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THE USE OF ULTRASOUND FOR HETEROGENEOUSLY CATALYZED HYDROGENATION REACTIONS USING MICROREACTORS.

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ABSTRACT

The MAPSYN European project aims at nitrogen-fixation reactions intensified by plasma and selective hydrogenations intensified by microwaves and ultrasound, being energy efficiency a key aspect. The use of microreactors has emerged as an option for this purpose. They display many benefit such as enhanced surface-to-volume ratios, excellent mass- and heat-transfer capabilities and better reaction yields. However, possible drawbacks of microreactors are inefficient reactant mixing and clogging of microchannels when solid-forming reactions are performed or solid (catalysts) suspensions are used. It is well known that sonication promotes efficient mixing, catalyst reactivation, and an eventual intensification of chemical processes.

RESUMEN

El proyecto europeo MAPSYN pretende desarrollar reacciones de fijación de nitrógeno intensificadas por plasma e hidrogenaciones selectivas intensificadas por microondas y ultrasonidos con alta eficiencia energética. Se propone para ello usar microrreactores por su mayor razón superficie/volumen, excelente transporte de calor y de masa y mejores rendimientos de reacción. Sin embargo, presentan algunos inconvenientes como la ineficiente mezcla de reactivos y la posible obstrucción de los microcanales en reacciones con sólidos en suspensión (catalizadores) o con formación de precipitados. La sonicación promueve un eficiente efecto de mezcla, la reactivación del catalizador y una eventual intensificación de los procesos químicos.

1. INTRODUCTION

Chemical industry needs improvements, especially in Europe, for many reasons and in particular because of rising energy costs. Nowadays the raw and fine chemicals production requires new, cheaper and more environmentally sustainable technologies compatible with the use of heterogeneous catalysts with a focus on reactor engineering aspects and non-conventional energy sources. In fact, optimization of conventional technologies can be achieved by using alternative forms of energy that offer the possibility of process intensification.

Among the different processes involved in the production of chemical raw materials, nitrogen-fixation reactions are particularly important. Nitrogen can be fixed in the form of different compounds from ammonia or nitric acid to hydrogen cyanide that can be used for large-scale applications, not only in chemical production industries but also in a wide variety of manufacturing industries. One of the most interesting and challenging processes is the production of nitrogen oxides by the direct reaction of nitrogen and oxygen in the air because of the availability and low cost of the reactants. Taking into account that the thermal reaction is highly endothermic and proceeds at very high temperatures, it is important to find a suitable procedure of process intensification with a reduced energy input.

Heterogeneously catalyzed reactions systems are industrially are of the most important classes of reactions, and a large number of commodities ranging from bulk chemicals and pharmaceutical products synthesis to alimentary preparation, are based on them. More specifically, the syntheses of fine chemicals and pharmaceuticals usually include the dangerous catalytic hydrogenation of organic compounds, which is classically carried out under a hydrogen atmosphere, often at elevated temperature in pressure-resistant reactors. The usually slow heating or cooling rates of those reactors can negatively affect the selectivity. The unwanted by-products formed require the introduction of new separation steps. The deactivation of the solid catalyst is also an important problem. Intensification leading to safe, energy-efficient hydrogenation processes is certainly welcome in the chemical industries where these transformations are very important.

In this context, chip-based microreactors can exhibit significant advantages over classical reactors because the reaction conditions in the microchannels are different to those in large-scale reactors. Properties such as fast and efficient heat and mass transfers due to short diffusion distances, and high surface/volume ratios can significantly improve organic synthetic processes or other applications [1]. Admittedly, one of the biggest hurdles in the development of microchannel flow chemistry is the handling of solids, which can be catalysts, reagents, products, and by-products. For example, microchannels can be irreversible clogged by the formation of precipitates during the reaction. In addition, microreactors can suffer from inefficient reactant mixing. To prevent these problems, ultrasonic irradiation has been suggested as an option, not only because of its well-known mixing effect, but also because of catalyst reactivation and eventual intensification of chemical processes by mass transfer enhancement.

The European Commission in its 7th Framework Program promotes the use of alternative energies for chemical industry in its call behind (NMP.2012.3.0-1; highly efficient chemical syntheses using alternative energy forms). The MAPSYN project (Microwave, Acoustic and Plasma assisted SYNtheses) was chosen for funding in this context and is presented here. The main goal of the MAPSYN project is to develop novel procedures for selective heterogeneously catalyzed hydrogenations and for nitrogen fixation reactions using non-conventional energy sources such as plasma, ultrasound and microwave irradiation. The different intensification procedures should be efficient from energetic and environmental viewpoints. The MAPSYN project aims not only to the development of a multifaceted strategy and a net of collaborations, but also to catalysts selection, laboratory experiments of synthesis, and physical modeling, characterization, and reactor fabrication that enable partners to develop and test module reactor type devices [2].

The consortium of the 3.5-year MAPSYN project is formed by 12 partners including research & development centers, small and medium enterprises, academic and large industry partners: C-Tech Innovation (Project coordinator, UK), Technische Universiteit Eindhoven (Technical lead. Plasma and microwave experts, NL), Evonik Industries (N-fixation end user, DE), Institut für Mikrotechnik Mainz (Microreactor construction, DE), University of Hull (Catalyst formulation, UK), DSM (Hydrogenation end user, NL), Coventry University (Sonic chemistry, UK), Syrris (Microreactor and PI expertise, UK), Università degli Studi di Torino (Organic chemistry hydrogenation, IT), UWE (Plasma engineers, DE/IT), Konstandin & Partner engineering GmbH (Rig build engineers, DE), and the University of Alicante (Acoustics and modeling, ES)

2. PLASMA PROCESSING APPLIED TO NITROGEN-FIXATION REACTIONS

Most of the raw simple chemicals formed by fixing atmospheric nitrogen (NO, NH_3, HCN or HNO_3) are of interest for the MAPSYN project. However, nitrogen has a very high dissociation energy that should be overcome to yield industrially competitive processes for atmospheric nitrogen fixation. Plasma intensification is a promising approach. When enough electrical energy is supplied to a gas, highly excited atomic, molecular, ionic and radical species are generated. Plasma is the term used to refer to this state of matter. Under plasma conditions, fast reactions occur. Already in 1904 Birkeland and Eyde used an industrial plasma reactor for nitric oxide synthesis from air [3]. This nitrogen fixation reaction had poor energy efficiency compared to the classical Haber process with ammonia and it was abandoned by industry. However, a large number of publications on plasma nitrogen-fixation appeared mainly at the end of the 20th century as a consequence of advances in the understanding of the plasma reaction kinetics.

3. MICROWAVE AND ULTRASOUND APPLIED TO HYDROGENATION REACTIONS

Microwave irradiation leads to efficient internal heating with a homogenous heating profile, avoiding the thermal gradients produced by the conventional heat transfer methods, proven to be in many cases rather slow and inefficient. The heating caused by microwaves is a consequence of radiation absorption in terms of dipole rotation and ion displacements. The frequency of common microwave ovens (2.45 GHz) is lower than the energy needed to break chemical bonds and therefore the effect of microwaves over chemical reactions is mainly related to the heating process. The efficiency of the microwave irradiation depends on the local strength of the electromagnetic field and on the permittivity and permeability of the system, which in practical terms means that both the nature of the reactants and the geometry of the microwave reactor affect the heat generation. Microwave heating, not only dramatically enhances the rate of most chemical reactions, but can also increase yields and selectivity. In addition, microwave irradiation of heterogeneously catalyzed reactions creates hot spots on metal sites at the catalyst surface, giving rise to intense temperature gradients between the catalyst and the bulk. This selective heating can dramatically promote chemical reactions.

In recent years, the chemical and mechanical effects of ultrasound have been applied in general chemical synthesis, heterogeneous catalysis, as well as in catalyst production, and pollutant remediation. In the case of power ultrasound, there is no direct interaction between the energy emitted by the transducer and matter at molecular level and most of the chemical effects are produced by the collapse of cavitation bubbles. For homogeneous sonochemical reactions of liquids has been reported in the literature that chemicals react: inside the cavitation bubbles, at the bubble gas–liquid interface and in the liquid bulk. For heterogeneous liquid–liquid or liquid–solid systems the interphase plays an important role in their sonochemical behavior [4]. Importantly, the collapse of the cavitating bubbles also generates mechanical effects such as shock waves and shear forces, and also streaming and microjets when solids are present, which mainly contribute to the mixing effect and to particle erosion, fragmentation and cleaning.
In heterogeneous catalysis, one of the most prominent cost-increasing factors is the need of catalyst regeneration and replacement because of catalyst deactivation. The mechanical effects caused by cavitation at liquid–solid interfaces (streaming, microjetting and erosion) have been used by researchers to solve that problem. Ultrasound can also enhance mass transfer and reaction rates, even if it does not affect the reaction chemically.

Among the large number of heterogeneously catalyzed reactions, catalytic hydrogenation reactions are of special interest. As mentioned above, the temperature and pressure-resistant classic reactors used for catalytic hydrogenations are manufactured with thick walls, and the usually rather slow energy transfer rate can negatively affect selectivity. Unwanted by-products can be formed, which increases the separation and purification costs, rendering the whole process unaffordable. Over the past decade several authors have reviewed modern green and efficient catalytic hydrogenations processes, including reactions assisted by microwaves, by

ultrasound [5] or by the use of novel gas-liquid microreactors [6]. Specifically, it has been reported that the enhancement of mass transfer and the reactivation of the catalyst by ultrasound irradiation help the sonochemical hydrogenations to proceed at room temperature [7]. Recently a batch sonoreactor for catalytic hydrogenations under moderate pressure (up to 7 bar) has been developed at the University of Turin, Fig. 1.

Figure 1. Ultrasound reactor for low-pressure hydrogenation reactions. Reprinted with permission from [2]. Copyright 2013 Elsevier.

MAPSYN will focus on the olefinic alcohol formation by selective hydrogenation of the corresponding acetylenic substrate. This is one of the most important industrial steps in the synthesis of vitamins A and E. 2-Methyl-3-butyn-2-ol (MBY) will be used as a model substrate for studying selective hydrogenation reactions and catalyst effectiveness.

4. MICROREACTORS COUPLED WITH ULTRASONIC AND MICROWAVE IRRADIATIONS

On the basis of their mode of operation, chemical reactors can be classified into continuous and batch-type reactors. According to their size, they can also be classified into traditional reactors or microreactors. Traditional reactors present several drawbacks related to mixing, temperature profile, thermal management, long residence time, safety, efficiency, waste and monitoring that can be overcome by using microreactors. These miniaturized reactors have micrometric dimension channels and reaction volumes in the nanoliter to microliter range. The miniaturization of chemical reactors has many benefits and now they are finding their way into research laboratories and industrial facilities where they can be found frequently integrated into pilot plants or production lines. As a result of the small reactants volumes used, a diminution of waste and environmental hazards are observed. As a result of the high surface area/volume ratio, an efficient contact and mixing control of the reagents produces reactivity enhancement. Moreover, microreactors facilitate an easy control of flow rate and residence time (directly proportional to the length of the microchannel), and a control over pressure, temperature or concentration gradients. They are also characterized by low manufacturing, operating, and maintenance costs, as well as low power consumption [1]. In addition, the ease of scaling through the concept of numbering up is another feature of microreactors. This is a particularly attractive advantage, as it saves both time and cost during process development and optimization.

In spite of the attractive features of microreactors, most chemical reactors with ultrasound or microwave intensification used for hydrogenation reactions keep on being batch-type reactors. An additional problem with these reactors is the difficulty in scaling them up from the laboratory to the production scale. Among the underlying reasons, we find that the ultrasonic field distribution strongly depends on the reactor geometry and that the penetration depth of microwaves into absorbing materials is limited. In fact, depending on the dielectric properties of the materials, microwave penetration is only of a few centimeters at 2.45 GHz. Therefore, for large-size batch reactors, it is not possible to obtain a homogeneous temperature profile using

traditional heating methods or microwave irradiation. In addition, the mixing efficiency of reaction solutions decreases when the batch-type reactors are scaled up. A continuous flow process is expected to mitigate most of the general drawbacks presented above for batch reactors, and to improve the efficiency of the processes. Moreover, with a microchannel flow reactor the problem of the penetration depth of microwaves is avoided and the energy transfer rate increases, making easier to achieve controlled temperature profiles.

Among the different microreactor designs, the falling film microreactor (FFMR), shown in Figure 2, arises as one the most studied configurations, being in principle appropriate for carrying out hydrogenations as it is well-suited for liquid/gas reactions [8]. In our particular case, the reactant liquid would be an acetylenic alcohol and the gas, pure hydrogen. In the FFR, the liquid flows downward due to gravity through microchannels carved on a plate, while a rectangular-shaped open space lies between the microchannel plate and the top cover of the housing through which the reactant gas flows. On the back side of the microstructured chamber a cooling fluid flows (heat exchanger), whereas the top cover of the reactor housing is equipped with a quartz window suitable for excitation or monitoring of the reacting system.

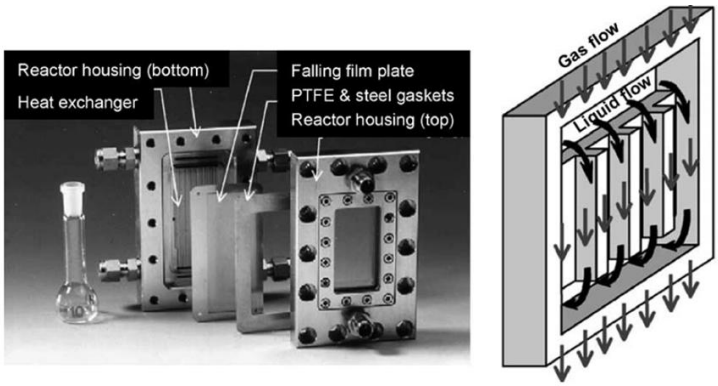

Figure 2. Components and scheme of the microstructured FFMR film reactor. Reprinted with permission from [1]. Copyright 2004 Wiley.

In the framework of the MAPSYN project, the microreactor should also be adequate for the incorporation of heterogeneous catalysts, either immobilized or suspended in the reactant liquid. In addition, the microreactor needs to be compatible with the incorporation of microwave and/or ultrasound irradiation. The clogging of the microchannels when solid-forming reactions are carried out or solid catalysts suspensions are used, are also drawbacks. Ultrasound irradiation can help overcome these problems and for that reasons the MAPSYN project includes this technique for intensify the catalytic hydrogenation reactions to be carried out in microreactors.

In the past, ultrasound irradiation has been combined with microreactors with the aim of preventing clogging and of intensifying processes. However in most cases, the microreactor was a capillary immersed in an ultrasonic bath. In the literature, only a few papers where the transducer is directly attached to the microreactor plate can be found: (i) In the simplest design, the transducer ultrasound waves (24 kHz) are indirectly transmitted via pressurized water placed between the steel jacket and the glass capillary containing the reactive mixture, Figure 3(a) [7]; (ii) In a second example, the transducer has been coupled to a more sophisticated microreactor by integrating it in the microchannel plate forming the microreactor, Figure 3(b) [8]; (iii) In the last example, the piezoelectric actuator has been integrated in a stack microreactor, Figure 3(c) [9]. In the second configuration either one or four transducers have been employed. For a preliminary acoustic study of these reactor see communication “Estudio acústico de reactores químicos ultrasónicos” AEV-1 005.

(a)

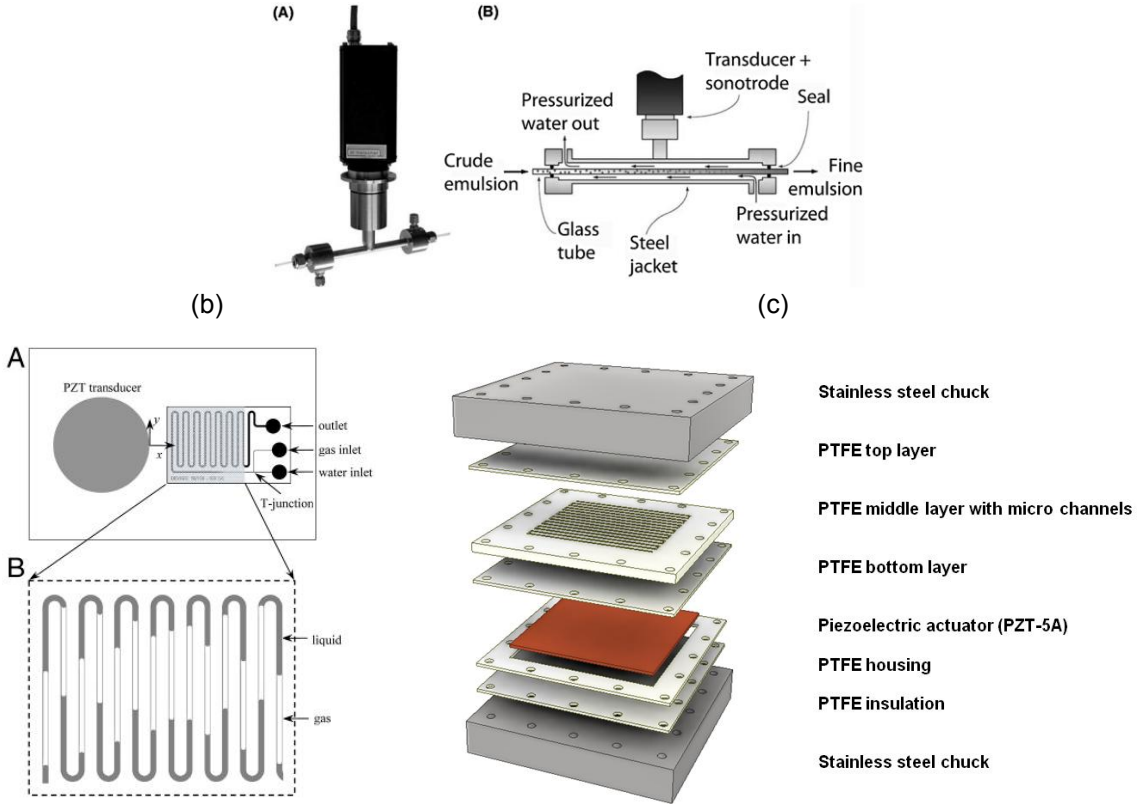

Figure 3. Transducers coupled to microreactor designs. (a) Ultrasound transmitted indirectly through pressurized water. Reprinted with permission from [9] Copyright Elsevier 2006; (b) piezoelectric integrated in the microchannel plate. Reprinted with permission from [10] Copyright PNAS 2010; (c) piezoelectric integrated in a stack microreactor.

One of the tasks to be carried out at the Universidad de Alicante in the framework of the MAPSYN project consists in the acoustic modeling and analysis of selected microreactor designs. Preliminary results have been obtained with an FFMR including a transducer on the back of the reaction plate. It should be taken into account that, as the final design should allow for both ultrasound and microwave irradiation, integrating the actuator in the carved microchannels plate is plausible, Figure 3(b). The problem of making compatible the piezoelectric material and microwaves can be solved easily if the part(s) of the plate with the actuator are placed outside the microwave cavity. Moreover by placing the piezoelectric actuator in the microreactor plate, higher energy efficiency for the transmission of the acoustic power to the reactants, and a better control of other operating variables are expected. Although some preliminary data have been obtained for this reactor configuration, further work should be done within the MAPSYN project framework.

The compatibility with microwave irradiation should also be taken into account when choosing the microreactor construction material. It should be completely microwave transparent, an excellent conductor of ultrasound, with high elasticity, and good chemical resistance. It should also be easy to manufacture. For the preliminary work presented here, arbitrary values of the physical properties, typical of ceramic materials, have been chosen.

The FFMR sketch shown in Figure 4 has been drawn in accordance to the dimensions described in the literature from its manufacturer (Institut für Mikrotechnik, Mainz). We have included a PZT actuator 1 mm in thickness (with or without PTFE joints) integrated in the stack microreactor. For the given dimensions, the acoustic field distribution was obtained by FEM (Finite Element Modeling) simulation. Specifically, the Piezoelectric Interaction module included in COMSOL MULTIPHYSICS was employed to obtain the spatial distribution of the acoustic pressure in the working fluids and the deformation of the solid parts of the microreactor. A linear

acoustic model has been employed and all the details of the calculations and boundary conditions are analogous to those described in “Searching for synergies between microreactors and ultrasound” ULT-0 013 communication.

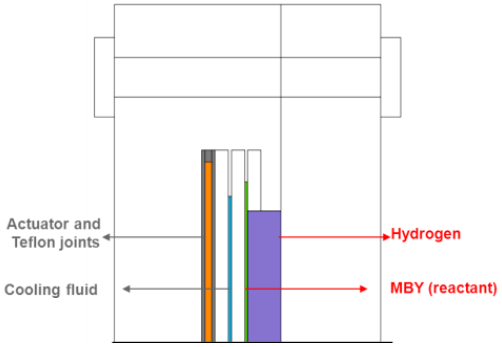

Figure 4. Representation of a cross section of the assembled falling film microreactor.

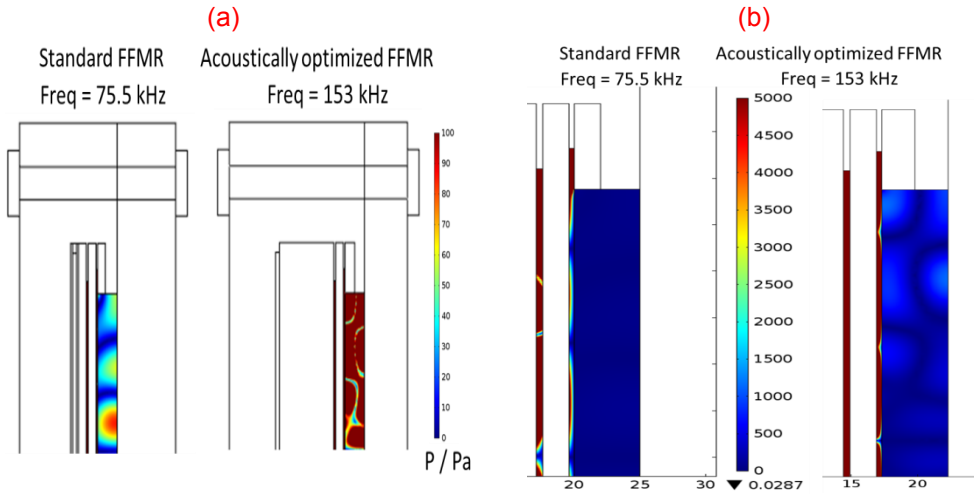

Figure 5. Comparison between the standard and the acoustically optimized FFMR. Acoustic pressure field (a) in the gas phase, and (b) in the liquid phase.

For the original design four main resonance frequencies in the range 65-90kHz have been found. At the optimum resonance frequency (74.5 kHz), the acoustic pressure in both reactive liquid and reactive gas is low and is not distributed homogeneously along the microchannel. The dimensions of the components of the reactor should be optimized to obtain the maximum possible acoustic pressure in the liquid. In order to approximately maintain the dimensions of the standard FFMR size, the frequency chosen to optimize the reactor was increased up to 153 kHz. The Langevin model was employed for the approximate sizing of the microreactor. Figure 5 also shows the calculated acoustic pressure for the acoustically optimized FFMR (frequency: 153 kHz) for both the gas and liquid phases. As observed, proper location and sizing of the different parts of the FFMR makes the sound pressure at the fluids much higher than for the standard original design.

5. CONCLUSIONS

In this contribution we have presented the main objectives and methods of the European project MAPSYN in which, among other things, process intensification by the application of ultrasound irradiation is planned for carrying out heterogenously catalyzed hydrogenations in

microreactors. Preliminary results shown here on acoustic optimization highlight the need of a proper sizing of the microreactor from an acoustic point of view. Acoustic optimization has been carried out by FEM simulations by means of the COMSOL MULTIPHYSICS software package. More refined calculations will be undertaken when the construction material and design of the microreactor are chosen. However, the ideas delineated here illustrate the approach to be followed.

6. ACKNOWLEDGEMENTS

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