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# The central role of materials in heterogeneous catalytic intensified processes

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ABSTRACT

The development of an intensified process, it is not only a question of finding synergies between process intensification and catalyst, but also finding the most suitable material for the framework conditions of the new process, which in most cases differs from the conventional process. In this paper I present lessons learnt and future perspectives in heterogeneous catalysis for different intensification strategies including, membrane reactors, structured reactors and process electrification with microwaves.

## 1. Introduction

Given the significant challenges facing by the chemical industry, including high energy demands and the need for safe and environmentally sustainable processes, process intensification (PI) is emerging as one of the most promising solutions. PI consists of redesigning industrial processes for the development of more sustainable chemical industry, leading to substantially smaller, cleaner and more energy efficient technology, as defined by Stankiewicz and Moujlin [1]. It involves the development of processing methods and equipment, but not necessarily the chemistry of the process. The question is, in the case of heterogeneous catalytic processes, with the new redesign reactors and processes… Are we changing the conditions around the catalyst, which is the responsible of the chemical transformation? If the answer is yes, then we must revisit the composition, shape, or even active phase of the catalyst for the new intensified process.

More recently Van Gerven and Stankiewicz [2] presented a holistic vision on PI, defining four principles for PI, making use of fundamental approaches in four domains, spatial, thermodynamic, functional, and temporal, being the pillars of PI. These principles should apply at different scales, ranging from molecular scale, to meso and macroscale. Considering this vision, the design of catalytic materials for intensified process, applies at molecular scale in the four mentioned domains.

The design of new catalysts alone is not considered process intensification; rather, it is the development of catalytic materials for PI related technologies and processes. In this article, I presented examples that I have experienced firsthand over the 25 years of my research career in chemical engineering, in different technologies and processes, i.e. membrane reactors, microreactors and microwave heating applied to heterogeneous catalysis. These examples show that the development of a suitable catalytic material is crucial for the success of the intensified process.

## 2. Membrane reactors

Chemical reactions are not always 100% selective to the desired product and commonly, after reaction, there are separation processes to purify the stream and obtain the desired product. Separation processes represent 60 to 80% of the CAPEX (equipment) and OPEX (energy requirement) of production costs in Chemical Process Industry (CPI) plants [3]. The integration of reaction and separation is a perfect example of process intensification. Membranes offer the possibility of two separate compartments in the reactor, giving rise to new reactor concepts.

### 2.1. Membrane reactors for oxygen distribution in catalytic selective oxidations

In selective catalytic oxidations, hydrocarbons are converted into useful products, at relatively high temperatures, in the presence of oxygen, and inevitably carbon dioxide, a non-desired by-product is formed. Looking at the kinetics of these reactions, it is observed that the partial order of oxygen in the selective oxidation is lower than the non-selective towards $CO_2$. In this sense, working under low partial pressure of oxygen would favor the selective path. This concept was successfully developed for selective oxidations, methane oxidative coupling and

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oxidative dehydrogenation (ODH) of several hydrocarbons, ethane, propane, and butane, increasing selectivity and yield to the desired product [4]. These reactions follow a redox Mars Van Krevelen, MVK mechanism, and the lattice oxygen of the catalyst is the responsible of the C-H activation [5].

In the case of the selective oxidation of butane to maleic anhydride (MA), also obeys the hypothesis of lower reaction order for the oxygen in the selective reaction and follows also a MVK mechanism in a redox catalyst, based on vanadium phosphorous oxides (VPO). In this case, comparing to ODH reactions, three oxygen atoms are inserted in the maleic anhydride molecule, thus a stoichiometrically higher amount of oxygen it is required. The typical composition of the feed in the industrial reactor for MA production consists of 1.5-1.8% butane in air, due to the low flammability limit of butane (1.8% in air). With the above considerations, a different paradigm was proposed in the butane to MA membrane reactor, since oxygen could be distributed, higher concentrations of butane could be fed avoiding flammability limits, increasing productivity for the same reaction volume, and obtaining a more concentrated product. The results were promising, with a MA yield of 14.2% feeding 10% butane [6]. However, the new reaction atmosphere, with less oxygen surrounding the conventional VPO catalyst resulted in the appearance of $V^{3+}$ phases, decreasing the selectivity to maleic anhydride [7]. This is an example where the catalyst was not specifically design for the intensify process version. Possible solutions to improve the material were the addition of promoters that help to maintain a higher oxidation degree of the catalyst [8] or adding $CO_2$ that can oxidize the catalyst surface under high butane concentrations, rendering it more selective [9].

### *2.2. Membrane reactors for selective product removal, shifting equilibrium conditions*

Thermodynamics defines the theoretical limits of a chemical reaction, dictating the maximum conversion achievable for a certain temperature and pressure. Given this, the only thing that can be done to increase conversion, is to dream and attempt to "trick" thermodynamics by changing the situation in an "apparent" way. This is possible again with the help of a membrane that creates two different compartments. The products are selectively removed shifting the equilibrium to new product formation. There are several examples for selective product removal, separation of hydrogen, with Pd membranes, in dehydrogenation reactions or in methane reforming [10], and separation of water in esterification reactions. The separation of water, with zeolite A (Si/Ai=1) membranes by pervaporation, the only industrial application reported for zeolite membranes [11]. Unfortunately, as the Si/Al ratio decreases the stability in acidic media decreases and zeolite A is not stable to operate under acidic conditions, as it is the case of acid esterification reactions. Again, here it is necessary to adapt the material to the specific application. There is tradeoff between membrane hydrophilicity and acid resistance, that can be tuned with Si/Al ratio. The zeolite mordenite (MOR) with a Si/Al ratio that can varied from 5 to 20 was a proper selection. The esterification of acetic acid in a zeolite MOR membrane reactor, operating in continuous mode, showed a conversion of 90%, overcoming 70% equilibrium conversion at the given reaction conditions, with stable operation for 5 days [12].

## 3. Structured reactors: microreactors and monoliths

Microchannel process technology provides process intensification by improving heat and mass transfer across a variety of chemical reactions [13]. Process intensification by miniaturization allows inherently safer reactors and decentralized distributed production. These microreactors have features in the range of microns to hundreds or thousands of microns [14]. Considering these dimensions, the conventional catalyst chips and pellets produced with sizes typically in the range of thousands of micrometrics are not an option. Different strategies were carried out for the deposition of catalysts in the micrometric channels, starting from the conventional wash coating methods early developed for monolithic exhaust gas converters and creating porous layers by anodization of the metallic surface. The ability to integrate catalyst uniformly is a key aspect for scaling up this technology and the adhesion of the catalyst to the surface, generally a dissimilar material, is a challenge [15]. Based on our previous experience in the development of zeolite membranes, we developed an in-situ synthesis strategy which allows strong adhesion of the catalyst to the surface and a conformational growth on microchannel plates and monolithic structures [16,17]. To check the adhesion of the layers we perform a test that consists of ultrasonication of the catalyst zeolite coated microchannel plates. The adherence percentage was defined as the weight percentage of the material applied through wash-coating or hydrothermal synthesis that remained intact after sonication. In the case of washcoating only 5% of the material remained vs. values of around 98% obtained for different zeolites, mordenite, zeolite Y and titanosilicate ETS-10 [18]. Process intensification by miniaturization is undoubtedly a successful story, with Velocys company producing the world's most compact Fischer-Tropsch reactor for the synthesis of hydrocarbons. The fact that the reactor plus catalyst assembly are included in the patent [19], reinforces the idea that the development of the catalytic material goes hand in hand with the intensification technology itself.

## 4. Electrification by microwave heating in heterogeneous G-S catalytic reactors

Microwave radiation is introduced as a method for intensifying heating in chemical processes. In solid-gas reactions, the selective heating of the solid offers an energy-saving advantage. Additionally, the temperature difference between the solid and the gas can enhance selectivity, providing further benefits [20]. Knowing microwave heating mechanism in catalytic solids is crucial to understand and control the process.

The loss processes that result in the deposition of heat in the catalyst, occur by different mechanisms. Dielectric loss processes can be divided into “dipolar” and “charge carrier” [21]. Two of the most common catalyst supports alumina and silica are perfect insulators, in principle with no charges available. In this case the only possibility to be heated up, is thanks to the interaction through dipoles created on defects or functional groups at the surface, i.e. hydroxyl groups or other polar groups anchored to the surface. The higher the number of functional groups, the higher the temperature that could be achieved. This was clearly demonstrated by functionalization of mesoporous silica with different silanes containing either, one, two or three amino groups [22].

Metals, perfect conductors, are very well known as catalyst, containing electrons that can move freely. However, penetration depth or skin depth, which is the depth below the surface of a conductor where the current density is reduced to about $1/e$ (37%) is very small, in the order of 3μm. Consequently, it is possible to heat micro and nanoparticles to a certain extent that depends on the support, size, and shape of the nanoparticle. Ano et al. developed a method to measure in situ the temperature of supported Pt NPs under MW irradiation based on operando XAFS, registering an average temperature gradient between NP and the support of 26K and 132K for $Pt/Al_2O_3$ and $Pt/SiO_2$ [23].The authors further extend the study and found that temperature achieved on the Pt NPs is a function of the particle size and the conductivity of the support [24]. The most important MW heating mechanism in catalyst, involving charge carriers, occurs in semiconductors and solids containing mobile cations, by a space-charge recombination mechanism, in which the electric field coerces the movement of charge (electrons or ions). Among these solids, zeolites hold a special and highly significant place among solid catalysts in chemical industry. Under MW heating, initially zeolites are heated up because of their high-water content, once the zeolite has been dehydrated, the cations moving inside the negative zeolite cage structure, with different positions available, are the responsible of the heating. In fact, depending on the type and size of the cations, the heating could be tuned. Calculating the energy barriers for cation-hopping to potential exchange positions using DFT provides valuable insights into the underlying phenomena [25]. For example, in zeolite A, reducing the number of cations, because of the presence of $Ca^{2+}$ divalent cations (Zeolite 5A) results in a reduced deposition of MW energy, and lower heating. Similarly, bigger $K^{+}$ cations (Zeolite 3A) induce stronger electrostatic repulsion, constraining the cation mobility. Finally, Zeolite 4A containing mostly $Na^{+}$ cations, has the highest cation mobility and heats up more effectively. In fact, MW heating of zeolite 4A and 3A at temperature above 400-500°C, results in thermal runaway and only 5A cannot reach thermal runaway [26]. If the dielectric properties of the materials, as a function of temperature are known, it is possible to simulate with multiphysics software tools, MW heating in a certain cavity and predict thermal runaway [27].

We also studied the MW heating of a series of mixed oxides perovskites, $LaXO_3$ (X=Cr, Mn,Fe, Co and Ni) [20]. Under the same conditions Fe and Cr perovskites, that behave as insulators, slightly heat up. $LaNiO_3$ perovskite, with metallic behaviour, is heated, and the semiconductor perovskites Mn and Co heat up more efficiently. In the case of $LaCoO_3$ a thermal runaway it is observed. This phenomenon was related to a metal to insulator transition that occurs in this perovskite together with a Jahn Teller distortion mechanism.

These two examples illustrate how in the case of charge carriers in semiconductor solids, small changes in materials composition, may have a dramatic impact on the mechanism of charge carriers in solids and its evolution with temperature, leading to runaway thermal situations detrimental to the safety of the chemical process. Measuring dielectric properties as a function of temperature is a good practice to know, in advance, the behaviour of the materials under MW heating [28]. The measurement of the temperature it is a critical aspect to understand and explain the catalytic activity results under MW heating to compare them with conventional heating [29–31]. Because of the interferences of thermocouples with electromagnetic fiber, the measure should be done with infrared thermometers, either optical fibers or thermographic cameras, able to observe the 2D surface of the catalyst.

The combination of structured reactors and MW heating is a very promising approach. It is possible to distribute homogenously highly MW absorbent nanoparticles, on the channels avoiding hot spot formation [29]. On the other hand, in case the catalytic solid it is not a good MW absorber; it could be deposit on a SiC monolith as good MW absorber providing the advantage of temperature gradient between the gas and solid. In the collaborative EU ADREM project, a structured reactor heated by MWs operated unmanned and continuously during 100h for dehydroaromatization of methane [32] The control system included programmed generation cycles and a temperature control loop connected to thermographic camera.

### *4.1. Recent advancements and future trends*

After reviewing various process intensification technologies, the question is whether we have already implemented them in the industry in new, redesigned sustainable chemical processes. What are the remaining challenges?

In no case have membrane reactors for selective oxidation or oxidative hydrogenation been industrialized, in fact oxidative dehydrogenation itself is not an industrial process. However, significant progress is being made in the development of membrane reactors for hydrogen production. Important developments at Eindhoven University of Technology (TU/e), in the group of Fausto Gallucci and Tecnalia with Pd membranes [33] for hydrogen production and purification have led to the creation of the spin-off company H2SITE which produces high purity $H_2$ (99,997%) at low cost (0,4€/$Nm^3$) [34] using a technology based on Pd alloy membranes. In dehydrogenation of propane a scalable electrified carbon membrane reactor has been recently proposed by the group of Prof. Liu [35]. Developments in membrane reactor technology and its potential in the chemical industry are reviewed recently by the group of Prof. Gallucci at TU/e [36]. It is also important to mention the consortium in the EU project MACBETH (Membranes And Catalysts Beyond Economic and Technological Hurdles) [37] reaching TRL7 different catalytic membrane applications, with several companies involved and coordinated by Evonik.

Although zeolite membranes have been reported industrial application in pervaporation in 2001 [11], the market has not advanced in this regard, the cost of ceramic membranes remains an obstacle that can only be overcome if the application justifies it and the process improvements or energy savings justify it. The zeolite synthesis hydrothermal method is relatively energy intensive and faces difficulties in scale-up and reproducibility of defect free zeolite membranes [38,39]. Recent advances in the synthesis of chabazite membranes for industrial $CO_2/CH_4$ separation are very promising [40].

The technology of catalytic microreactors is a reality in the miniaturization of gas to liquid platforms, including Fischer Tropsch and sustainable SAF production [41,42]. Other important areas where this technology could be expanded are biological processes and pharmaceutical industries. In this case with the preparation of active pharmaceutical ingredients API, including the end-to-end manufacturing, reducing waste by producing only as needed [43]. Concerning the integration of catalyst in structured reactors and monoliths, the 3D printing technology offers a new way of scale-up with desired controlled geometries [44–47]. One important challenge is the incorporation of the required active phases during the preparation of the printing paste with the adequate rheological properties. The formulations may change dramatically from one material to the other.

Microwave heating is a technology already implemented at industrial scale in food technology and vulcanization. In chemical processes the Microwave Chemical Company developed a plant for the production of 1,000 tons of high-quality, high-purity sucrose fatty acid esters per year [48]. The literature above mentioned, has proven the advantages of energy savings and selectivity control in MW heated G-S catalytic processes. To implement this intensification tool, a profound knowledge on the heating mechanism and solid transformations occurring under MW heating is necessary, not only to avoid thermal runaway, but also to create new materials, thanks to the interaction with the electromagnetic field and/or fast MW heating rates [49,50]. To avoid hot-spots, the deposition of the catalyst in structured reactors and the use of fluidized bed reactors that promote mixture and homogeneous temperature are better alternatives compared to conventional fixed bed reactors. Horkoshi et al. studied the Variable Frequency Microwave (VFM) radiation, to provide a homogenous electric field distribution which contributes to the suppression of hot-spots and scale-up of MW systems [51]. The design of MW cavity with homogeneous field distribution that could be scale-up to meaningful volumetric dimensions of the reactor, considering the wavelength of the radiation, is the main challenge for industrial utilization of MWs in G-S heterogeneous catalytic processes. The group of D.Vlachos at University of Delaware recently reviewed MW heated reactors highlighting the importance of adequate simulation tools [52]. There are active efforts to translate microwave-heated processes into industry, in particular several demonstration projects in plastic waste to value applications, including a MW PET depolymerization plant (GR3N project https://gr3n-recycling.com/ and MW assisted plastic waste pyrolysis included in PLASTICE project https://plastice.eu/ exemplified the advantages of MWs, offering faster heating and the integration of renewable electricity.

## Declaration of competing interest

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

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## References

[1] A.I. Stankiewicz, J.A. Moulijn, Process intensification: transforming chemical engineering, Chem. Eng. Prog. 96 (1) (2000) 22–33.

[2] T. Van Gerven, A. Stankiewicz, Structure, energy, synergy, time-the fundamentals of process intensification, Ind. Eng. Chem. Res. 48 (5) (2009) 2465–2474, https://doi.org/10.1021/ie801501y.

[3] E. Favre, Specialty Grand Challenges in Separation Processes, Front. Chem. Eng. 2 (March) (2020) 1–4, https://doi.org/10.3389/fceng.2020.00001.

[4] J. Coronas, J. Santamaría, Catalytic reactors based on porous ceramic membranes, Catal. Today 51 (3–4) (1999) 377–389, https://doi.org/10.1016/S0920-5861(99)00090-5.

[5] K.D. Chen, A. Khodakov, J. Yang, A. Bell, E. Iglesia, Isotopic tracer studies of oxidative dehydrogenation pathways on Mo-based catalysts, J. Catal. 186 (1999) 325–333.

[6] R. Mallada, M. Menéndez, J. Santamaría, Use of membrane reactors for the oxidation of butane to maleic anhydride under high butane concentrations, Catal. Today 56 (1–3) (2000), https://doi.org/10.1016/S0920-5861(99)00276-X.

[7] R. Mallada, S. Sajip, C.J. Kiely, M. Menéndez, J. Santamaría, Influence of the reaction atmosphere on the characteristics and performance of VPO catalysts, J. Catal. 196 (1) (2000), https://doi.org/10.1006/jcat.2000.3010.

[8] N. Ballarini, F. Cavani, C. Cortelli, S. Ligi, F. Pierelli, F. Trifirò, C. Fumagalli, G. Mazzoni, T. Monti, VPO catalyst for n-butane oxidation to maleic anhydride: A goal achieved, or a still open challenge? Top. Catal. 38 (1–3) (2006) 147–156, https://doi.org/10.1007/s11244-006-0080-z.

[9] R. Mallada, M. Menéndez, J. Santamaría, On the favourable effect of $CO_2$ addition in the oxidation of butane to maleic anhydride using membrane reactors, Appl. Catal. A: Gen. 231 (1–2) (2002), https://doi.org/10.1016/S0926-860X(02)00007-8.

[10] A. Iulianelli, S. Liguori, J. Wilcox, A. Basile, Advances on methane steam reforming to produce hydrogen through membrane reactors technology: A review, Catal. Rev. - Sci. Eng. 58 (1) (2016) 1–35, https://doi.org/10.1080/01614940.2015.1099882.

[11] Y. Morigami, M. Kondo, J. Abe, H. Kita, K. Okamoto, The first large-scale pervaporation plant using tubular-type module with zeolite NaA membrane, Sep. Purif. Technol. 25 (1–3) (2001) 251–260, https://doi.org/10.1016/S1383-5866(01)00109-5.

[12] O. de la Iglesia, R. Mallada, M. Menéndez, J. Coronas, Continuous zeolite membrane reactor for esterification of ethanol and acetic acid, Chem. Eng. J. 131 (2007) 1–3, https://doi.org/10.1016/j.cej.2006.12.015.

[13] J.J. Lerou, A.L. Tonkovich, L. Silva, S. Perry, J. McDaniel, Microchannel reactor architecture enables greener processes, Chem. Eng. Sci. 65 (1) (2010) 380–385, https://doi.org/10.1016/j.ces.2009.07.020.

[14] A. Gavriilidis, P. Angeli, E. Cao, K.K. Yeong, Y.S.S Wan, Technology and applications of microengineered reactors, Chem. Eng. Res. Des. 80 (1) (2002) 3–30, https://doi.org/10.1205/026387602753393196.

[15] A. Tonkovich, D. Kuhlmann, A. Rogers, J. McDaniel, S. Fitzgerald, R. Arora, T. Yuschak, Microchannel technology scale-up to commerical capacity, Chem. Eng. Res. Des. 83 (6 A) (2005) 634–639, https://doi.org/10.1205/cherd.04354.

[16] M.A. Ulla, E. Miro, R. Mallada, J. Coronas, J. Santamaría, Preparation of highly accessible mordenite coatings on ceramic monoliths at loadings exceeding 50% by weight, Chem. Commun. 4 (2004) 5, https://doi.org/10.1039/b315386j.

[17] O. de la Iglesia, V. Sebastián, R. Mallada, G. Nikolaidis, J. Coronas, G. Kolb, R. Zapf, V. Hessel, J. Santamaría, Preparation of Pt/ZSM-5 films on stainless steel microreactors, Catal. Today 125 (2007) 1–2, https://doi.org/10.1016/j.cattod.2007.03.015.

[18] V. Sebastián, O. de la Iglesia, R. Mallada, L. Casado, G. Kolb, V. Hessel, J. Santamaría, Preparation of zeolite films as catalytic coatings on microreactor channels, Microporous Mesoporous Mater. 115 (2008) 1–2, https://doi.org/10.1016/j.micromeso.2007.12.039.

[19] Tonkovich A.L. et al. US patent US2004033455A1. Integr. combust. react. methods conduct. simultaneous endothermic exothermic react.. Publication date 2004-02-19.

[20] J. Gracia, M. Escuin, R. Mallada, N. Navascues, J. Santamaria, Nano-heaters: New insights on the outstanding deposition of dielectric energy on perovskite nanoparticles, Nano Energy (2016) 20, https://doi.org/10.1016/j.nanoen.2015.11.040.

[21] Referencia del libro Horikoshi.

[22] H. Nigar, B. Garcia-Baños, F.L. Peñaranda-Foix, J.M. Catalá-Civera, R. Mallada, J. Santamaría, Amine-functionalized mesoporous silica: A material capable of $CO_2$ adsorption and fast regeneration by microwave heating, AIChE J. 62 (2) (2016), https://doi.org/10.1002/aic.15118.

[23] T. Ano, S. Tsubaki, A. Liu, M. Matsuhisa, S. Fujii, K. Motokura, W.-J. Chun, Y. Wada, Probing the temperature of supported platinum nanoparticles under microwave irradiation by in situ and operando XAFS, Commun. Chem. 3 (1) (2020), https://doi.org/10.1038/s42004-020-0333-y.

[24] T. Ano, S. Tsubaki, S. Fujii, Y. Wada, Designing local microwave heating of metal nanoparticles/metal oxide substrate composites, J. Phys. Chem. C 125 (43) (2021) 23720–23728, https://doi.org/10.1021/acs.jpcc.1c06650.

[25] J. Gracia, M. Escuin, R. Mallada, N. Navascues, J. Santamaría, Heating of zeolites under microwave irradiation: A density functional theory approach to the ion movements responsible of the dielectric loss in Na, K, and Ca A-zeolites, J. Phys. Chem. C 117 (30) (2013), https://doi.org/10.1021/jp406390b.

[26] T. Ohgushi, S. Komarneni, A.S. Bhalla, Mechanism of microwave heating of zeolite A, J. Porous Mater. 8 (1) (2001) 23–35, https://doi.org/10.1023/A:1026518200875.

[27] H. Nigar, G.S.J. Sturm, B. Garcia-Baños, F.L. Peñaranda-Foix, J.M. Catalá-Civera, R. Mallada, A. Stankiewicz, J. Santamaría, Numerical analysis of microwave heating cavity: Combining electromagnetic energy, heat transfer and fluid dynamics for a NaY zeolite fixed-bed, Applied Thermal Engineering, 2019, https://doi.org/10.1016/j.applthermaleng.2019.03.117.

[28] J.M. Catalá-Civera, A.J. Canós, P. Plaza-González, J.D. Gutiérrez, B. García-Baños, F.L. Peñaranda-Foix, Dynamic measurement of dielectric properties of materials at high temperature during microwave heating in a dual mode cylindrical cavity, IEEE Trans. Microw. Theory Tech. 63 (9) (2015) 2905–2914, https://doi.org/10.1109/TMTT.2015.2453263.

[29] A. Ramírez, J.L. Hueso, R. Mallada, J. Santamaría, Ethylene epoxidation in microwave heated structured reactors, Catal. Today (2016) 273, https://doi.org/10.1016/j.cattod.2016.01.007.

[30] A. Ramirez, J.L. Hueso, R. Mallada, J. Santamaria, In situ temperature measurements in microwave-heated gas-solid catalytic systems. Detection of hot spots and solid-fluid temperature gradients in the ethylene epoxidation reaction, Chem. Eng. J. (2017) 316, https://doi.org/10.1016/j.cej.2017.01.077.

[31] B. García-Baños, J.J. Reinosa, F.L. Peñaranda-Foix, J.F. Fernández, J.M. Catalá-Civera, Temperature assessment of microwave-enhanced heating processes, Sci. Rep. 9 (1) (2019), https://doi.org/10.1038/s41598-019-47296-0.

[32] I. Julian, C.M. Pedersen, A.B. Jensen, A.K. Baden, J.L. Hueso, A.V. Friderichsen, H. Birkedal, R. Mallada, J. Santamaria, From bench scale to pilot plant: A 150x scaled-up configuration of a microwave-driven structured reactor for methane dehydroaromatization, Catal. Today 383 (2022) 21–30, https://doi.org/10.1016/j.cattod.2021.04.013.

[33] E. Fernandez, A. Helmi, J.A. Medrano, K. Coenen, A. Arratibel, J. Melendez, N.C. A. de Nooijer, V. Spallina, J.L. Viviente, J. Zuñiga, D.A. Pacheco Tanaka, F. Gallucci, Palladium based membranes and membrane reactors for hydrogen production and purification: An overview of research activities at Tecnalia and TU/e, Int. J. Hydrog. Energy 42 (19) (2017) 13763–13776, https://doi.org/10.1016/j.ijhydene.2017.03.067.

[34] H2SITE: On-site generation of high purity hydrogen https://www.tecnalia.com/en/partly-owned-companies/h2site-on-site-generation-of-high-purity-hydrogen, Accessed 8 September 2024.

[35] L. Liu, A. Bhowmick, S. Cheng, B.H. Blazquez, Y. Pan, J. Zhang, Y. Zhang, Y. Shu, D.T. Tran, Y. Luo, M. Ierapetritou, C. Zhang, D. Liu, Alkane dehydrogenation in scalable and electrifiable carbon membrane reactor, Cell Rep. Phys. Sci. 4 (12) (2023) 101692, https://doi.org/10.1016/j.xcrp.2023.101692.

[36] S. Richard, P. Olivier, M. Jégoux, C. Makhloufi, F. Gallucci, Membrane reactors technologies for e-fuel production & processing: A review, Int. J. Hydrog. Energy 112 (2025) 446–467, https://doi.org/10.1016/j.ijhydene.2025.01.361.

[37] MACBETH project https://www.macbeth-project.eu/ Accessed December 14, 2025.

[38] A. Navajas, R. Mallada, C. Téllez, J. Coronas, M. Menéndez, J. Santamaría, Study on the reproducibility of mordenite tubular membranes used in the dehydration of ethanol, J. Membr. Sci. 299 (2007) 1–2, https://doi.org/10.1016/j.memsci.2007.04.038.

[39] Y. Li, M. Zhu, N. Hu, F. Zhang, T. Wu, X. Chen, H. Kita, Scale-up of high performance mordenite membranes for dehydration of water-acetic acid mixtures, J. Membr. Sci. 564 (July) (2018) 174–183, https://doi.org/10.1016/j.memsci.2018.07.024.

[40] M. Sinaei Nobandegani, L. Yu, J. Hedlund, Zeolite membrane process for industrial CO2/CH4 separation, Chem. Eng. J. 446 (P4) (2022) 137223, https://doi.org/10.1016/j.cej.2022.137223.

[41] D. Braide, C. Panaritis, G. Patience, D.C. Boffito, Gas to liquids (GTL) microrefinery technologies: A review and perspective on socio-economic implications, Fuel 375 (August) (2024) 132385, https://doi.org/10.1016/j.fuel.2024.132385.

[42] https://velocys.com/projects/ Accessed February 2025.

[43] A. Hyer, D. Gregory, K. Kay, Q. Le, J. Turnage, F. Gupton, J.K. Ferri, Continuous Manufacturing of Active Pharmaceutical Ingredients: Current Trends and Perspectives, Adv. Synth. Catal. 366 (3) (2024) 357–389, https://doi.org/10.1002/adsc.202301137.

[44] Z. Dong, Z. Wen, F. Zhao, S. Kuhn, T. Noël, Scale-up of micro- and milli-reactors: An overview of strategies, design principles and applications, Chem. Eng. Sci.: X 10 (2021) 100097, https://doi.org/10.1016/j.cesx.2021.100097.

[45] M.B. Montaner, S.T. Hilton, Recent advances in 3D printing for continuous flow chemistry, Curr. Opin. Green Sustain. Chem. 47 (2024) 100923, https://doi.org/10.1016/j.cogsc.2024.100923.

[46] M.B. Montaner, M.R. Penny, S.T. Hilton, Digitisation of a modular plug and play 3D printed continuous flow system for chemical synthesis, Digit. Discov. 2 (6) (2023) 1797–1805, https://doi.org/10.1039/d3dd00128h.

[47] A. Potdar, L.C.J. Thomassen, S. Kuhn, Scalability of 3D printed structured porous milli-scale reactors, Chem. Eng. J. 363 (2019) 337–348, https://doi.org/10.1016/j.cej.2019.01.082. October 2018.

[48] https://mwcc.jp/post_achievements_en/project05_synthetic/Accessed, December 2025.

[49] A. Domínguez-Saldaña, A.J. Carrillo, M. Balaguer, L. Navarrete, J. Santos, D. Catalán-Martínez, B. García-Baños, P.J. Plaza-González, J.D. Gutierrez-Cano, F. Peñaranda, J.M. Catalá-Civera, J.M. Serra, Microwave-driven reduction accelerates oxygen exchange in perovskite oxides, ACS Appl. Mater. Interfaces 16 (50) (2024) 69324–69332, https://doi.org/10.1021/acsami.4c15150.

[50] A. López-García, A. Domínguez-Saldaña, A.J. Carrillo, L. Navarrete, M.I. Valls, B. García-Baños, P.J. Plaza-Gonzalez, J.M. Catala-Civera, J.M. Serra, Microwave-driven exsolution of Ni nanoparticles in A-site deficient perovskites, ACS. Nano 17 (23) (2023) 23955–23964, https://doi.org/10.1021/acsnano.3c08534.

[51] S. Horikoshi, H. Mura, N. Serpone, Three-dimensional observations of the electric field distribution of variable frequency microwaves, and scaling-up organic syntheses, Commun. Chem. 6 (1) (2023), https://doi.org/10.1038/s42004-023-01062-6.

[52] H. Goyal, T.-Y. Chen, W. Chen, D.G. Vlachos, A review of microwave-assisted process intensified multiphase reactors, Chem. Eng. J. 430 (2022) 133183, https://doi.org/10.1016/j.cej.2021.133183.