Perspective

Practical Challenges in the Energy-Based Control of Molecular Transformations in Chemical Reactors

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Introduction

Control of the rate and the distribution of products in chemical reactions is a mainstay of chemical reaction engineering. Over the last decades, vast progress has been made in the use of increasingly sophisticated techniques to dictate the path and outcome of these reactions. Among other things, microreactor technologies have emerged as attractive alternatives to conventional reactors.[1]

A few years ago, Özkan et al[2] envisaged the future generation of chemical reactors—"perfect reactors"—in which the geometry of molecular collisions is controlled while the energy is transferred selectively from the source to the required molecules in the required form, in the required amount, at the required moment, and at the required position. In this article, we focus on the possibilities of executing the enhanced control of the molecular orientation and activation with different forms of energy: electromagnetic or electric fields. We identify the challenges of bringing those novel methods to industrial-scale applications. Obviously, the controlled geometry of molecular collisions and selective activation are not the only constituents of "perfect reactors." Other elements, such as mixing, concentration distribution, residence times, heat removal, and *in situ* product separation, play important roles, too. These elements, however, are beyond the scope of this article.

Some of the techniques discussed here, for example, molecular beams (MBs), Laval nozzles, and laser excitation, have been developed and investigated by chemical physicists but have not gained any significant attention in the chemical engineering literature so far. We briefly introduce those techniques to the readers and examine their practical applicability in chemical processing. We address both homogeneous and heterogeneous systems. In the former ones, the coupling between the energy and the molecules has a direct character, whereas in the latter ones, the coupling is indirect and proceeds via intermediation by a material, usually a catalyst.

Fundamental insights from chemical physics, catalysis, and chemical, electrical, and materials engineering provide exciting opportunities for the development of new classes of chemical reactors with enhanced control of molecular events. As we discuss further on in this article, microchannel or millichannel systems are expected to play an important role in these developments.

Energy-Based Methods for Orienting and Activating Molecules: The Options

Orienting molecules with electric fields

Obviously, the mutual orientation of molecules at the moment of their collision influences the effectiveness of that collision and, hence, the reaction outcome.[2] The simplest manner of orienting molecules in space is to place dipolar molecules in a uniform electric field. Neutral molecules interact with electric fields through their charge distribution via the so-called Stark effect.

Figure 1 shows the dependence of the angle between the dipole and the field (θ) and the energy of the molecular dipole in the electric field according to the so-called Langevin formula:

$$\langle \mu \cos\theta \rangle = \mu \left(\coth \frac{\mu E}{kT} - \frac{kT}{\mu E} \right) \tag{1}$$

where μ is dipole moment, k is the Boltzmann constant and T is the temperature.

According to Figure 1, to generate a polarized distribution of molecules from a random distribution, the energy of interaction (μE, where E is the field strength) must be larger than the thermal energy (kT), that is, $\frac{\mu E}{kT} \gg 1$. In other words, for large Es and very low Ts, the average dipole moment would be equal to the built-in dipole moment; that is, all of the dipoles would be strictly parallel to the field. The questions

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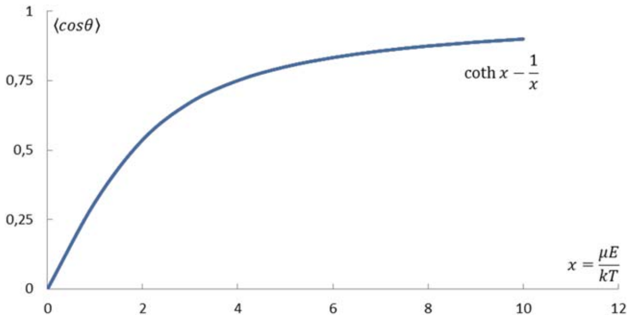

Figure 1. Average dipole orientation of molecules in an electric field according to the Langevin formula (Eq. 1).

are what range of $x = \frac{\mu E}{kT}$ values is accessible for real conditions and materials and how close to the saturation limit of Langevin function $L(x) = \coth x - \frac{1}{x} = 1$ we can get.

As an example, Figure 2 shows the average dipole orientation plotted as a function of the temperature for H_2O. The picture is not encouraging. For instance, at $T = 300$ K, kT is 209 cm^{-1}. For H_2O molecules ($\mu = 1.82$D) and an electric E of 10^5 V/cm, the value of $\frac{\mu E}{kT}$ is only 0.015. Under these conditions, the average dipole orientation is 0.005; this shows that the degree of orientation of water molecules at room temperature and high electric E is very low (a perfect orientation corresponds to $\langle \cos\theta \rangle = 1$).

Clearly, to make a reasonable use of the electric field-based orientation, the cooling of the molecules is needed. To reach sufficiently low effective temperatures without significant condensation or clustering of the reactants, two supersonic gas-expansion techniques have been developed: Laval nozzle expansion and molecular beam (MB) expansion (Figure 3).

Laval nozzle expansion is realized via the isentropic expansion of a gas mixture from a high-pressure reservoir through a shaped convergent–divergent nozzle (Figure 3) into a large vacuum chamber.[3,4] This process provides a jet of relatively dense (typically 10^{16} to 2×10^{17} molecules/cm^3) and strongly cooled gas moving at supersonic speed. An important inconvenience of this cooling method is that the gas throughput and pumping requirements are huge, and this makes it very expensive to run.

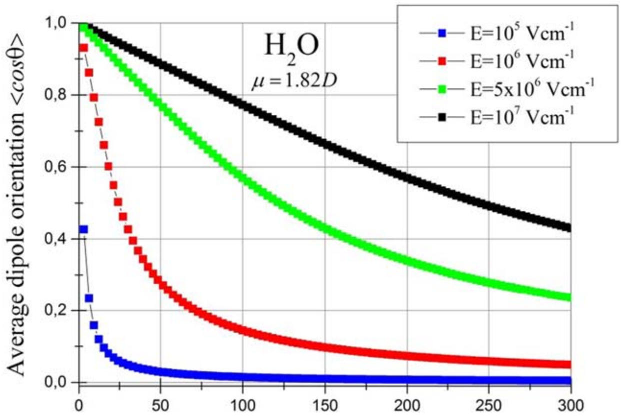

Figure 2. Average dipole orientation of H_2O plotted as a function of temperature for several electric Es: $E = 10^5$ V/cm (blue), 10^6 V/cm (red), 5×10^6 V/cm (green), and 10^7 V/cm (black).

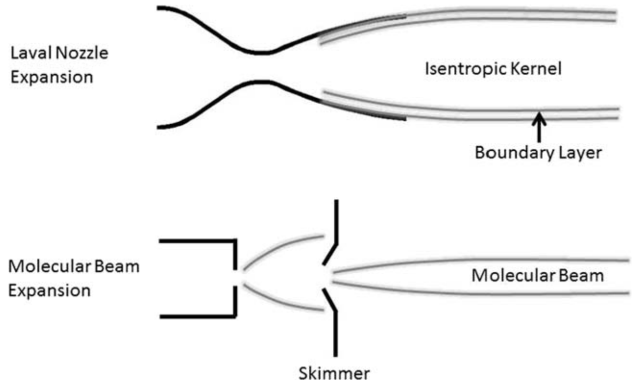

Figure 3. Schematic diagram of nozzles used to generate different supersonic gas expansions: Laval nozzle and MB.

MBs, on the other hand, are not only a source of extremely cold particles, but they also narrow the velocity distribution and produce a kind of molecular plug flow; this allows molecules to be prepared in a collision-free environment with a well-defined velocity. MBs are formed by the expansion of a gas from a reservoir at high pressure through a small orifice (400–1200 μm) into vacuum, as schematically shown in Figure 3. Because the nozzle diameter is greater than the mean path of the molecules in the source, multiple collisions occur around the throat of the orifice. These collisions convert a large part of the total energy that is available per molecule into kinetic energy along the MB axis, and this results in a highly directed flow of molecules that are internally very cold. The translational and rotational temperatures can be lower than 1 K, whereas the vibrational temperatures are usually somewhat higher. For small molecules such as ammonia or CO, densities of about 10^{13} molecules/cm^3 can be reached with MBs.

Molecular surgery: selective activation with lasers

For enhanced molecular-level control, the energy level of the molecules should be distributed as narrowly as possible.[2] As schematically illustrated in Figure 4, the most efficient approach would be to bring the molecules to a well-defined initial energy level [Figure 4(b)] and activate them selectively [Figure 4(c)].

The first step can be realized by means of the cooling of the reactants to very low temperatures, as described in the

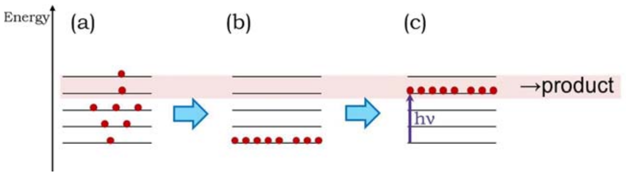

Figure 4. Schematic representation of the molecular energy distribution in a (a) conventional reactor and (b,c) perfect reactor.

previous section. The required, tunable energy for the second step can be provided by light. Laser radiation has five distinct features; this makes it unique with respect to all other light sources, such as light emitting diodes (LEDs) or discharge lamps. Laser light is monochromatic, directional, coherent, and high power and may be pulsed. *Monochromatic* means that the light emitted is extremely pure and has a very narrow line width. For comparison, in the UV region, the typical line width of the laser is 0.1 nm, whereas in the case of the LED, it is 10 nm. This very narrow line width of laser light is unique in terms of selective molecular bond cleavage. For example, it was shown that the selective breaking of either O—H or O—D bond in the bimolecular reaction of HOD with hydrogen atoms depends on the laser wavelength used.[5,6] In another example, carbonyl sulfide molecules were first aligned and oriented in an electric field and then dissociated by a laser beam.[7] In a study by Kandel and Zare,[8] laser-induced C—H stretching vibration in methane during its chlorination reaction introduced so-called stripping collisions with chlorine atoms. An increase of the reaction rate by a factor of more than 100 was subsequently observed. This all indicates that a careful design of the reaction at the molecular level with molecules well prepared to interact with selected laser wavelength can radically improve the reaction performance.

Shooting with electrons: The plasmas

Nonthermal plasma reveals the outstanding characteristics of the generation of particles that carry enough energy to execute chemical reactions that are often impossible to perform under conventional conditions. Unlike thermal plasmas, which provide high power levels, nonthermal plasmas are less powerful but have the benefit of securing more selectivity, which is very much needed in chemical applications. In general, a higher level of nonequilibrium results in better selectivity for chemistry. In nonthermal plasmas, only a tiny fraction (a few percentage) of gas molecules is ionized, and the thermodynamic equilibrium is far from being reached. In such a case, the electrons are at higher temperature than the ionic and neutral species. The temperatures of ions and neutrals usually take lower values close to that of the ambient environment, that is, from room temperature up to 1000 K, whereas the electrons can feature temperatures above 10,000 K. The energy is transferred between the discharge and the atoms or molecules through electron impact.[9–14] It is commonly responsible for the well-known process of dissociation that leads to the breaking of molecular bonds and the generation of chemical products during the chemical reactions. Another elementary process that plays a fundamental role in the chemical applications of nonthermal plasma is vibrational excitation.[15] For example, at electron temperatures of around 1 eV, which are quite common for nonequilibrium plasmas, nearly all electron and implicitly discharge energy is transferred into the vibrational stimulation of the reagent molecules. However, vibrational excitation should not be seen as a direct process but rather as a multistep mechanism accompanied by vibrational–vibrational and vibrational–translational relaxation processes. This can be seen, for instance, in the chemical processing of CO_2 gas that is vibrationally excited to a dissociation extent.[16,17]

Liquid-phase reactions and the so-called microwave effects

The ongoing discussion in the literature concerns the mechanisms behind the spectacular enhancement effects in many liquid-phase reactions observed with microwaves, where factors from several to more than a thousand have been reported. Among the mechanisms of the enhanced activation by microwave microscopic hot spots, molecular agitation, improved transport properties of molecules, positioning of the transitions states, and a decrease in the activation energy in the Arrhenius law have been hypothesized.[18–23] Nowadays, the standpoint prevails that the effect of microwaves has a purely thermal character.[24,25] Accordingly, ionic liquids are being proposed as doping agents for the systems in which the reacting species are neither polar nor ionic.[26] In view of our own experimental experience with microwaves, we indeed suspect that many of the nonthermal microwave effects reported were due to incorrect temperature measurements. However, occasionally interesting cases have been reported that could not be explained simply by erroneous temperature measurements. For example, in one of our studies, a homogeneous zinc triflate catalyst repeatedly exhibited a significant microwave enhancement effect in an esterification reaction, whereas other homogeneous catalysts investigated in exactly the same system did not show any effect at all.[27] Such observations definitely warrant further studies.

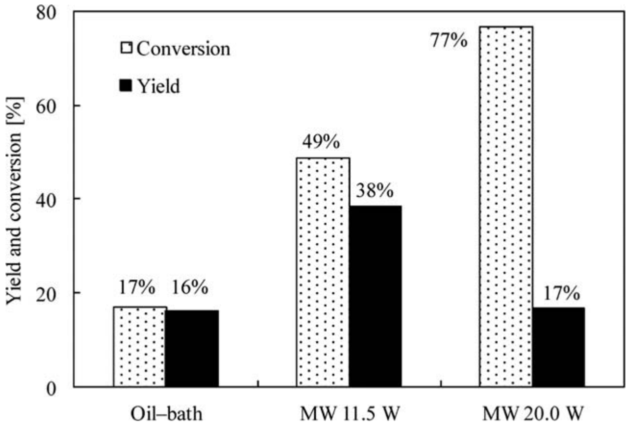

Figure 5. Microwave effect on the conversion and yield of a Sonogashira coupling reaction.

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Localized heating of heterogeneous catalysts

The same microwaves can be applied to the activation of heterogeneously catalyzed reactions, and a considerable increase in the reaction rate (of 20–100 fold) and/or the product yield compared to events with conventional heating has commonly been reported.[28–31] Figure 5 presents an example of the microwave effect on the conversion and yield of the Sonogashira coupling reaction on a Pd catalyst carried out at the same average bulk temperature of the reactant solution.[31]

Effects such as the previous one are usually attributed to selective microwave–catalyst interaction. The selective heating of solid catalysts may lead to catalyst superheating and, consequently, to higher reaction rates. These effects have been observed when the catalysts contain metallic or carbon (nano)particles, which selectively dissipate microwaves into

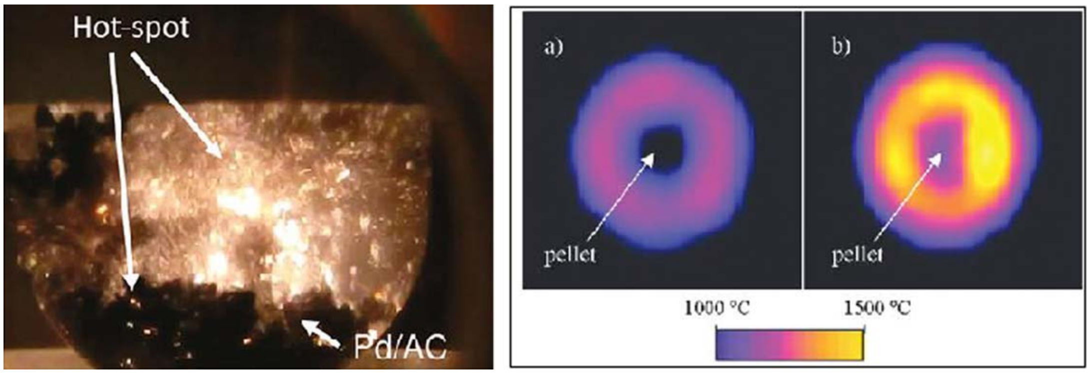

Figure 6. Left: Evidence of arcing on the Pd/activated carbon (AC) catalyst. Right: Thermal images showing the preferential absorption of microwaves by graphite surrounding a much colder pellet: (a) after 3 and (b) 5 s of heating.

Left side reprinted with permission from Horikoshi S, Horikoshi S, Osawa A, Abe M, Serpone N. On the generation of hot-spots by microwave electric and magnetic fields and their impact on a microwave-assisted heterogeneous reaction in the presence of metallic Pd nanoparticles on an activated carbon support. *J Phys Chem C*. 2011;115:23030-5.[32] Right side reprinted with permission from Vallance SR, Kitchen HJ, Ritter C, Kingman S, Dimitrakis G, Gregory DH. Probing the microwave interaction mechanisms and reaction pathways in the energy-efficient, ultra-rapid synthesis of tungsten carbide. *Green Chem*. 2012;14:2184-92.[33]

thermal energy. In addition, local plasma (ie, arcing or microplasmas) can be created with an additional energetic drive for the chemical reactions (Figure 6).[32]

Frequently, researchers make use of already known reaction kinetics from thermal catalytic studies to back-calculate the catalyst temperature on the basis of the conversion achieved under microwave heating.[34,35] Experimental approaches to the verification of local hot-spot formation make use of infrared and high-speed cameras. Microwave heating at nanoparticle scale has been theoretically investigated by Keblinski et al.[36] The authors proposed a characteristic heating time and temperature estimation method for electromagnetically heated nanoparticles (Eqs. 2 and 3). They reported that the temperature increase in the vicinity of a metal nanoparticle was negligible. On the contrary, the superposition of heating by a group of nanoparticles dispersed in a macroscopic region induced a global temperature increase, which was orders of magnitude larger than that adjacent to a metal nanoparticle:[36]

$$t_{\text{global}} = \frac{r_p^2}{\alpha} \tag{2}$$

$$T_{\text{system}} - T_{\text{fluid}} = \frac{\frac{dQ_{\text{particle}}}{dt} R^2 \rho_N}{2\lambda} \tag{3}$$

where t_{global} is the characteristic time for the system to obtain a stable temperature, r_p is the radius of the particle, α is the thermal diffusivity of the fluid, $T_{\text{system}} - T_{\text{fluid}}$ is the temperature difference between the surface of the particle and the colder fluid, $\frac{dQ_{\text{particle}}}{dt}$ is the power absorbed by each particle, R is the radius of the heated region, ρ_N is the density of the particles, and λ is the thermal conductivity of the fluid.

Aside from the higher reaction rates and conversion, localized catalyst heating may have a positive effect on the product selectivity. As an example, we refer to the work of Marotta et al.[37] on carbon formation mechanisms on metal catalysts. The authors applied joule heating to nickel and copper–nickel catalysts to carry out ethylene hydrogenation. The aim was to selectively activate the catalyst while keeping the gas phase relatively cold to minimize unwanted thermal decomposition reactions in the gas phase and pyrolytic carbon formation (Figure 7). Indeed, a higher ethane yield and lower solid carbon deposits, exclusively of catalytic origin, were obtained in comparison to those in the conventionally heated process. Furthermore, the dramatic changes in the gas selectivity for the same catalyst activity suggested that the current flow through the support induced not only resistive heating but also electronic perturbations in the metal particles.[37] Selective catalyst heating by means of microwaves to maintain a temperature difference between the catalyst and the gas phase has been studied as well (eg, Garcia et al.[38]).

Activating catalysts with light: Future roles for plasmonic structures?

In the field of synthetic organic chemistry, light with a sufficiently high energy (deep UV) has been used to directly activate the molecules.[39] Photochemical conversion can also be induced by the activation of a catalyst, typically a

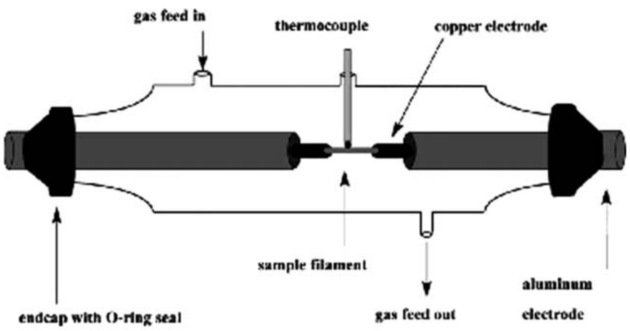

Figure 7. Localized catalyst unit heating by means of an electrical current flow.

Reprinted with permission from Marotta CL, Terry R, Baker K. The use of a localized heating protocol in heterogeneous catalysis. *J Mol Catal A*. 2003;195:209-18.[37]

semiconductor, rather than the reactant. Here, the absorption of a photon with sufficient energy leads to a charge separation because of the promotion of an electron from the valence band of the semiconductor catalyst to the conduction band; this generates a hole in the valence band. To have a photocatalyzed reaction, electron–hole recombination, subsequent to the initial charge separation, must be prevented as much as possible. By far, the dominant research area of photocatalysis has been the photodegradation of organic compounds either in air or in water. However, the possibility of inducing selective, synthetically useful redox transformations has attracted more and more attention. Last but not least, photocatalysis can allow the conversion of solar energy into chemical energy in, for example, water splitting or CO_2 activation.

Two major difficulties in classical photocatalysis are their low photocatalytic efficiency and the energy band positions of the materials and reactants. The energy band positions of the photocatalyst determine its cutoff photon absorption wavelength, whereas those of the redox group relative to those of photocatalyst determine whether a specific reduction or oxidation reaction is possible and efficient. Commonly used photocatalysts, such as TiO_2 and ZnO, absorb UV light only ($\sim$3.2 eV). This requires special artificial light sources, and it also means that very few solar photons ($\sim$4%) could be used to activate these catalysts (the visible range of solar light represents an abundant, largely untapped energy source for photocatalysis). Moreover, the determination of higher efficiency schemes for electron–hole separation is still needed to realize more efficient conversion of light energy in photocatalytic devices with low fabrication costs.

It has been demonstrated recently that noble metal nanostructures show considerable potential in this field because of their unique optical properties.[40] Metal nanostructures are able to absorb light at specific wavelengths across an extensive region of the electromagnetic spectrum to produce electron density waves; this depends on their composition, size, geometry, and dielectric environment.[41–43] These distinctive properties make metal nanostructures excellent candidate substrates in the field of photocatalysis.[44]

When light interacts with metal nanostructures that are smaller than the incident wavelength, the resonant, photon-induced collective oscillations of metal valence electrons are generated, known as *localized surface plasmon resonances* (LSPRs).[45] LSPRs are characterized by the ability to concentrate the energy of incoming photons in small volumes surrounding the nanostructure, which is observed as a huge enhancement in the electromagnetic fields. Consequently, such nanostructures can act as very efficient light-trapping components.

There are two main incentives for the development of plasmon-enhanced photocatalysis. The first one is to extend the effective optical band gap of the catalyst (from the UV to the visible range). The second one is to considerably enhance the separation of the photo-induced electrons and holes and to suppress their recombination by the formation of Schottky junctions.[46] In addition to that, metal nanoparticles can act as antennas that localize the optical energy and, because of that fact, smaller amounts of semiconductor are needed to achieve complete light absorption. Moreover, larger metal particles can efficiently scatter unabsorbed photons; this increases the path length of light through the semiconductor and produces more absorption near the semiconductor surface.[46,47] For instance, it was observed[48] that the scattering of Ag nanocubes enhanced the absorption of photons at 400–500 nm by up to 25%. Furthermore, the plasmons created an intense local electric field, which favored the photocatalytic reactions in several ways. For instance, it induced the polarization of the reactant molecules, which enhanced their adsorption on the photocatalyst surface. It also created local hot spots that increased the mass transfer of the reactants and, therefore, increased the reaction rates.[46]

From Theory to Practice: The Way Ahead

Industrial relevance

As we have seen previously, various energy-based methods for the molecular control of chemical reactions have been developed and studied in chemical physics, synthetic chemistry, and catalysis. The most important question, however, is whether and which of those approaches and methods could potentially provide a basis for enhanced molecular control in the manufacturing of chemical products. The gaps between the fundamental research and practical applications that need to be bridged, and the challenges ahead vary widely. Table 1 gives a brief overview of industrially relevant reactions and processes that have been addressed with the energy-based reaction control technologies discussed in this article. In the table, we also provide, as illustration, some exemplary quantitative comparisons reported in the literature.

The challenges

In the electric-field-based control of homogeneous gas-phase reactions, the first issue fundamental to production-scale feasibility is the molecular density of the stream passing through the reactor. Molecular densities in conventional processes running under normal pressure are usually somewhere between 10^{18} and 10^{19} molecules/cm^3. Molecular densities in standard MBs (ca. 10^{13} molecules/cm^3) are far too low for practical applications. On the other hand, the highest molecular densities achievable from Laval nozzles (ca. 10^{17} molecules/cm^3) come fairly close to the values seen in conventional processes. Unfortunately, the high operating costs of Laval nozzle technology and certain technical issues (eg, the distortion of the boundary layers by the electric field) make this option unfeasible. The strength of the electric fields necessary to orient even simple dipolar molecules appears too high to apply it in commercial equipment, although the concepts of honeycomb multibeam hexapole electric fields to process larger throughputs are known (see Figure 8).

An open question is whether the orientation of molecules with electric fields at reasonable molecular densities and temperatures could be successfully realized in microchannel or millichannel systems, where the voltages applied do not need to be extremely high because of small characteristic dimensions and where the physical barriers (channel walls) to some degree constrain the freedom of molecular movements. Those issues are currently being investigated in our group in an electric field-assisted millichannel reactor

Table 1. Application Potential of Energy-Based Reaction Control

	Energy	Reactions and processes studied	Effects observed	Comparison with conventional technology (illustrative example)
Homogeneous	Electric field Laser	CO_2 splitting, H_2O splitting, steam reforming, dry reforming	Higher selectivities and low-temperature processes	Not available: fundamental exploratory phase
	Plasma	CO_2 splitting; H_2O splitting; steam reforming; dry reforming; nonoxidative methane coupling; biomass gasification; transformations of coal to syngas, hydrocarbons from heavy oil, propane to C_{4+}, and hydrogen from propane; CO_2 reduction with hydrogen	Higher conversion, higher selectivity, lower temperatures, cleaner products	Oxidative conversion of hexane to olefins on Li/MgO catalyst selectivity to $C_2^=$-$C_5^=$ at 500°C: 21.2% conventional and 43.9% with plasma.[49] Hydrogen-rich syngas from coals. Cold gas efficiency $<$ 70% conventional and 84% with plasma.[50]
	Microwaves	Fine-chemical and pharmaceutical synthesis, polymerizations, polycondensations	Shorter processing times, better yield/selectivity, higher molecular weights, better product form, lower energy consumption	Oxidation of benzyl alcohol to benzyl aldehyde in a microchannel reactor with a conversion of 8.37% with conventional heating and 75.39% with microwave (MW) heating.[51]Poly(butylene succinate) with a molecular weight of about 1×10^4 after 5 h of conventional heating and a molecular weight of about 1.65×10^4 after 1 h of microwave heating.[52]
Heterogeneous	Microwaves (catalytic)	Methane oxidative and nonoxidative coupling, methane oxidation, methane steam and dry reforming, transformation of biogas to syngas, methanol steam reforming, HCN synthesis, propane oxidation, ethane/propane/*n*-butane dehydrogenation, *o*-xylene/toluene oxidation, ethyl benzene dehydrogenation	Higher conversion, better selectivity, reduction in reaction temperature	Methane dry reforming at 600°C CH_4 conversion: 35% conventional and 57% with MW. CO_2 conversion: 52% conventional and 62% with MW. H_2/CO ratio = 0.69 conventional and 0.78 with MW.[53] Oxidative dehydrogenation of ethyl benzene at 350°C conversion: 15% conventional and 27% with MW. Selectivity to styrene: 53% conventional and 92% with MW.[54]
	Photocatalysis	Environmental reactions, oxidations, water and CO_2 splitting	Low temperature, better selectivity, low energy consumption	Cyclohexane oxidation to cyclohexanone: conventional: conversion = 9% and selectivity = 70% (including cyclohexanol). Photocatalysis on NaY zeolite with visible light: conversion $>$ 40% and selectivity = 100% to cyclohexanone.[55]

coupled to a MB[57] (Figure 9). Furthermore, in structured, small-scale systems, such as microreactors, laser light could potentially be used for the selective excitation of molecules, as it has recently been shown for a liquid-phase photochemical process.[58]

In larger scale processes, the use of shape-selective, nanostructured (catalytic) materials to temporarily immobilize the molecules in certain position at the moment of their activation evidently presents a better option than that of electric fields. The synergistic combination of such nanostructured materials for molecular orientation with one or another form of electromagnetic energy for selective activation of the molecules is definitely worth further studies.

Nonthermal plasma has proven its application potential in the chemical processing of important molecular gases, such as CO_2, CO, H_2O, and NO_2, that have an impact on environmental chemistry. It becomes an interesting option for steam and dry reforming, and one of the numerous examples is the syngas generation from propane through the use of nonthermal plasma at atmospheric pressure and low temperature.[59] The reforming process delivers molecular hydrogen as the main product at concentrations as high as 50% and methane, carbon dioxide, and other hydrocarbons as side products at concentrations as low as 6%. Table 2 shows an interesting comparison of the economy of the methane steam reforming with oxygen (SRO) process (Haldor Topsøe) and of the integrated syngas-to-liquids process in small distributed systems, including gas treatment (GT) and solide oxide fuels cells (SOFC) in conventional catalytic and plasma reactors.[60]

Next to it, plasma can be applied to generate high-purity syngas from waste. Thermal plasma units for the gasification of municipal solid waste are already operating on the commercial scale.[61] The nonthermal plasma can be advantageously used for the conversion of waste biomass to syngas

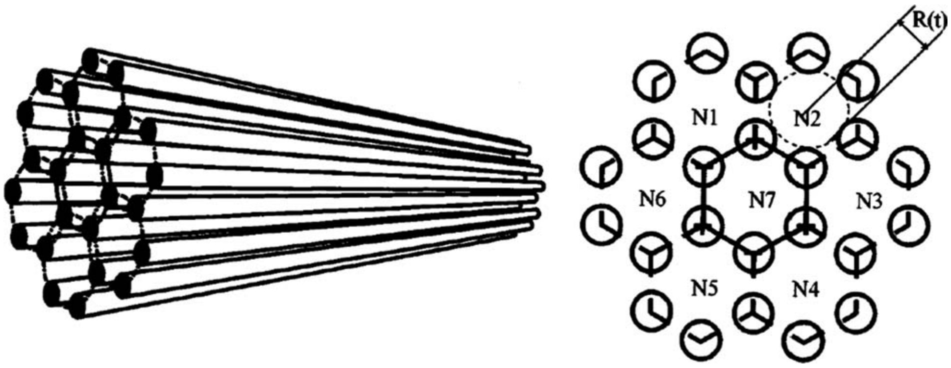

Figure 8. Multibeam hexapole honeycomb device for orienting molecules in a static electric field (R(t) is distance between the hexapole axis and the rod surface, Ni is the number of the MB-line).

Reprinted with permission from Shimizu Y, Che DC, Hashinokuchi M, et al. Electrostatic hexapole state selector: honeycomb field for integrating intensity of oriented molecular beams. *Rev Sci Instrum*. 2003;74:3749-52.[56]

with low tar generation and with high energy recovery levels. Table 3 presents some experimental results from a continuous, microwave-induced plasma gasification unit for waste biomass gasification, developed in our group in collaboration with the Bill and Melinda Gates Foundation.[62] The results confirm the low tar generation (low CH_4 concentration) and high energy recovery levels.

In all plasma applications to chemical processing, it is essential to select the proper type of plasma through control of the input power (direct current, radio-frequency (RF), microwave), operating pressure, temperature, and degree of ionization (weak, partial, or fully ionized). An absolutely crucial role is played by the reactor design, which should deliver an optimal plasma zone configuration and residence times therein and enable the control of the behavior of the electrons, which represent the main energy-exchange carriers in the reaction environment. There are very many plasma reactor designs that have been developed and compared in the literature; see, for instance, the comparative study on nonthermal plasma-assisted reforming technologies by Petitpas et al.[63] On the other hand, the miniaturization of plasmas coupled with microfluidics and microelectronics technology should deliver much better precision in the control of hot electrons and the short-living species generated in plasma-assisted processes. Microplasma reactors (eg, Figure 10) can offer advantages for the chemical processing of hydrocarbons for conversion into the hydrogen-rich products needed in energy applications, such as combustion and fuel cells.[64] Microchannel structures offer, among other things, the possibility of the use of high-pressure microplasmas that allow the prevention of instability problems and the maintenance of a self-sustained discharge.[65,66] In addition, very efficient heat removal can be realized in such systems.

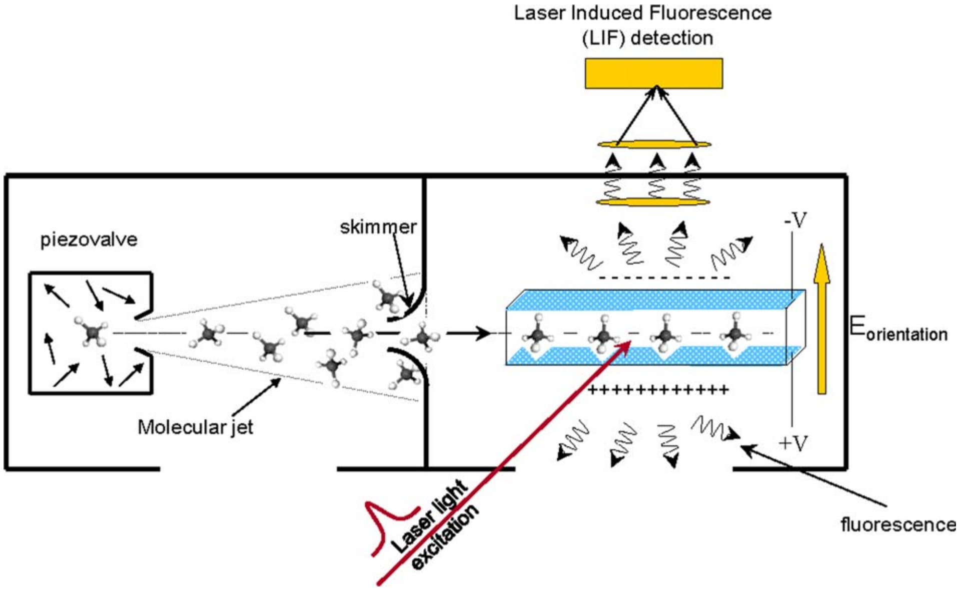

Figure 9. Scheme of the experimental setup used to investigate the electric field-based molecular orientation and laser-based activation in millichannels.

Table 2. Comparison of the Economy of the SRO Process in Conventional and in Plasma Reactors[60]

	SRO investment cost (euro/N m^3 h^{-1} H_2)	H_2 cost (euro/Nm^3)	SOFC–GT–SRO system investment cost (euro/W)
Chemical reactors	750–900	0.05–0.08	5.12
Plasma reactors	65	0.23	4.59

Table 3. Waste Biomass to Syngas Transformation via MW-Induced Plasma: Exemplary Results from Our Own Research[62]

Forward microwave power	4 kW	4 kW
Plasma agent	N_2	Air
Product gas composition	20 L/min	15 L/min
H_2	13.6%	23.3%
CO	16.6%	34.5%
CO_2	0.3%	4.4%
CH_4	0.1%	1.0%
Energy recovery (lower heating value versus. net microwave power)	99%	184%

Shrinking the size of plasma reactors offers also the opportunity for low-power operation. The electric field strength in the space between two electrodes grows inversely proportional to the space width, so it is possible to exceed the ionization potential of the carrier gas and sustain the discharge through the application of a lower voltage. Therefore, microplasmas can be operated at consistently lower power, and this leads to lower operating costs. The main drawback, however, stems from the fact that plasmas are normally extinguished by recombination at the walls because of the process of ambipolar diffusion of electrons and ions. Wall collisions are magnified by the larger surface-to-volume ratio of the microchannels. During the downsizing of the reactor, a high E can be used to some extent to create new charges in the bulk and, hence, compensate the loss at the walls. In this regard, the proper regime of operation, in which low-voltage nonthermal plasma can deliver a high output, is determined by whether the timescale of the reaction kinetics is comparable to or faster than that of the ambipolar diffusion. Hence, a comparison of these timescales needs to be addressed.[65]

In the field of heterogeneous gas-phase chemistry, nonthermal plasma is usually more energy expensive than thermal catalysis, as the required energy for the conversion of a reactant molecule through electron-impact dissociation or ionization reactions is multifold higher compared to the energy needed to heat the reactant molecule from room temperature to the reaction temperature in a catalytic reactor.

Therefore, in a plasma catalytic reactor, the chemistry task should mainly be taken over by the catalyst itself, whereas the role of the plasma should be to increase the internal energy of the reactants by means of vibrational excitation reactions. In turn, selective vibrational heating depends on the proper control of the electron density and energy distribution functions. Conventional nonthermal plasma sources, such as DBD or coronal discharge, do not enable energy-effective product yields at present. The discovery and application of novel plasma activation methods to catalytic reactors is needed. The starting point can be the methods that have been used by plasma physicists for control of the electron energy distribution function and electron temperature in rather simplified systems (single gas-phase components, eg, H_2 or Ar). Information on relevant methods, such as the application of a double power source, fast electron injection, discharge current obstruction, negatively biased grids, selective electron absorption, and magnetic filters, can be found in the literature.[68,69]

The second challenge toward the realization of efficient plasma catalytic reactors is the development of reactor designs with very high catalytic surface areas. Because of the very short lifetime of vibrationally excited species ($<10^{-7}$ s), the contact area between the gas and catalytic phases should be as high as possible. On this ground, structured microreactors or millireactors seem to be the most suitable reactor concepts for plasma catalytic chemistry.

The primary challenges of the improved reaction control in microwave-assisted processes, both homogeneous and

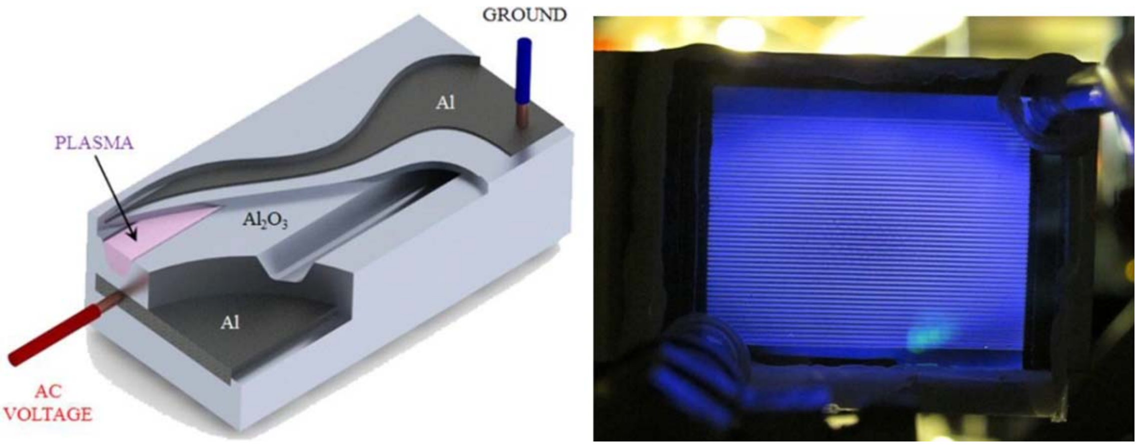

Figure 10. Microplasma reactor for ozone generation: Cutaway view and a 48-channel planar array of Al/Al_2O_3 microchannels.

Reprinted with permission from Kim MH, Cho JH, Ban SB, et al. Efficient generation of ozone in arrays of microchannel plasmas. *J Phys D*. 2013;46:305201.[67]

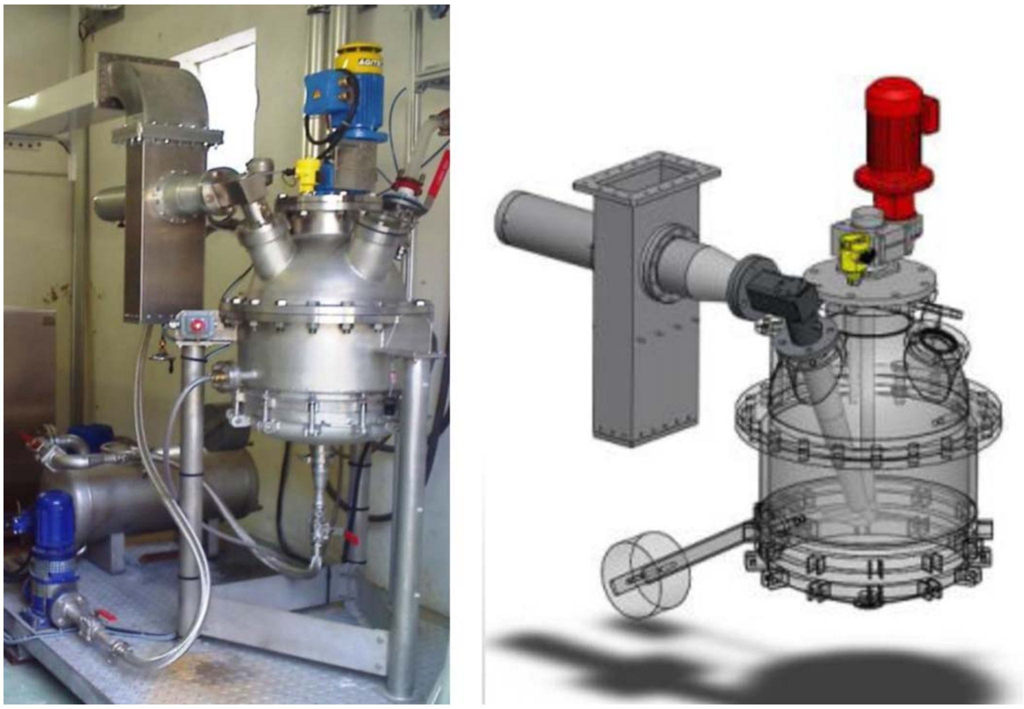

Figure 11. Pilot-scale microwave reactor with INTLI developed by SAIREM (France; Radoiu et al[70]).

Reprinted with permission from SAIREM SAS.

heterogeneous, are the introduction of the microwaves into the reactor and the control of the field uniformity there. Obviously, the placement of a reactor inside a microwave cavity puts clear constraints on the material from which the reactor is made (it must be transparent to microwaves) and, consequently, on the processing conditions there (temperatures and pressures). One of the ways to circumvent this problem is the internal transmission line (INTLI) concept,[70] in which the microwave is brought into the reactor by a specially shaped waveguide (Figure 11). In this concept, the reactor vessel can obviously be made of steel, can be pressurized, and so on. In addition, the controllable energy transfer to the medium along the length of the lossy transmission line is not only beneficial in terms of uniformity, but it also reduces the total power consumption by minimization of the reflected power. Our study on polyester preparation in the INTLI reactor showed that the reflected power there was almost fourfold lower compared to a conventional multimode cavity.[71]

On the other hand, the field and, therefore, the intensity of irradiation in typical multimode microwave equipment, from kitchen appliances up to large-scale industrial ovens, is highly nonuniform. Such nonuniformity may be acceptable in operations such as drying, thawing, or pasteurization, but it is surely not acceptable in the case of chemical reactions. Here, not only the nonuniformity of the field itself plays a role but also the orientation of the flowing reactants with respect to the field. This issue is illustrated in Figure 12 from our own research, which shows the heat generation in a single-millitube flow reactor placed in a rectangular resonant microwave cavity. One can clearly see that the heat generation occurred almost exclusively in the vertical part near the

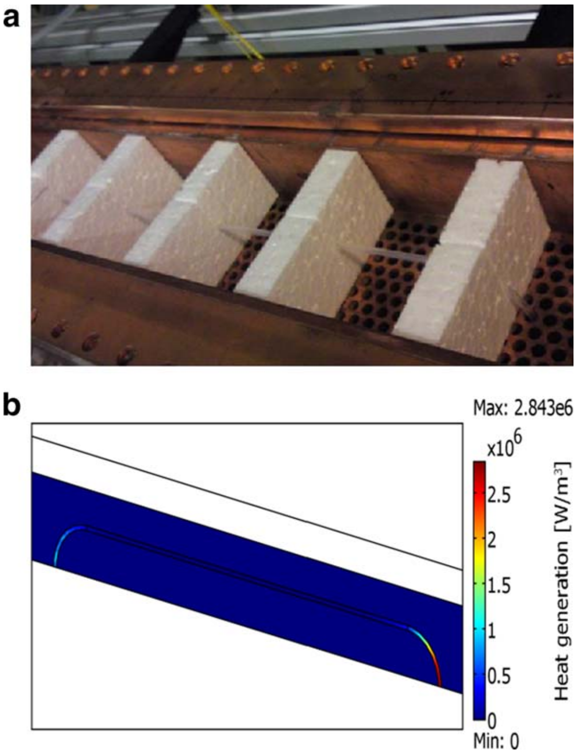

Figure 12. Heat generation in a millireactor tube placed in a rectangular cavity: (a) experimental setup and (b) numerical simulation (Sturm[72]).

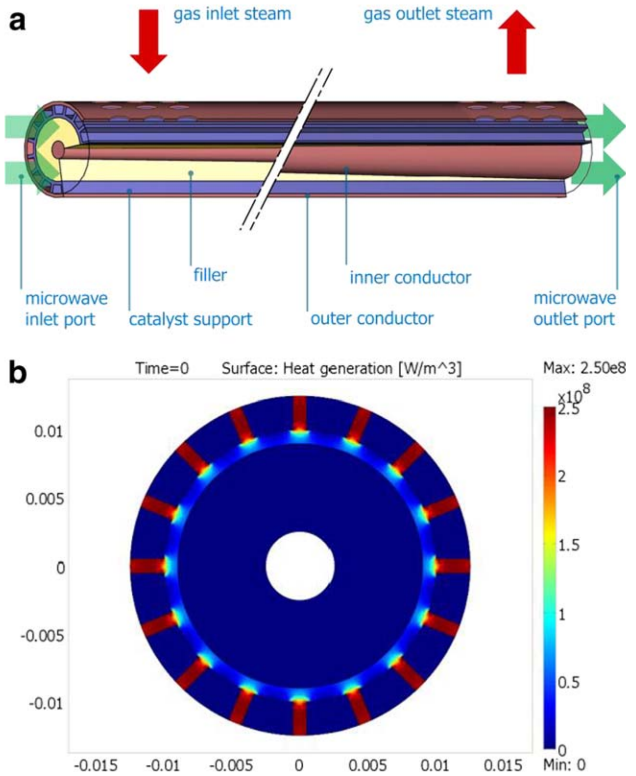

Figure 13. (a) TWR for gas-phase heterogeneous catalysis. (b) Heating rate distribution over the channels of the reactor.

inlet, which was more or less parallel to the field direction. In the horizontal part of the reactor (perpendicular to the field), heating practically did not occur. The simulation results shown in Figure 12(b) were validated experimentally.[72]

The concept that successfully addresses both the previous issues is the traveling wave reactor (TWR), shown in Figure 13(a), in the version for heterogeneous catalytic reactions.[72] Similarly to a coaxial cable, a TWR consists of outer and inner conductors with filler between them. A monolithic support with catalytic microchannels/millichannels is placed on the filler, and the microwave is allowed to travel along those channels. With a full cylindrical symmetry, the channels placed at the same radius are evenly irradiated with microwaves, as shown in Figure 13(b). Additionally, one can manipulate the diameter of the inner conductor to compensate for attenuation. For large-scale applications, bundles of TWRs (similar to multitubular reactor designs) are envisaged.

On the other hand, in heterogeneous catalytic systems, guidelines for the rational design of microwave-receptive catalysts that can attain the optimum heating rate and pattern for a given process do not exist. The key dielectric properties (real and complex permittivity for the prediction of the interaction of the material with the microwave field and the induced heating rate) are seldom measured. Dielectric characterization, when done, is done at room temperature and under nonreactive conditions. Consequently, the dielectric property values obtained may not be representative of those during the process. There is a need to develop instrumentation that enables the measurements of the dielectric properties of microwave-irradiated catalytic reactors under real process conditions over a wide frequency range. The process conditions concern the actual reaction temperature, which may be several hundred degrees Celsius, and the exposure of catalyst to reactants and products in gas or liquid form.[73] In the next step, the results should be used to guide the development of new models based on effective medium theories,[74] which will correlate the dielectric properties of catalyst composites as function of the catalyst size, shape, composition, and temperature.

In photocatalysis, the effective illumination of the catalyst and, consequently, photon transfer remain the main challenge. Nanoscale illumination of the catalyst (integration of an electroluminescent light source and catalyst surface) postulated by Van Gerven et al.[75] still waits for its first feasible realizations.

On the other hand, the pioneering applications of hot-electron-induced photochemistry on nanoparticles have been recently demonstrated in gas-phase heterogeneous catalysis for the oxidation of ethylene on Ag nanocubes,[76,77] the room temperature dissociation of H_2 on Au,[78] and water splitting.[79,80] It should be noted that the dissociation of H_2 is one of the most important and challenging reactions for heterogeneous catalysis, with the activation energy (4.51 eV) being too large to surmount the use of a thermally induced process.

Although rather complex and still in its infancy, plasmonic photocatalysis has already demonstrated its capability to tackle the problems of low photocatalytic efficiency and low response to visible light. Significant enhancements in the photocatalytic efficiency, typically up to 10 times, have been obtained; see the review by Zhang et al.[81] and the references therein. However, there are a number of important challenges in the application of plasmonic-enhanced photoreactors on an industrial scale. A limiting factor in the use of metal nanostructures for light trapping is the high spatial localization of the LSPR-modified density of states (channels for storing and/or routing the electromagnetic energy in a given medium). Accordingly, the performance of a thick layer of adsorbate can primarily be boosted via the LSPR-induced photon scattering, which has been successfully used to engineer plasmonic antireflection coatings. Another important challenge in plasmon-enhanced photocatalysis is the relatively high level of dissipative energy losses (eg, hot electrons cooling, light scattering, localized heating of nanoparticles). Generated hot electrons have to be extracted out before they cool down; this happens on picosecond timescale in most metals. In our opinion, there is plenty of room for further fundamental and applied studies. Also, new reactor designs, especially for plasmonic photocatalysis, certainly need more attention.

Summary and Take-Home Message

In Table 4, we summarize our discussion on the challenges of energy-based methods for reaction control. Although pilot-scale or commercial-scale applications have already been reported for most of the technologies presented,

Table 4. Status and Challenges of Energy-Based Reaction Control

Energy	Status	Main challenges	Way forward
Electric field Laser	Fundamental studies with MB	Feasible maximum throughput, attainable molecular density of the stream, necessary electric field strength	Microchannels/millichannels in combination with the electric field
Plasma	Bench-to-pilot scale and isolated cases of commercial-scale applications have been reported.	Control of the plasma field distribution and contact times, catalyst design, ultrashort lifetimes of species generated, energy utilization efficiency	Novel reactor designs and catalyst development
Microwaves	Bench-to-pilot scale and isolated cases of commercial-scale applications have been reported.	Feeding of microwaves into the reactor, penetration depth, control of the microwave field distribution, catalyst design, energy efficiency	Novel reactor designs (eg, traveling wave) and the development of microwave-responsive catalysts
Photocatalysis	Commercial scale in some (mostly environmental) applications	Photon-transfer limitation (light source–catalyst configuration), effective optical band gap, electron–hole recombination	Novel reactor designs, development of catalysts with *in situ* illumination, plasmonic enhancement

the challenges are still tremendous. The way forward for addressing those challenges basically boils down to reactor design, catalyst design, or both. Obviously, a deeper understanding of the underlying mechanisms and phenomena is an absolute prerequisite for moving forward. For that deeper understanding, new instrumentation needs to be developed to observe, measure, and control at the time and space scales of molecular events.

In this article, we have emphasized the essential connections between the chemical physics, catalysis, and chemical engineering and have examined the technical feasibility of controlling the reacting molecules by different energy fields. Perfect reactors still appear to be quite far away. They exist only in physicists' labs so far and are limited to small, simple molecules only. As of today, there are no methods of practical significance, catalysts included, which can fully control chemical reactions at the molecular level. Complex downstream processing systems in chemical plants are clear proof of that. The energy-based methods discussed in this article will not solve that problem on their own either. As has been shown, most of them do not provide molecular control *pur sang,* although they are definitely able to significantly improve the outcome of many industrially relevant reactions by influencing the local reaction and heating rate conditions on the nanoscale/microscale and/or by bringing molecules into energy states not achievable with conventional heating. These methods will not replace the catalysis in chemical industries, but they can help catalysis to reach beyond the limits it has today. They can also intensify noncatalytic processes, such as gasification or pyrolysis. More symbiotic research between catalysis, physics, and chemical engineering is postulated. A better understanding of the underlying phenomena and interrelations between the catalysis and various energy forms is a prerequisite here. Concurrent development of tailored, energy-responsive catalysts and novel reactor concepts with enhanced field control should lead to new quality in chemical processing. With electricity becoming the most widely available, versatile energy form of energy on Earth, the electricity-based methods discussed in this article may play an important role in the development of flexible, distributed production units for the clean manufacturing of fuels and chemicals in various environments. Microstructured and millistructured systems will be important elements in that development.

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