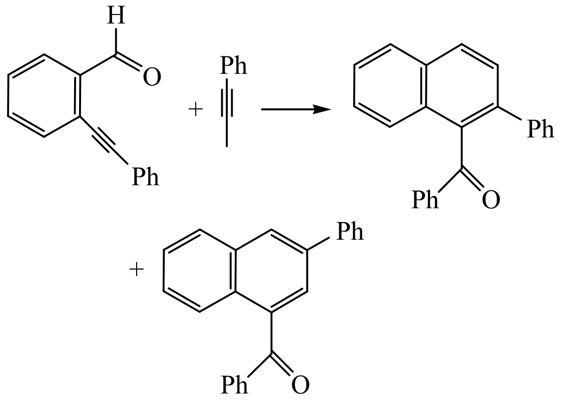
Gold Films

A high catalytic activity of thin gold films deposited on the inner wall of glass capillaries of 1.18 mm in diameter was observed in MW-assisted hydrosilylation of alkynes (Si–R coupling) [39]:

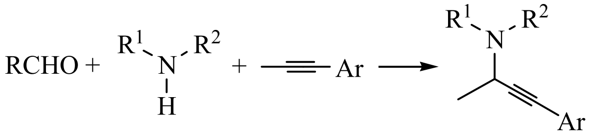


The gold film was obtained by the reduction of gold chloride with solvents (for example, ethylene glycol) at 180°C. After 30 min the temperature was decreased, residual solvent was purged-off from the capillary, and calcination at 400°C was performed. In a single-mode microwave at 180°C, the yields of target products were more than 25% higher compared to conventional heating. No catalyst deactivation was observed during experiments. Evidence for the high stability of thin gold films was obtained by elemental analysis of solutions at the outlet at the reactor.

Since 2002 there has been growing interest in research on cycloaddition of acetylene derivatives [40]:



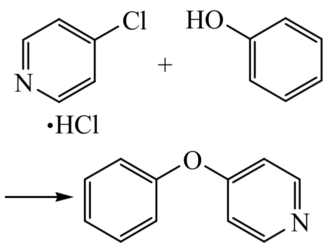
Shore et al. [41] successfully deposited thin films to obtain two-layer Au/Ag films inside capillaries 1.7 mm in diameter: First an inner silver layer was formed and then, after calcination at 500°C, it was coated with a gold film by the reduction of $AuCl_3$ in a 2% aqueous sodium citrate solution. An efficient synthesis of propargylamines from aldehydes, amines, and acetylene derivatives (molar ratio in 1.0:1.2: 1.5, respectively) in a continuous-flow microreactor was proposed [42]:



Thin Au (or Cu) films were used as catalysts. It was found that exposure to MW irradiation in a single-mode MW cavity can bring the temperature of the metal film to more than 900°C. Therewith, oxides formed from the Cu films can be involved in the catalytic cycle. The yields of propargylamines varied in the range 65–80%, depending on the reactants.

Mesoporous Films Containing Metal Nanoparticles

In our laboratory we have studied the Ullmann synthesis of bi- and polynuclear aromatic compounds [43]:



It should be noted that since the discovery of Ullmann reactions at the beginning of the 20th century, copper powders have been used as catalysts. At present homogeneous catalysts employing the Cu(II)/Cu(I) redox cycle are applied. Copper nanoparticles have

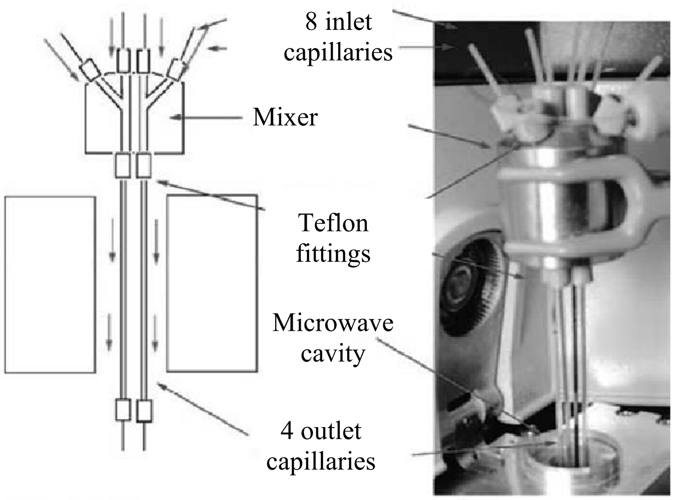


Fig. 3. Scheme of a continuous-flow microreactor for combinatorial organic synthesis in a single-mode MW cavity. The image was adapted from [47] upon the authorization of Wiley−VCH.

only recently started to be applied to catalyze the Ullmann synthesis.

Comparative analysis shows that the yield of 4-phenoxypyridine in the Ullmann synthesis in a multimode MW cavity increases from 20 to 80% if a 3-μm copper gauze catalyst is replaced by 10-nm copper nanoparticles stabilized by poly(vinylpyrrolidone) [44].

For the synthesis of 4-phenoxypyridine in a continuous-flow microreactor, poly(vinylpyrrolidone)-stabilized Cu nanoparticles were deposited on a mesoporous film obtained by dip-coating (250-μm nonporous silica microspheres). The use of the deposited catalyst made it possible to enhance the efficiency of a fixed-catalyst-bed continuous-flow glass reactor 5 mm in diameter, located in a multimode cavity. Thus, the conversion of 4-chloropyridine in a continuous-flow reactor was above 70% at 130°C and a contact time of 15 min, and increased to 80% in the case of a $CuZn/TiO_2$ bimetallic catalyst [45]. A high stability of deposited mono- and bimetallic catalysts during the reaction should be mentioned.

Along with the development of catalytic films, our laboratory performs research into improvement of adsorption characteristics of Co–Ni–Zn ferrite films obtained by spin-coating on silicon substrates [45, 46]. Varying the precursor ratio allowed the microwave absorption maximum to be shifted by a few GHz. In the future, catalytic films can be deposited on the ferrite films and thus considerably reduce consumption of noble metals in microreactors.

Combinatorial Organic Synthesis

The main principle of combinatorial chemistry — parallel synthesis of relatively small (2×4) libraries of diaryl compounds — was successfully realized by combining micro reaction technique, catalysis, and MW heating [47]. Comer and Organ [47] employed homogeneous catalysts in C–C bond coupling in continuous-flow microreactors 200–1200 μm in diameter. Several microchannels were simultaneously placed into a single-mode cavity (Fig. 3). The flow rate was varied in the range 2–40 μl min^{-1}, depending of the concentration of the reactants and the intensity of MW irradiation.

A MultiSynth single-mode apparatus was used to study the influence of reaction conditions on the yield of the Suzuki reaction [48]. It was observed that during simultaneous heating of several reactors in a multimode cavity, rather large temperature differences between individual reactors were observed reactions were performed in solvents poorly absorbing MW irradiation. Minor additives of strongly absorbing solvents provided a virtually uniform heating of individual reactors. In a follow-up study a batch reactor was used in a multimode cavity to develop a kilo-scale synthesis [49].

Scale-up of Microwave-Assisted Processes

One of the directions of intense development of chemical microreactor engineering is scale-up of organic synthesis [7, 50]. A major advantage of microreactors consists in that a customer obtains ready modules with all required engineering equipment, which can be assembled like Lego bricks [50]. Another advantage is the possibility to disassemble the process line after some time and use other catalytic microreactors for a new process. Such approach is practiced in fine chemicals synthesis, where most chemical reactions are performed in batch reactors. The maximum load of the largest modern device is 20 ml, which is a multimode device suitable for eight parallel reactions. Normal loads are generally no do not exceed 0.25–5.0 ml, since in larger reactors the reaction mixture undergoes fast MW heating only near walls, while heating inside the reactor occurs exclusively by convection.

In most cases, performance can be enhanced by using a continuous-flow reactors. The product yields in upscaled reactors are unaffected only under the conditions of vigorous reactant mixing and uniform heating [51]. These conditions are hardly realizable in continuous-flow reactors larger than 11 in volume. Therefore, the problem of enhancing efficiency of continuous-flow processes is solved by placing several small reactors into a multimode cavity. Unlike batch reactors, continuous-flow reactors allow use of heterogeneous catalysts deposited as thin films on the inner surface of the reactors [52].

CONCLUSIONS

Further progress of MW-assisted processes seems to be associated with the integration of MW technique with automated process control, which will lead to the development of automated industrial processes with a maximum utilization of the energy of microwaves. The Voyager equipment allows fully automated laboratory experiments in batch reactors [20]. To protect the magnetron from reflected power, reflected power control is applied. As the reflected power grows, the input power is automatically reduced. Continuous temperature, pressure, and radiation power control, as well as forced cooling provide safe and efficient operation of the MW reaction system.

Heterogeneous catalysts as thin metal films and metal nanoparticles on mesoporous supports allow considerable simplification of production processes by excluding the stages of separation of the catalyst and the reaction mixture in the Suzuki, Ullmann, and Diels−Alder reactions, as well as in certain hydrosilylation and cycloaddition reactions. Since under MW irradiation the local temperature of metal nanoparticles can be much higher than the average temperature of the reaction mixture, strong acceleration of surface reactions occurs, which reduces contact time and generally enhances reaction selectivity. The fast mass transfer in microreactors allows reactions to be performed in the kinetic regime. Thus, by exploring a catalytic reaction with known kinetics one can calculate the local temperature of the catalyst under MW irradiation, which is required for exact calculation of catalytic “microwave” microreactors (μ^2-reactors).

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