



The potential of catalysis for closing the loop in human space exploration

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ARTICLE INFO

Keywords:

Heterogeneous catalysis
Human space exploration
Life support
Catalysis
Green chemistry
Sustainability in space

ABSTRACT

This mini-review provides a perspective on how catalysis can contribute to the challenge of human space exploration, i.e. to the establishment of a space habitat on the Moon in the near future and the realization of a journey to Mars in the far future. The role of catalysis for space exploration is reviewed along elemental resource provisions for human life that are based on catalytic chemical processes. As a secondary effect, learning about catalysis under the high constraints of the sustainability requirements inherent to long-term space missions can be beneficial for the advancement of currently developed catalytic processes for a green, circular economy on Earth. In-depth research into catalysis for space applications could therefore also provide answers to urgent industrial, environmental and social sustainability challenges on our planet e.g., as expressed by the United Nations Sustainability Development Goals. Even for today's short-term space missions, catalysis already plays a key role in the *Environmental Control and Life Support System* (ECLSS) on the *International Space Station* (ISS) and moreover, in fuel and propellant synthesis as well as the recycling of combustion products such as CO₂.

1. Introduction

This mini-review does explicitly not go into depth concerning the use of catalysis for energy-related issues of spacecrafts and space habitats, as they have been intensively described elsewhere and are central research and development issues of the last five decades of space missions. Therefore, it excludes, for example, catalysed H₂ and O₂ formation (from water by electrolysis and fuel cells), CO₂ conversion to form H₂ through the water-gas shift reaction or the use of catalysts for rocket propellant production such as highly refined kerosene (RP-1, Rocket Propellant-1) [1–4].

Instead, this review aims at providing a holistic view of the inherent role catalysis has in space, centred around the manifold needs of the human (astronaut) lifestyle and quality of life. The involved chemical conversions as well as the resource materials and products for human comfort are substantially different to those used for rocket propulsion and space energy provision. Homogeneous catalysis such as enzyme- and - more generally - biocatalysis as well as classical heterogeneous catalysis such as (photo-)electrocatalysis could play major roles in future

space missions for chemical synthesis and recycling [5–8]. The required safety, stability, and efficiency as well as the supply isolation of catalytic processes in space - either in a habitat or on a long-duration space flight - emphasise the necessity of high system circularities, high atom economies, the recyclability of reaction components [9] and the avoidance of waste.

This review will summarise ongoing challenges and opportunities associated with catalysis in space environments for human survival and comfort. It will provide an outlook to areas in which catalysis could also play a role in future space missions, and thus, define the gap that is not tackled by current research.

1.1. Definition of elemental and comfort life support in human space exploration

Nature has manifold catalysts operating in their metabolic cycles on Earth to support human life. Industrial chemistry and catalysis provide additions to that. A spacecraft or space habitat represents a microenvironment, and consequently, it offers a reduced complexity for catalytic

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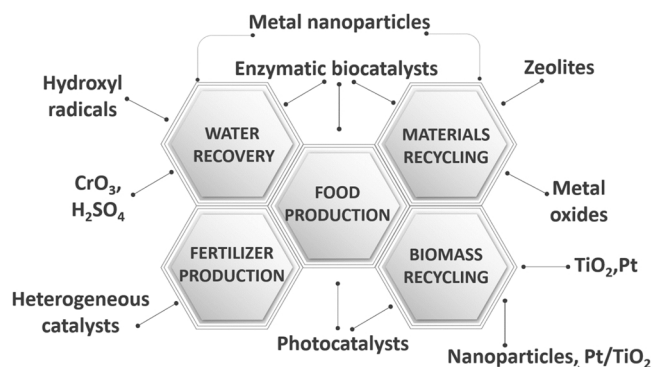


Fig. 1. Space resource catalysis for human space exploration. This figure provides an overview of the role of catalysis in elemental life support required for human survival as well as life comfort in space.

processes in comparison to Earth. Therefore, the minimum demands for human survival and comfort define the threshold in the simplification of space catalysis. It is our opinion that the provision of catalysis merely for human survival is not sufficient (as it is on Earth), as it is only the addition of human comfort that facilitates the high performance of an astronaut. Rephrased, human comfort is a part of human survival. On that note, the role of catalysis for human comfort in space has hardly been investigated.

The elemental life support processes for a space habitats and spacecrafts provide a microcosm for the life cycles of the life-supporting elements N, C and O. At first, the space microenvironment has to provide clean water, an atmosphere containing 20.95 % oxygen (Fig. 1) and a possibility to recycle atmospheric carbon dioxide. Plant growth could contribute to the maintenance of the atmospheric composition and the provision of nutritious food. Fertilisers have to be available to support and sustain plant growth. All elements - from packaging materials to tanks, cupboard-sized containers and large housing - require encasement to shield against the harsh space conditions. Given their light weight, wealth of manufacturing, and established terrestrial processes of recycling, possible construction and all-purpose materials in space are polymers. Catalysis will be central to both, the synthesis of these basic components as well as to their recycling.

Comfort life support goes one step further and includes elements which are required for a long-term stay in a habitat or onboard a spacecraft to allow a comfortable life and to enhance the astronaut's performance and well-being. From a chemical perspective, this includes e.g., the provision of pharmaceuticals, advanced building and shielding materials, paints and adhesives. Given the large variety of catalytic processes involved in elemental and comfort life support systems, this review will only provide a brief overview over some relevant processes.

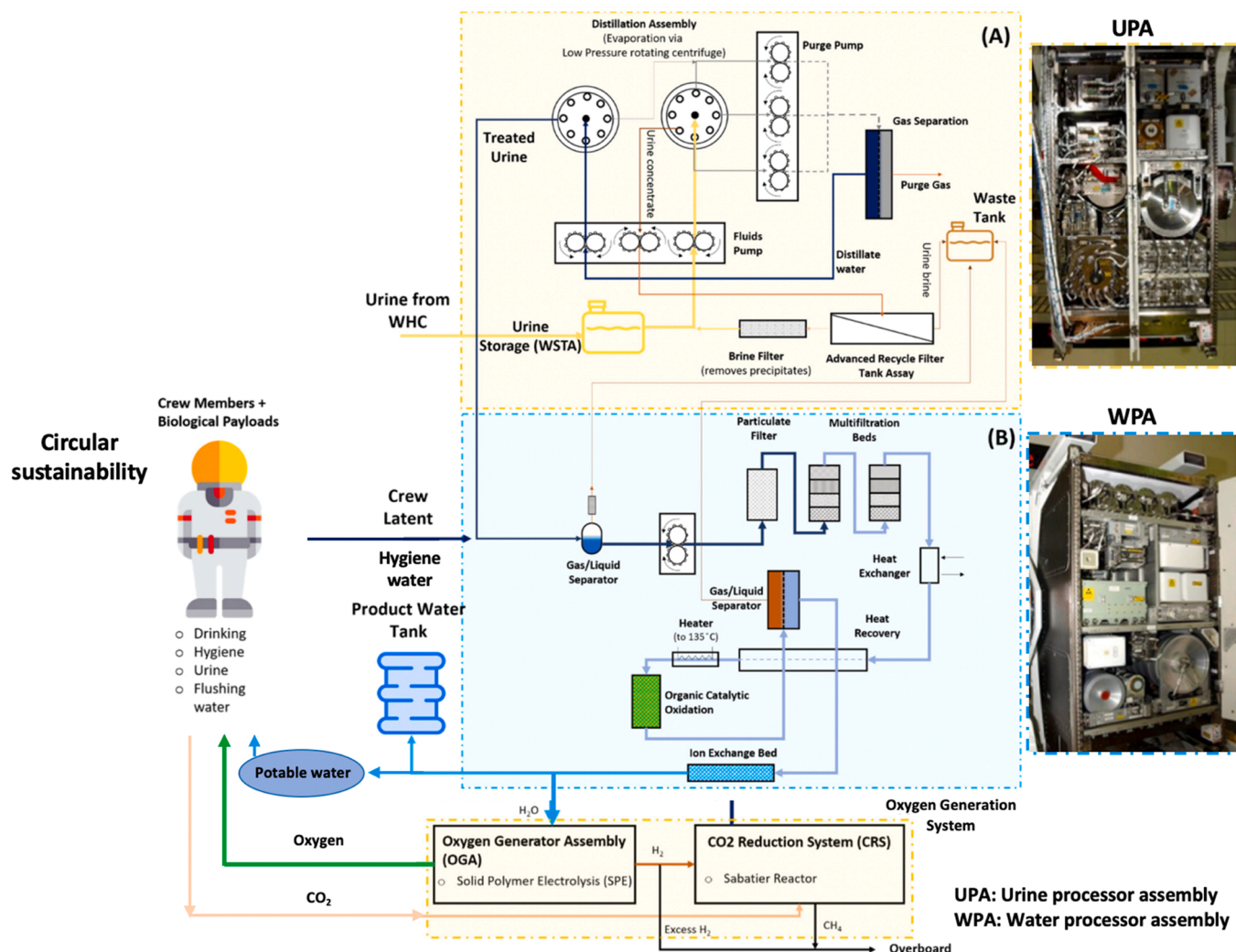


Fig. 2. Simplified recycling loops to support human life in a spacecraft. Adapted from [12] with kind permission from MDPI.

1.2. Defining the gaps in the life-support space loops

Many catalytic processes for human space exploration have hardly been moved beyond a technology readiness level (TRL) of 3, meaning, the confirmation of a proof of principle. Whereas elementary, catalytic life support processes such as water electrolysis for oxygen production and the recycling of carbon dioxide in a Sabatier reactor already operate in space, other processes such as catalytic waste recycling have not reached a sufficiently high TRL yet. Quantitative, open-public data on the productivity and sustainability/circularity assessment are rare or not existent and require further investigations.

Another area where this is the case is space farming [10,11]. A long history of plant growth in space and specific space garden environments have been established to support crop growth over the past five decades. There is however still a gap within space farming technology developments e.g., in the sense of an intensified horticulture for hydroponics and aeroponics to produce plants which can configure dishes and nourish humans. The commonly used terms ‘space gardens’ and ‘plant habitat’ describe the state of the art well. Currently existing systems aim at providing a proof of principle and a bridge to a future pilot system. Furthermore, artificial nitrogen fixation and fertiliser production need to be established and maintained in a spacecraft or habitat which is particularly significant for long-distance manned space travel. This is however not yet a priority of space farming investigations.

Circularity concerns have been initiated by proposing model process designs for space manufactories including the recycling element. Up to date, a quantitative assessment of the degree of circularity has been reported only rarely. It should however be noted that even for similar chemical process cycles on Earth, hardly any quantitative circularity reports have been compiled (albeit life cycle assessments are common). On a positive note, space science could therefore act as frontier to promote circularity investigations on Earth.

2. Clean water management in space - enzymatic and metal-supported catalysis

Clean water is the human body fluid and the carrier of nutrients and metabolic processes in plant life. Knowledge transfer on water management for future long-term space missions can occur from the current wastewater management on the *International Space Station* (ISS) to future technological developments, where enzymatic catalysis and titania-based noble-metal photocatalysts could play a role.

Water recycling is of key importance for future human space exploration: currently, the required resupply of air, food, and water accounts for 15 kg/d on the ISS, which is estimated to be able to be reduced to 1 kg/d with an optimized recycling system (Fig. 2) [12]. Water is the primary consumable of all life-support elements in space and a reliable and effective water purification and recovery system is essential.

The currently used *Water Recovery System* (WRS) on the ISS contains the *Water Processor Assembly* (WPA) which processes cabin air humidity condensate, waste hygiene distillate and product water from the Sabatier reactor and the *Urine Processor Assembly* (UPA), which processes crew urine distillate [13,14]. Current technologies to recover water from urine utilize chemical additives for pre-treatment such as chromium trioxide and sulfuric acid before water can be recovered using *Vapor Compression Distillation* (VCD) [15].

In order to simplify the process and recycle wastewater in fewer steps, enzymatic systems coupled with electrolyzers have been proposed for future life support systems: Cabrera et al. [16,17] have utilised urease, an enzyme catalysing the conversion of urea to ammonia, and *Proteus Vulgaris* bacteria to create an ureolysis system to recycle urine. The bacteria are used to catalyse the conversion of urea to ammonia in a bioreactor and the produced ammonia is consecutively oxidized in an electrochemical reactor. This self-sustaining system is currently under investigation for scale-up in microgravity environments [15]. The group has also investigated electrochemical ammonia oxidation in

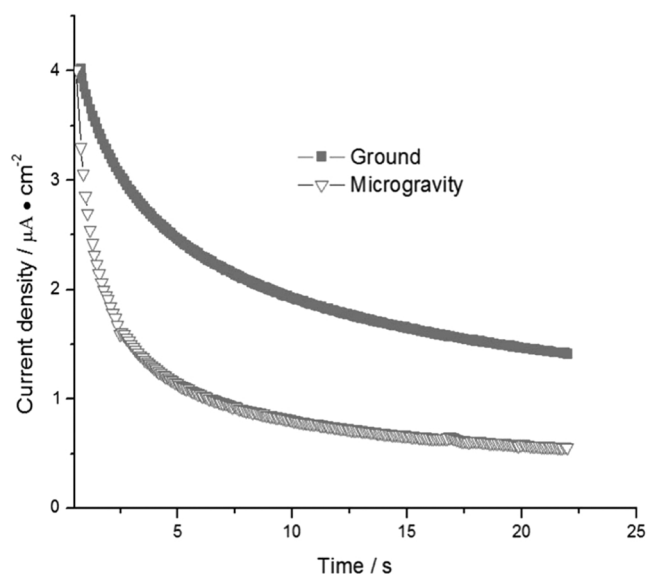


Fig. 3. Chronoamperometric characteristics of the ammonia oxidation reaction on Pt nanoparticles supported by mesoporous carbon (MPC) under microgravity and ground conditions. From [16] with kind permission of Springer Nature Switzerland AG.

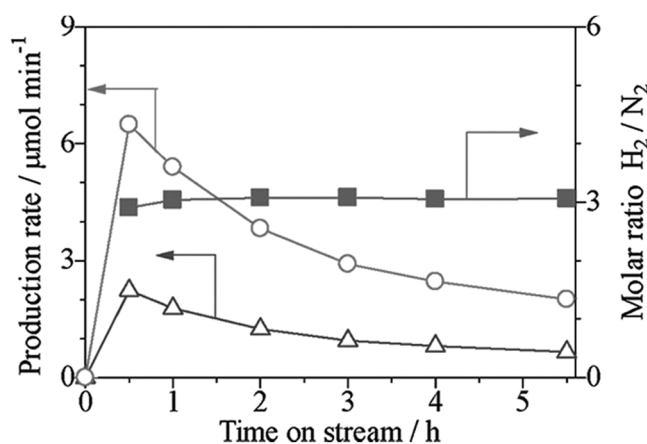


Fig. 4. Photocatalytic ammonia decomposition using Pt/TiO₂ nanoparticles in a fixed bed flow reactor. Hydrogen (H₂) production is shown in circles, nitrogen (N₂) in triangles, H₂/N₂ production in squares. From [20] with kind permission of the American Chemical Society.

microgravity environments. Studies carried out by Poventud-Estrada et al. [18] showed that the current density of the ammonia oxidation reaction (AOR) generally decreased in parabolic flight experiments, involving Pt nanoparticles supported by modified mesoporous carbon (MPC) as electrocatalysts (Fig. 3).

This decrease in current density is depended on the MPC pore diameter: in comparison to terrestrial control experiments, the decrease varied between 25 % and 63 %, whereas the smallest current density decrease was observed with Pt catalysts prepared with a large MPC pore diameter (137 Å) [18]. This leads to the hypothesis that N₂(g) formation inside the pores causes a small convection which results in a diffusional contribution to mass transfer and the removal of N₂(g) from the electrode surface. The observation illustrates how important the nanotopography of (electro-)catalysts for space applications is as the systems need to defy the near-absence of buoyancy in microgravity environment.

The heterogeneous photocatalytic oxidation of ammonia has attracted attention over the last years due to the possibility of generating in-situ oxidative hydroxyl radicals (•OH), the general easy operation

Chemistry on Mars: in-situ resource utilisation of the Martian atmosphere with Microwave plasma

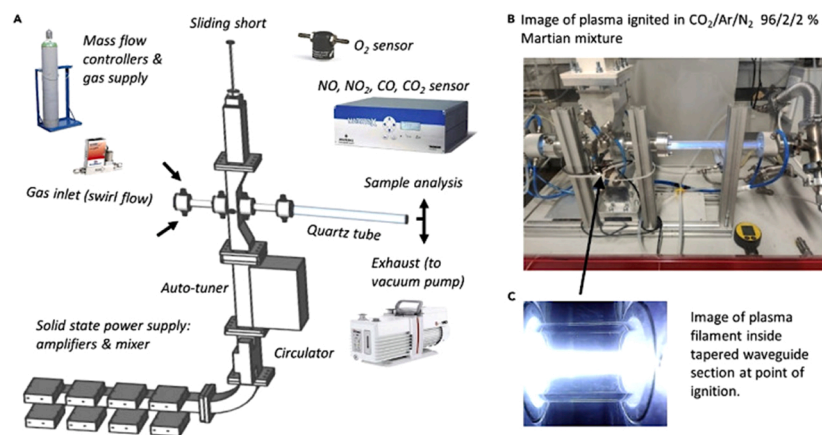
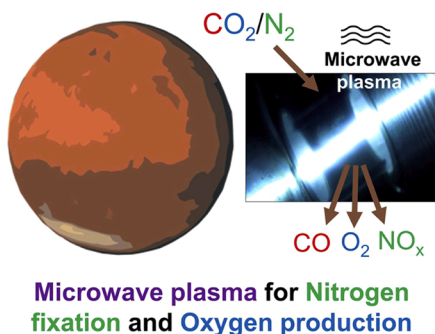


Fig. 5. Left: Motivation for using plasma catalysis in the Martian atmosphere: carbon dioxide (CO₂) could be converted into oxygen (O₂) and carbon monoxide (CO), and nitrogen (N₂) to nitrogen oxides (NO_x). Nitrogen dioxide (NO₂) can then form nitric acid after absorption in water. Right: Microwave plasma system technology for use in space catalysis. From [30] with kind permission of Cell Press.

and control of the set-up as well as the low energy and cost demands [19, 20]. Given the possibility of directly utilising sunlight for the reaction and thereby reducing the overall energy input, it also represents an interesting option for space applications. Under alkaline conditions, the hydroxyl radicals generated e.g., through TiO₂-based photocatalysts, can react with ammonia at a relative fast reaction rate ($k = (2.7 \pm 0.4) \times 10^7 / M \text{ s}$ at pH 11.3 [20]) to nitrite, nitrate ions and N₂(g) [19]. The product selectivity towards N₂(g) production remains hereby one of the main obstacles. Nobel metals loaded onto the photocatalyst have been investigated as electron traps which inhibit the charge carrier recombination and enhance the photocatalytic activity. Yuzawa et al. [20] have observed the decomposition of ammonia to N₂(g) and H₂(g) on TiO₂/Pt nanoparticles under UV light and anoxic conditions, proposing that the amide radical ($\bullet\text{NH}_2$) is the active intermediate species firstly formed upon oxidation of a photoformed hole or surface hydroxyl radical (Fig. 4).

This leads further on to the formation of diazene (N₂H₂) via hydrazine and finally, to the formation of the two products. Despite recent advances, the photocatalytic approach to the AOR is still under development and requires further research as well for terrestrial applications. An ‘intermediate’ solution between the photocatalytic and the electrocatalytic AOR is represented by the photoelectrocatalytic pathway, where integrated semiconductor-electrocatalyst systems operate in analogy to nature’s photosynthetic processes and integrate the processes of light absorption, charge separation and (electro-)catalysis [21,22]. Given the weight and volume constraints for long duration space travels, they present a particularly interesting option. This has however not been explored for the AOR in greater depth.

Photocatalytic oxidation can also be used for air and wastewater treatment. The *High-Performance Photocatalytic Oxidation Reactor System* (HPPORS) was developed by *Pioneer Astronautics* to decompose airborne volatile organic compounds (VOCs) prior to the water processing systems [23]. The proposed HPPORS operates under ambient conditions of temperature and pressure using high-intensity light emitting diodes (LEDs) and visible light-activated photocatalysts. A high VOC conversion efficiency was demonstrated at a compact reactor volume and low pressure drop. The use of LED irradiation eliminates the conventional ultraviolet mercury lamp logistics and hazards [23]. Titanium dioxide (TiO₂) has been used as a common photocatalyst for VOC removal in air and water. When shifting the photocatalyst activity from ultraviolet (UV) to visible wavelengths, metal and non-metal materials have to supplement the TiO₂ photocatalyst.

The *Advanced Wastewater Photooxidation System* (AWPS) of *Pioneer Astronautics* is a system designed to oxidize and remove recalcitrant aqueous organic constituents in the water recovery post processing

system under ambient temperature and pressure conditions [24]. Long-lifetime UV LED light sources are used with a photocatalyst immobilized on a high surface area support.

3. Fertiliser production through dinitrogen fixation

The growth of plants in space requires fertilisers and, foremost, nitrogen (N), with ammonia being the key ingredient for N-based fertiliser production. Ammonia can be converted by oxidation to nitrate via the Oswald process. Apart from that, phosphorus (P) and potassium (K) fertilisers are needed as macronutrients for the growth of plants which are however not considered here.

The state of the art of ammonia production is the Haber-Bosch technology, but its high pressure and high temperature make it difficult to use in space. Dinitrogen fixation could instead be accomplished through (photo-)electrochemical reduction utilising sunlight as an energy source [25,26] or in a plasma-based process. The historic Birkeland-Eyde process [27] utilised an electric arc i.e., a thermal plasma, to produce nitrogen oxide (NO) and nitrogen dioxide (NO₂), which was then absorbed by water to yield nitric acid (HNO₃). Initially, it competed against the Haber-Bosch process for dinitrogen fixation, but the high energy demand and reactor maintenance costs were not competitive. Access to renewable electricity makes plasma-assisted ammonia production from dinitrogen potentially competitive again [28]. The fast turning on and off as well as the scalability for small communities could furthermore also be beneficial for space applications.

On Earth, nitrate (NO₃) formation through plasma catalysis has been brought to a technology readiness level of 3 and offers the opportunity for commercialisation. The EU project MAPSYN (*Microwave, Acoustic and Plasma SYNtheses*, [29]) aimed at nitrogen-fixation reactions intensified by plasma catalysis on an industrial pilot scale but did not report the final evidence for that. Generally, the role of the plasma is two-fold. The plasma itself presents a catalytic environment, composed of highly reactive species, including electrons, ions, and other excited species. The introduction of catalysts, as known from conventional catalysis, can support the plasma reaction intensification either in a two-fold action, firstly in a plasma step and then completing the conversion by catalysis (or vice versa) or - and preferentially - in a symbiotic action of plasma and catalysis at the same time and location. The latter has been coined as ‘plasma catalysis’.

As the Martian atmosphere contains dinitrogen (2.8 %) and oxygen (0.17 %), plasma catalysis could be used to form nitrous oxides and further on, nitrates, when dissolved in water. Kelly et al. [30] proposed the possibility of fixing nitrogen on Mars by using a microwave plasma which provides oxygen through CO₂ dissociation and nitrate-fertilisers

by converting nitrogen (N_2) to nitrogen oxides (NO_x), followed by water absorption as illustrated in Fig. 5. Guerra et al. [31] also discussed the potential of combining non-thermal plasma and membrane technology for the in-situ production of fuels, oxygen for air revitalization, fertilisers and building resources on Mars.

4. Crop growth in space - light-induced bio-catalysis

Future, long-term space missions to Moon and Mars require a life support system which can generate all essentials for human survival. Such a system also needs to include a compartment to produce plants as identified through the MELiSSA project (Micro-Ecological Life Support System Alternative) [32,33]. Plants offer a regenerative food source, oxygen production, and contribute to the purification of water and air. The question is how the diverse biocatalysts within green plants and cyanobacteria operate in outer space, with the most prominent ones being the enzymes of the photosynthetic catalytic system.

Stressors on Earth are a threat to plant growth. Nevertheless, plants typically manage to sustain growth even under stress conditions by adapting their metabolic cycle to the environment. In a similar way, plants can seemingly adapt to the unknown space stressors, although more research is needed here. Radiation stress is probably the largest threat in space. Manned space travel likely requires plant cultivation under conditions of prolonged exposure to ionising radiation that is caused by a diverse array of charged particles from both, within and outside the solar system [32,33]. Plants and their enzymatic catalyst system, Photosystem II (PSII), are well adapted to visible light stress. Profound expertise has been gained on the growth of different plant species through the investigation of the illumination period (photoperiod), the spectral composition of light and the lighting mode (pulsed or continuous, [34]). This involves fine tuning of the photosynthetic photon flux density (PPFD), the duration of lighting and number of cycles. In addition, supplemental lighting such as red light (600–660 nm) has been found to improve leaf growth [35].

In extension to visible light stress studies, UV light stress has been investigated as there is a higher amount of UV light present in space. Hardly experienced by plants on Earth, space radiation consists of ionising radiation such as alpha (α) particles, beta (β) particles (high-speed electrons or positrons), gamma (γ) rays, X-rays, and galactic cosmic rays (GRCs) as well as non-ionising radiation such as microwaves and infrared light. Alpha particles have a positive charge, which have great ionising power, but very little penetration due to their large mass [36]. Proton radiation has a positive effect on germination rate, but a negative effect on plant height and root and shoot weights [37]. Beta radiation can stimulate the growth at a low dose, but damage plant roots and shoots and hinder the growth of branches and leaves at high dose rates [38]. Gamma rays are not necessarily detrimental to crop growth, but the destructive nature of gamma rays is evident at higher doses [39,40]. Interestingly, not only negative results on plant growth are known from these stressors, but under certain conditions plants did grow well with exposure of cosmic ray-analogous radiation, mainly dependent on the level of doses.

Literature research reveals that if higher plants are provided with a controlled atmosphere, forced ventilation and a well-functioning water and nutrient delivery system, they adapt relatively well to space conditions in low Earth orbit, at least from one generation from seed to seed [41]. The focus of these investigations has primarily been on effects of reduced gravitation, the presence of a weak magnetic field (such as present on Moon and Mars) and radiation, as these parameters can affect the processes of gas exchange, photosynthesis and the transport of water and nutrients [41]. As reduced gravitational environments prevent buoyancy-driven thermal convection in the physical environment around and inside plant, it alters the exchange of gases and liquids and therefore, the substrate and product transfer to and from the catalytic center PSII as well as the availability of $CO_2(g)$ for the photosynthetic 'dark' reactions and oxygen for the plant's roots. Despite that plants

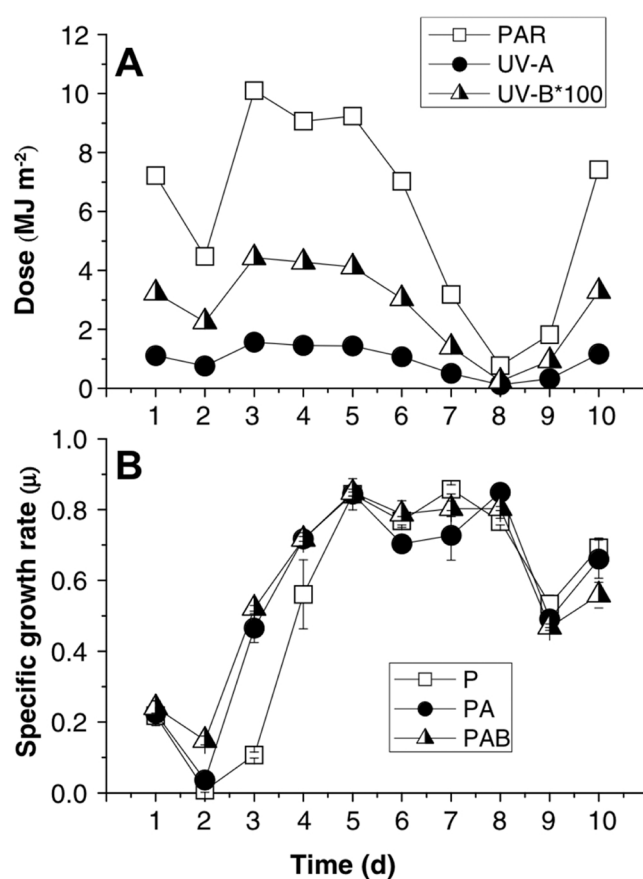


Fig. 6. Daily exposition doses (A) and specific growth rates of *H. akashiwo* (B) during exposure to different parts of the solar spectrum (PAB: 280–700 nm, PA: 320–700 nm, P: 400–700 nm) for 10 days. From [43] with kind permission of Elsevier.

generally adapt well to the environmental change onboard the ISS, the diffusion limitations cause root zone hypoxia which leads to alterations in the root and shoot physiology [42].

Although the actual photosynthetic processes involving light absorption, charge separation and water oxidation catalysis should not be altered by reduced gravitation, the actual solar irradiance spectrum on Moon and Mars differ with respect to the terrestrial one (AM 1.5 G) as briefly discussed above: the AM 0 spectrum available on the moon shows a larger contribution of solar ultraviolet radiation (UV-R, 280–400 nm), leading to a larger availability of high-energy photons as part of the photosynthetically active radiation (PAR, 400–700 nm). In contrary to the assumption that they could be utilised for the oxygen evolution reaction (OER) in PSII due to their high energy content, they activate photoprotection mechanisms: on short time scales, (<day), dynamic photoinhibition or even irreversible photodamage to PSII have been reported upon extensive UV-R exposure in macroalgae and microalgae due to the damage of the D1 protein in PSII [43].

Gao et al. [43] investigated the growth rate of the red algae *Heterosigma akashiwo* in dependence of solar ultraviolet radiation in long-term studies (Fig. 6). The mean daily irradiance values were 118, 18.7, and 0.53 W m^{-2} for PAR, UV-A (315–400 nm) and UV-B (280–315 nm), respectively. The specific growth rates for the cell cultures exposed to solar radiation for 10 days are shown in Fig. 6. Even though there was an initial decrease of the specific growth rate, μ , it showed a significant increase during the first half of the experiment, from < 0.2 to ca. 0.8 at day 5. During the second half (i.e., after day 5), μ was rather constant with the exception of a small decrease at the end of the experiment likely due to the appearance of clouds. Notably, during days 2, 3 and 4, the samples receiving UV-R had a higher μ than the ones

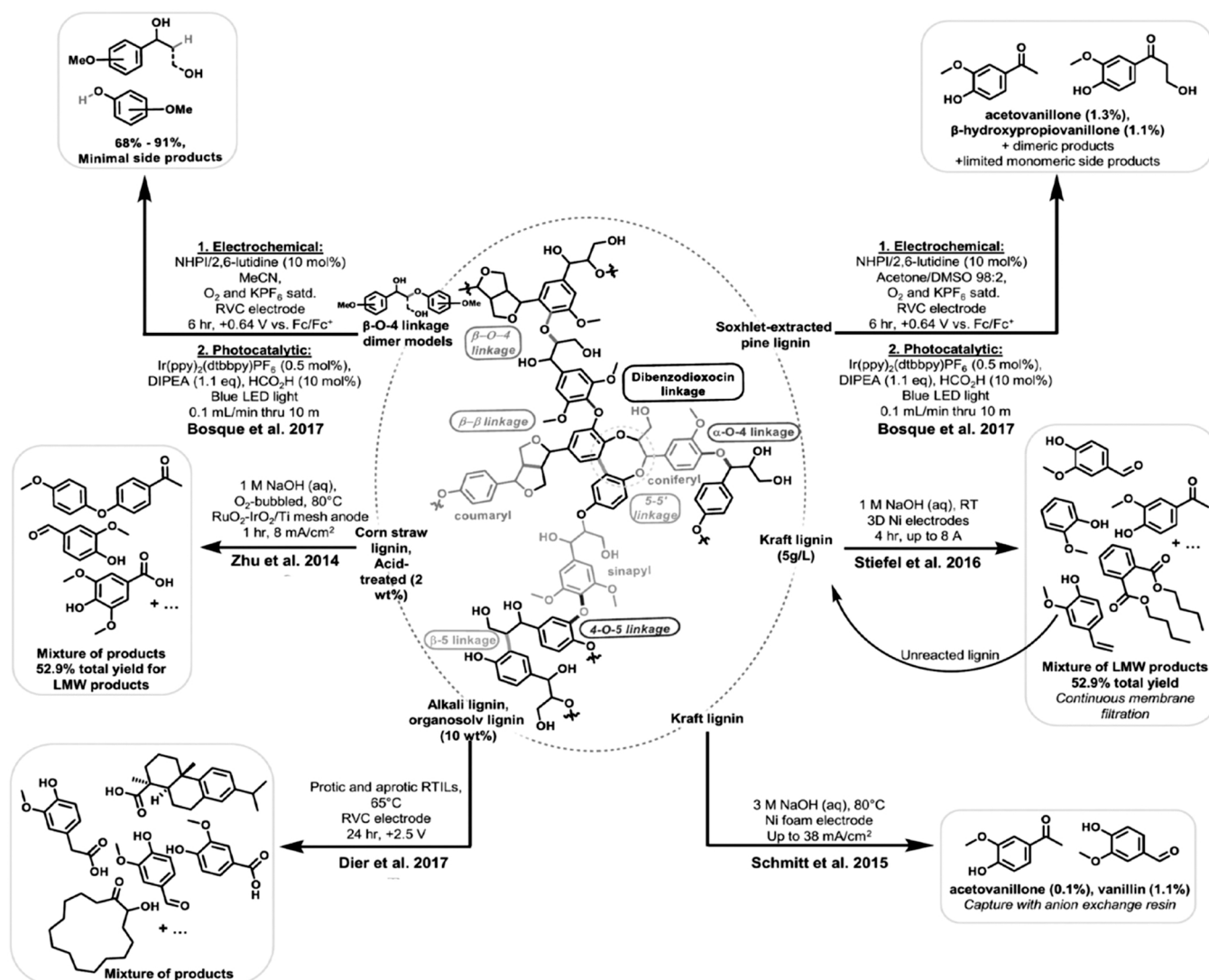


Fig. 7. Electrochemical depolymerization of lignin. From [48] with kind permission of the Royal Society of Chemistry.

exposed only to PAR. The growth rates reflected the amount of UV-absorbing compounds found in the cells: during long-time exposure, autotrophic organisms have the possibility of protecting themselves against UV-R e.g., through the synthesis of mycosporine-like amino acids (MAAs) [44]. These compounds can absorb UV-R at a wavelength range between 310 and 360 nm. It is however still uncertain how different species can utilize MAAs to cope with long-term UV-R exposure, their rate of production or even the cell quota necessary to guarantee protection. This area requires more in-depth research. Generally, it is however expected that the usage of solar irradiance filters and shielding against radiation damage e.g., through GCRs on Moon and Mars might be necessary to accommodate the plants requirements for optimal growth and O₂ production.

5. Materials recycling through heterogeneous and enzymatic catalysis

Terrestrially, metals and plastics constitute construction and all-purpose materials. They comprise major value components of household waste. The same holds for the 'household waste' on the ISS and other spacecrafts. A crew of four astronauts can generate up to 2500 kg of waste during a yearlong mission, which takes up space and represents a safety risk due to biological and physical hazards [45]. Currently, waste disposal on the ISS relies on the manual processing of trash by the

astronauts who place it into bags which are then loaded onto a designated vehicle for short-term storage. They are either sent down to Earth or burned up in the atmosphere. This way of disposing trash will not be available on long-term space missions and other methods are required with a stronger focus on recycling end-of life products and creating a more in-depth plan for refurbishing. The stronger focus on a circular economy also potentially requires a redesign of products in order to be more recycle-friendly, as many polymers and textiles usually decrease in quality after undergoing recycling.

Electrochemistry and - more precisely - (photo-)electrocatalysis offers a broad range of applications in waste recycling and materials processing in space as it typically avoids high temperatures and other harsh reaction conditions. Additionally, many (photo-)electrocatalytic reactions can be carried out in aqueous solutions, which represents a significant safety advantage.

Terrestrial techniques in use are slurry electrolysis and electrodeposition which have been used to collect minerals like manganese, aluminium, and antimony from complex mixtures [46]. Because metal ions have different deposition voltages, electrochemical techniques can separate mixed wastes containing a variety of metal ions. This works particularly well for Mn, but also Ti and Al can be recovered simultaneously e.g. from spacecraft parts using electrodeposition out of an HCl (aq) solution [47]. For elements such as Li, slurry electrolysis can be used for recovery e.g., from battery waste. Li is however still rarely

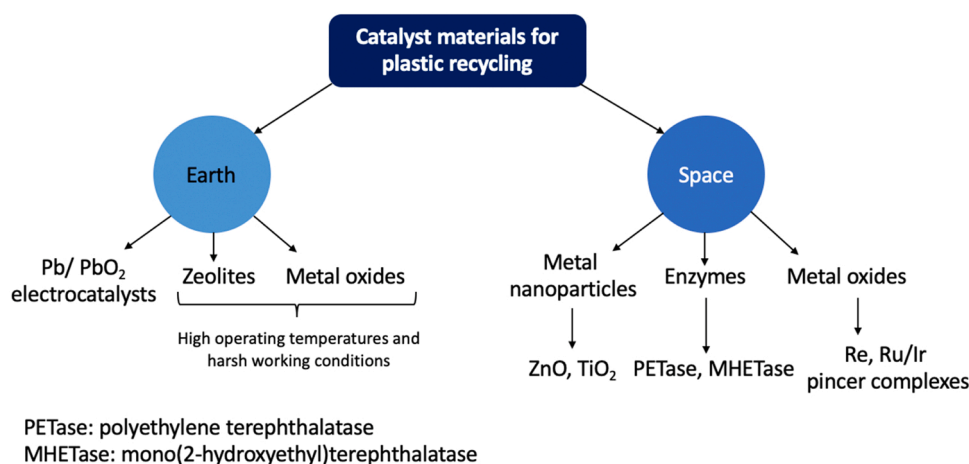


Fig. 8. Catalyst examples for plastic decomposition on Earth and potentially in space. Metal and metal oxides as well as enzymes could also operate in electrochemical set-ups.

recycled as well terrestrially and the recycling process urgently requires more in-depth research [46].

5.1. Plastic waste management in space

Plastic waste represents a largely untapped resource for manufacturing chemicals and fuels. Plastic recycling is majorly investigated in space, yet reports largely refer to web articles and journal articles remain rare.

Biodegradable polymers such as cellulose and lignin are generally easier to recycle via depolymerisation pathways. The electrocatalytic reduction has hereby also become of terrestrial interest as a less energy-intensive alternative [46]. Using 0.5 M sulfuric acid as the electrolyte under ambient conditions, Meng et al. [48] could e.g., decrease the degree of polymerisation (DP) of cotton cellulose from an average initial DP of 1100 to a final DP of 367 in 8 h, yielding 1.8 % of 5-hydroxy-methylfurfural (5-HMF). Using Lignin as a starting compound, different products can moreover be derived through various electrochemical pathways as shown in Fig. 7.

Terrestrial research on the heterogenous catalytic processing of plastic started to receive attention in the mid 1990s with a focus on pyrolysis and hydrocracking [48]. The major catalysts in use are zeolites, with metal oxides and supported metals playing a substantial role as well [48] (Fig. 8).

Glycolysis and hydrolysis represent the third most relevant route to plastic recycling which mostly focus on polyethylene terephthalate (PET) and polyurethane (PUR) i.e., oxygen-containing plastics [48]. Here, efficient catalysts comprise metal oxides and supported metal nanoparticles (NPs). The major obstacle behind the terrestrially utilized procedures are the high temperatures (e.g., for pyrolysis 300–500 °C [48]) and the usage of harsh conditions such as acids to mediate the cracking of plastic chains. This is unlikely to be feasible for space applications where safety and space constraints dominate. Enzymatic biocatalysis for plastic decomposition is currently under research, but bears the obstacle that most plastics are water insoluble and depolymerization enzymes have to react at the surface via an interfacial mechanism [49]. Beyond interfacial biocatalysis, processes involving enzymes in non-aqueous media or low-water systems have also been studied [50]. Here, enzyme immobilization on solid supports (so-called ‘bio-hybrid systems’) can enable protein stabilization for reactions in non-aqueous or low-water environments, where polymers can also be solubilized before the reaction [49].

Until today, most synthetic polymer deconstruction work has focused on PET conversion with hydrolases. Recently, Zhou et al. [51] have also reported the possibility of electrocatalytically upcycling PET

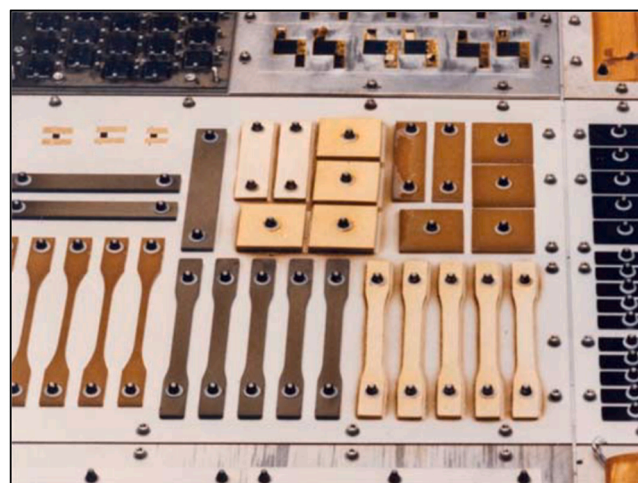


Fig. 9. Post-flight photograph of the Solar-Array Materials Passive Experiment that faced atomic oxygen exposure in low Earth Orbit (LEO). Volatile contamination from silicone on the materials became evident through oxidation by atomic oxygen which darkened through further UV radiation exposure. From [55] with kind permission of Springer Nature Switzerland AG.

plastic to potassium diformate, terephthalic acid and hydrogen using a nickel-modified cobalt phosphide (CoNi 0.25 P) electrocatalyst. This pathway could be particularly interesting for space applications as hydrogen is a sought-after fuel. Moran et al. [52] have also investigated the electrochemical oxidation of nylon, yielding 70 % of adipic acid. Nylon 6 and nylon 6.6 have been - since their discovery in 1931 - one of the most commonly used artificial fibres and are widely used as well in space. This yield compares well to non-electrochemical methods, where yields typically range from 0.33 % to 36.2 % [46].

The *Polymer Recycling System* (CPRS) of the *Made in Space Company* has been launched to the ISS to recycle polymer parts and plastic bags into a raw material for 3D printers. 3D prints made from *Braskem North America's Green Polyethylene*, derived from sugarcane, can be recycled. Earth applications may include 3D printed items in general hardware stores or items which are specifically made for expeditionary manufacturing on small surface ships and submarines and on offshore oil and gas platforms.

Additionally, a machine called *Refabricator* has been successfully installed on the ISS, which is a 3D printer and the first integrated recycler [53]. Its purpose is to recycle the plastic used in space to 3D printing materials and then remake the parts or tools needed. If such a

recycling machine could be combined with catalytic processing to deal with the plastic waste in the space, most of the plastic waste in space could be reused which would be suitable for the long-way space travel.

NASA has developed furthermore a *Catalytic Wet Air Oxidation* (CWAO) unit to decompose polymers into carbon dioxide, hydrogen and methane [54]. The reaction in the CWAO occurs at temperatures as low as 250 °C. Various catalysts are active for different targeted species e.g., ruthenium on a carbon support provides the highest carbon yield [54].

Photocatalytic pathways such as atomic oxygen/ultraviolet (UV) catalytic decomposition or bio-decomposition can principally use the strong radiation that is ‘naturally’ accessible in space while those factors, on their own and in combination, are known to be a threat to polymers, composites and other materials causing degradation [55]. Silicone outgassing is for example a common problem for adhesives and paints in space which causes further contamination: the volatile compounds in silicone react e.g., with atomic oxygen to silica which then darkens through further UV radiation exposure. This has been extensively studied after the retrieval of the Long Duration Exposure Facility (LDEF, Fig. 9).

Takagawa and Yokota [56] investigated the effect UV radiation and atomic oxygen exposure on polyimide erosion. They found that the UV- and atomic oxygen-exposed polyimide promoted the desorption of carbon oxides. By changing the relative intensity of atomic oxygen and UV, an up to 400 % increase in the erosion rate could be observed at high UV radiation intensity [56]. This indicates that the combination of atomic oxygen and UV radiation could have the potential to decompose plastic waste in space, whereas the decomposition rate could be adjusted by the UV radiation intensity. This effect could be further supported by the use of appropriate photocatalysts.

Biodeterioration of polymeric materials also occurs in space [57]. Bacterial biofilms form readily on surfaces of polymeric materials at a wide range of temperatures and relative humidity. In fact, the degradation of polymeric materials e.g., on the ISS is mostly a result of both, fungal and bacterial colonization as these microorganisms have been detected on spacecraft hardware and in the air. To take advantage of the biodegradation of polymers in the sense of waste removal, the decomposition rate has to be controlled and further accelerated using optimised biocatalysts and bioprocessing conditions.

5.2. Management of larger metal waste in space

Metal recycling is motivated by the near-future metal trash in space arising from the increasing number of satellites, currently about 600 a year according to the Swiss start-up company *ClearSpace SA* [58]. *Airbus* and *ClearSpace SA* are underway for a proof of concept for the removal of this space debris by their 100 kg *RemoveDEBRIS* satellite and ESA's *Vega* rocket, respectively [58], recovering the large amount of aluminium which is a major composite of satellites. Moreover, *Airbus* plans to use a harpoon to skewer satellite debris. The first test includes the recovery of a 100 kg component with a size of two metres and a weight of two tonnes which defines the commercial threshold for the *Airbus* recycling [58]. The company plans to bring a metal recycling device firstly to the ISS to start recycling metal parts and then operate it on the Moon in a next step. *ClearSpace* heads moreover for a robotic spacecraft with four articulated arms to remove debris [58].

6. Conclusions

Catalysis for human space exploration is still at its infancy, but further research and development in the area is inevitable for the realisation of long-term space missions and habitats as illustrated in this review. Imminent knowledge and research gaps in the field of space catalysis are pointed out and a selection of past and present achievements have been summarised. While there is profound experience from Earth-based processes, the space constraints on circularity and atom economy will likely require new concepts and approaches in catalysis.

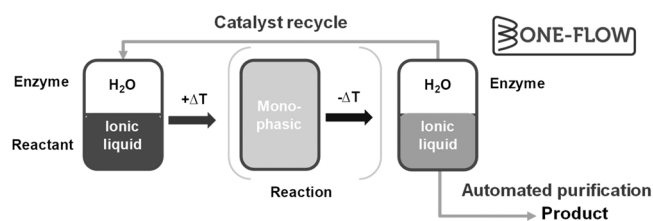


Fig. 10. A compartmentalised catalyst array concept as described in ONE-FLOW for the production of pharmaceuticals.

Few reports are however available with respect to tests in and for space and future terrestrially-based investigations need to consider the space environment to a much larger extent such as the reduced gravitational environment, space radiation and the required process compactness.

The experience with elementary life support in space and related catalysis is two-fold. The life support needs as demanded by current ISS operations are well investigated. This includes provision of clean water, clean and life-supportive atmosphere, and management of plastic waste. Moving from the supply view of short-term space exploration to one for a long-term presence of humans in space, comfort life support aspects involving food production and nutrient supply as well as recycling has to be explored more intensively in detail. Current proof-of-principle trials need to be transferred to real-case practices. This requires research on biological and enzymatic catalysis in space and integrated catalysis systems provided e.g., through (photo-)electrocatalysis.

7. Outlook

Space systems have to be close to circular, allowing only minute in-flows (resources) and minute outflows (waste) - if at all. Nature meets these high sustainability constraints by integrating many production (metabolic) cycles into one holistic sustainable system. Catalytic processes are arranged in vicinity to allow fast processing along a cascade of reactions. Space catalysts might profit from a similar concept. The EU project ONE-FLOW [59] aimed at such compartmentalised catalyst arrays to conduct bio-organic synthesis cascades within one single (flow) reactor (Fig. 10). Such a unified catalyst system would contribute to reducing system complexity in space. Despite that weight and volume constraints are not as relevant on Earth, the high circularity and atom economy constraints of catalytic processes in space are an excellent linkage to terrestrial green catalysis approaches and provide common research ground.

CRedit authorship contribution statement

KB and VH conceptualized the article. CZ, MEG, KB and VH wrote it and KB and VH edited the final version as well as the revision.

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.

Data availability

No data was used for the research described in the article.

Acknowledgements

KB would like to thank the *German Aerospace Center* (DLR) with funds provided by the Federal Ministry for Economic Affairs and Energy (BMWi), Germany, under Grant No. DLR 50WM2150 (project *LiMo*). VH acknowledges support from the ERC Synergy Grant *Surface-Confined*

fast modulated Plasma for process and Energy intensification (SCOPE) from the European Commission with Grant No. 810182.

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