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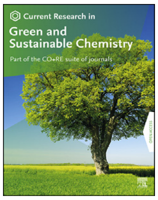

The reductive catalytic upcycling of polyolefin plastic waste

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ABSTRACT

Plastics, and polyolefins (POs) in particular, revolutionized the everyday life, and after use the waste accumulation is raising severe environmental concerns fostering an intense the research towards more sustainable and profitable recycling routes.

In this contribution, we focus the attention concerning recent advances on the reductive upgrading of POs promoted by heterogeneous catalysts, that is emerging as a valid alternative to pyrolysis since POs are transformed into valuable chemicals and fuels, allowing overcome the issue of elevated temperatures, as well as low selectivity and fast catalyst deactivation. As a matter of fact, the introduction of H_2 gas in the reactor allows to carry out PO degradation in milder conditions coupled with a higher control on the produced hydrocarbons, depending on the employed catalyst and the reaction parameters. Two main processes have been so far developed: hydrogenolysis and hydrocracking, respectively leading to formation of diesel and gasoline. At a molecular level, their difference relies on the different typologies of catalysts, which are monofunctional metal catalysts in the former case (where both surface hydrides and surface alkyl species are formed and recombine each other), and bifunctional acid/metal catalysts in the latter (where, after a carbocation is formed by protonation, the reaction proceeds by isomerization and scission). Despite the conceptually simple and univocal definition of the two mechanisms, several catalytic processes have been developed in the last years, varying for both reaction conditions and obtained products, thus generating a quite complex scenario.

Hereafter, the most significant results are reported to provide a consistent base for further progress.

1. The global context of polyolefin plastic waste

The advent of plastics revolutionized everyday life combining unrivalled functionalities with low cost, low weight and excellent barrier properties. At global level, 367 Mton/year of plastics are currently manufactured starting from fossil resources. However, millions of tons of mismanaged plastic waste accumulate in the environment causing problems throughout the ecosystem (Fig. 1) [1].

Polyolefins (POs) are a family of thermoplastics that include mainly polyethylene and polypropylene and are the most widely used commodity polymers with a plethora of applications spreading from films and rigid packaging, bottles and containers (for food products, detergents, cosmetics), single-used bags, electrical cable coatings, automotive parts, toys, etc. The most commons POs are low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), high density polyethylene (HDPE) and polypropylene (PP), accounting for about 50% of the global plastics demand (Fig. 1) [1]. In particular, POs generally used as textiles, packaging materials and many consumer goods (plastic bags, bottles, toys, etc. etc.) have an expected market size of USD 604 billion by 2030 with a CAGR of about 9.7% (Fig. 1) [2].

POs generate significant externalities along their whole life-cycle. In particular: i) POs production still relies on the use of fossil resources and is responsible for the emission of large amounts of greenhouse gases; ii) at the end of its lifetime (usually shorter than one year), only ca. 30% of PO wastes are recycled, while the remainings are often mismanaged causing the well-known degradation of natural systems [1]. Looking ahead, it is expected that the worldwide demand of POs will continue to grow at a high rate as the economy and the population also grow. However, the amount of POs littered in the environment cannot increase as well and an intelligent end-of-life management is foremost urgent. As a matter of fact, the European Union, standing up as a global leader towards a just, climate-neutral and resource-efficient economy, has

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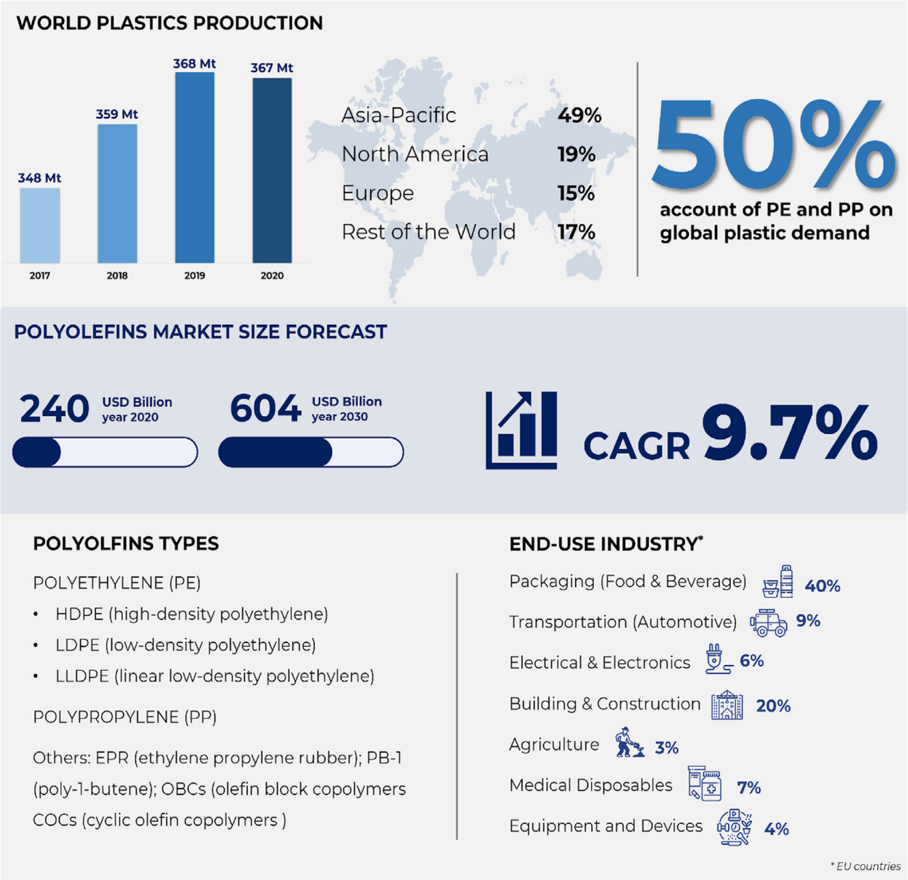


Fig. 1. World Plastic production, Polyolefins type, applications, end-use industry and relative market size forecast.

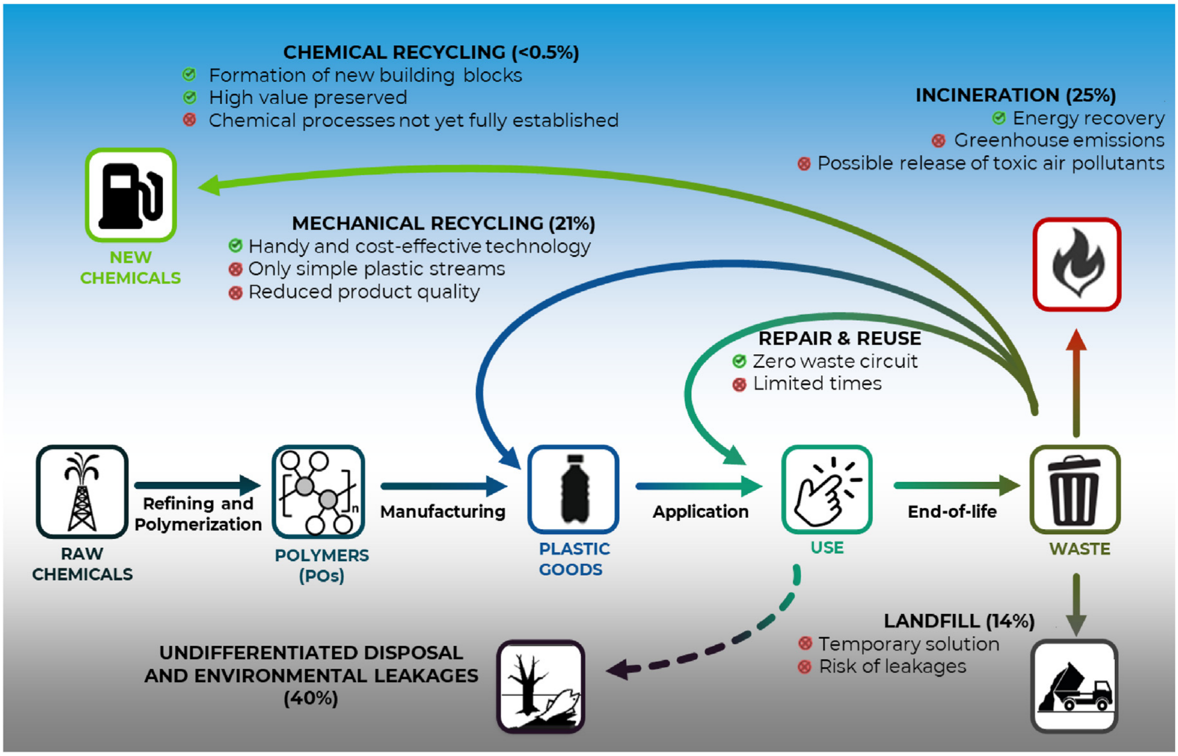


Fig. 2. The whole life-cycle of POs, with special emphasis to the practice after use [4,5].

identified plastics as a key product to act on, setting strict requirements for both waste reduction and recycled content in new products in the sectors of packaging, construction materials and vehicles. The implementation of these targets is based on extending the economic responsibility to plastic producers, increasing the awareness of the consumers and building up a capillary network of infrastructures for separate collection [3].

Fig. 2 displays the whole plastic chain, with special emphasis to the management of the end-life. According to Plastics Europe (a pan-European association of plastics manufacturers), in 2020 only two thirds of the plastics produced in Europe have been effectively sorted after use, while the rest has been racked up as undifferentiated disposal or leaked in the environment [4]. Surely, improving the end-life collection is a priority target for governments and it will responsibly involve the whole population. However this is not enough: new breakthroughs are needed in the industrial treatments of the plastic waste in order to preserve the high value of materials and to promote a real circular economy. Of course, the first action to realize is to repair and reuse, an increasingly fundamental strategy for extending the duration of plastic goods, although it is not sufficient with respect to the huge amount of irreparable waste inevitably generated every year (29.5 Mt in 2020 only in Europe) [4]. Surprisingly, 23% of the plastics properly sorted (i.e., the 14% of the whole annual production) is still destined to landfill, but this fraction is going to drastically reduce in the next future since it is just a temporary solution, requiring a huge land consumption and dissipating a potential resource, besides the risk of soil and groundwater contaminations if not prevented by costly measures [5]. Nowadays, the most common and profitable treatment for plastic waste is the incineration with energy recovery as heat and electricity, accounting for the 42% of the sorted plastics (25% of the total). Although this route cannot terminate plastic waste problems because of carbon emissions, increasing global warming and losing again a potential resource [5,6].

Therefore, recycling through specific routes for all the different plastic streams turns out to be the only possibility to maintain the plastic value chain. Currently, 35% of sorted plastics are recycled (21% of the total), but the perspective is to become the predominant route, almost doubling its volume in 2030 [4,5]. According to the ISO15270:2008 standard and ASTM D7209 definitions, three main types of recycling processes are identified based on mechanical, chemical and biological approaches [1,7]. So far, most of the recycling is mechanical, which is a handy and cost-effective technology, but it can be applied only to homogeneous and highly purified plastic streams, generally leading to a progressive degradation of the material properties in terms of mechanical and thermal resistance and appearance [6]. On the other hand, the chemical recycling, which so far accounts only for less than 1% of all matter, allows to transform plastic waste into valuable chemicals, which can serve as building blocks for new processes and manufactures [8]. It is worth noticing that chemical recycling follows specific routes for each class of plastic materials and this is the main reason for its limitation up to now [6].

2. The chemical upgrading of POs

Among chemical recycling processes, catalytic pyrolysis is surely a well-established approach for the upcycle of POs: this process converts long-chain polymers into small molecules (gases, liquids and aromatics) in the presence of a solid acid catalyst (either Lewis or Brønsted acid) at high temperature (above 300 °C) and proceeds through a carbocationic mechanism [7]. The production of liquid hydrocarbon fuels from the POs waste is technically feasible and has been already implemented at an industrial level. However, elevated temperatures not only make the pyrolysis process economically unsound, but also raise the challenge of selectivity control and catalyst fast deactivation.

The reductive upgrading of POs into liquid fuels – either gasoline (C5–C12) and/or diesel (C9–C22) – is an alternative process which is recently gaining attention since it entails H_2 to cleave the very stable C–C bonds of long polymer chains thus requiring milder temperature conditions with respect to those generally adopted in the pyrolysis.

The catalytic reductive upgrading of POs can be generally related to either hydrogenolysis or hydrocracking reactions. Both reductive technologies are aimed to the catalytic cleavage of internal C–C bonds since the terminal bond breaking leads to excessive formation of gaseous products. At present, most of the reactions reported in literature on the hydrogenolysis and hydrocracking of POs are performed without the need of external solvents. However, it has been recently demonstrated that reaction solvents may play a crucial role in (i) reducing mass transfer problems, (ii) improving the kinetics of the process and, most important, (iii) driving the product selectivity [9], similarly to the common practice in pyrolysis [10].

A schematic comparative representation of hydrogenolysis and hydrocracking processes as well as relative reaction products, conditions and catalysts used are reported in Fig. 3.

In terms of an exact definition, hydrogenolysis refers to the “lysis” of polymer chains in the presence of H_2 promoted by monofunctional metal catalysts, while the hydrocracking describes a depolymerization process where the cleavage of C–C bonds occurs on the acid functionalities on the catalysts surface followed by the metal-mediated hydrogenation of intermediates.

3. The basic catalysis of the reductive upcycling of POs

Fig. 4 displays the main reaction steps involved either in hydrogenolysis or hydrocracking processes, starting from the same polymer chain (linear PE is considered for simplicity). As already discussed, in the hydrogenolysis process the catalysis is exploited by a metal surface, while in the hydrocracking a combination of metal and acid functionalities is required. Anyhow, in both cases the polymer chain is initially activated by chemisorption onto the metal surface, by replacing two (or more) C–H bonds with as many C-metal ones [11]. Afterwards, the two processes follow different pathways.

In the case of hydrogenolysis, the dehydrogenation step is necessary because the cleavage of C–H bonds is considerably more favorable than the direct cleavage of C–C ones (ΔEa of 18.11 kJ/mol with respect to 88.93 kJ/mol) [12]. The most stable configuration for the polymer chain adsorbed on the metal surface is that occurring through two adjacent C atoms (the so called α,β configuration), although the backbone flexibility of the long chains could allow also different configurations, involving C atoms more distant that one from each other [13]. The adsorption onto the metal weakens the C–C bond, whose cleavage is now competitive with further C–H bond scission [12]. Depending on the H_2 pressure (and hence on the amount of radical H available on the metal surface), the chemisorbed polymer can evolve differently: at high hydrogen coverage, polymer fragments can easily be hydrogenated and then desorb from the surface, whereas at low hydrogen coverage, polymer fragments stay longer on the metal and further crack occurs forming short hydrocarbons [7]. Therefore, controlling H_2 pressure and/or choosing a catalyst with higher or lower H affinity are two effective tools for tuning the selectivity to products, for instance increasing the liquid yield (as then reported in Fig. 5) [14].

On the other hand, in the case of the hydrocracking the initial activation of the polymer chain by the metal serves to form the C═C double bond necessary for adding H^+ and thus generating the first carbocation [15]. Then the reaction proceeds either by skeletal isomerization (rearranging the chain to a more branched structure) or by β-scission (breaking the chain into two fragments, one ending with a vinyl group and the other one bearing the positive charge). Since the formation of primary carbocations is unfavored, isomerization prevails at the beginning. Four types of β-scission have been so far identified as possible, involving only secondary and tertiary ions (both as starting point and as result) [16]. All the four types of β-scission and the skeletal isomerization compete each other, randomly taking place at the same time within the reactor. Generally, β-scissions involving secondary carbocations are

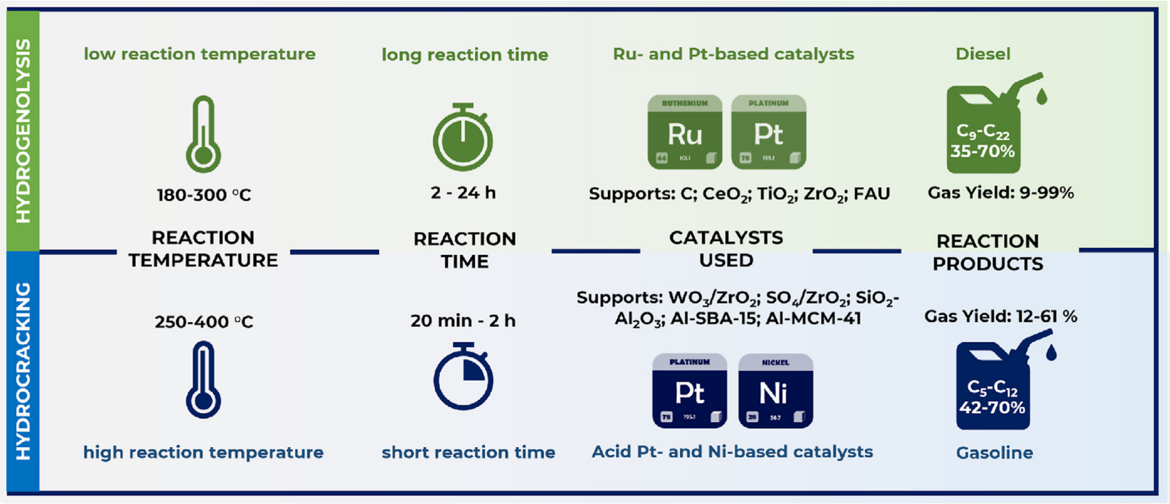


Fig. 3. Schematic comparative representation of hydrogenolysis and hydrocracking processes for reductive catalytic upgrading of POs.

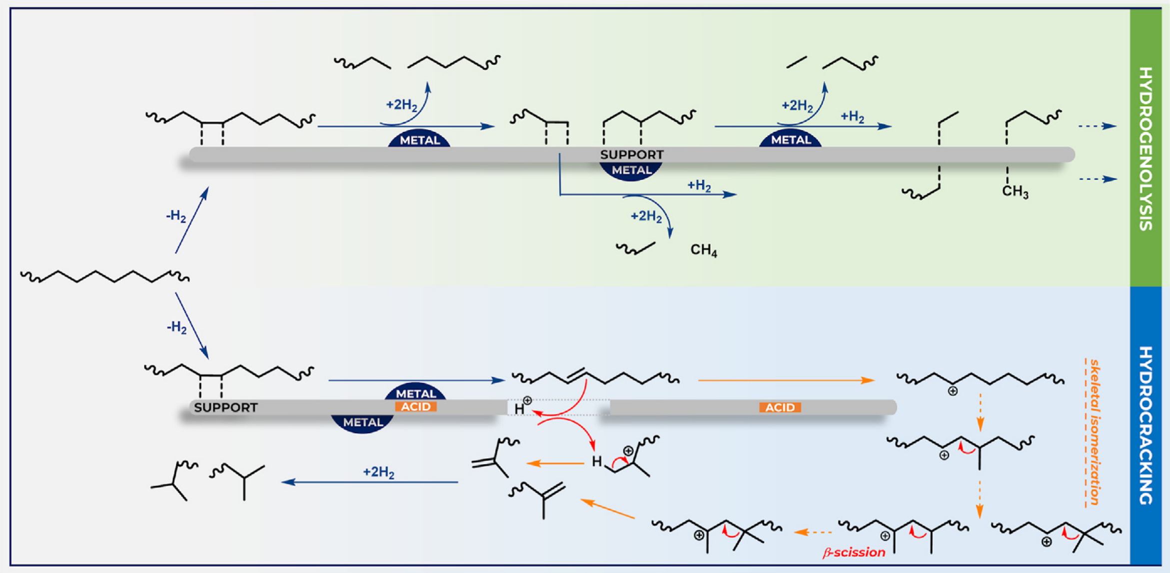


Fig. 4. Schematic representation of the reaction mechanisms for hydrogenolysis and hydrocracking processes, starting from the same generic PE chain.

slower than the isomerization, which in turn is slower than the β-scission involving only tertiary ions (which is thus considered as the most probable conclusion of the whole process), but the kinetics can change depending on the reaction conditions and on the used catalyst [15]. Finally the neutrality can be restored by transferring back the H^+ to the acid catalyst and all vinyl groups formed upon the carbocationic chemistry are hydrogenated by the metal catalyst [7].

4. The actually developed processes: hydrogenolysis vs hydrocracking

A summary of the reaction conditions adopted in the hydrogenolysis and hydrocracking processes is reported in Fig. 5.

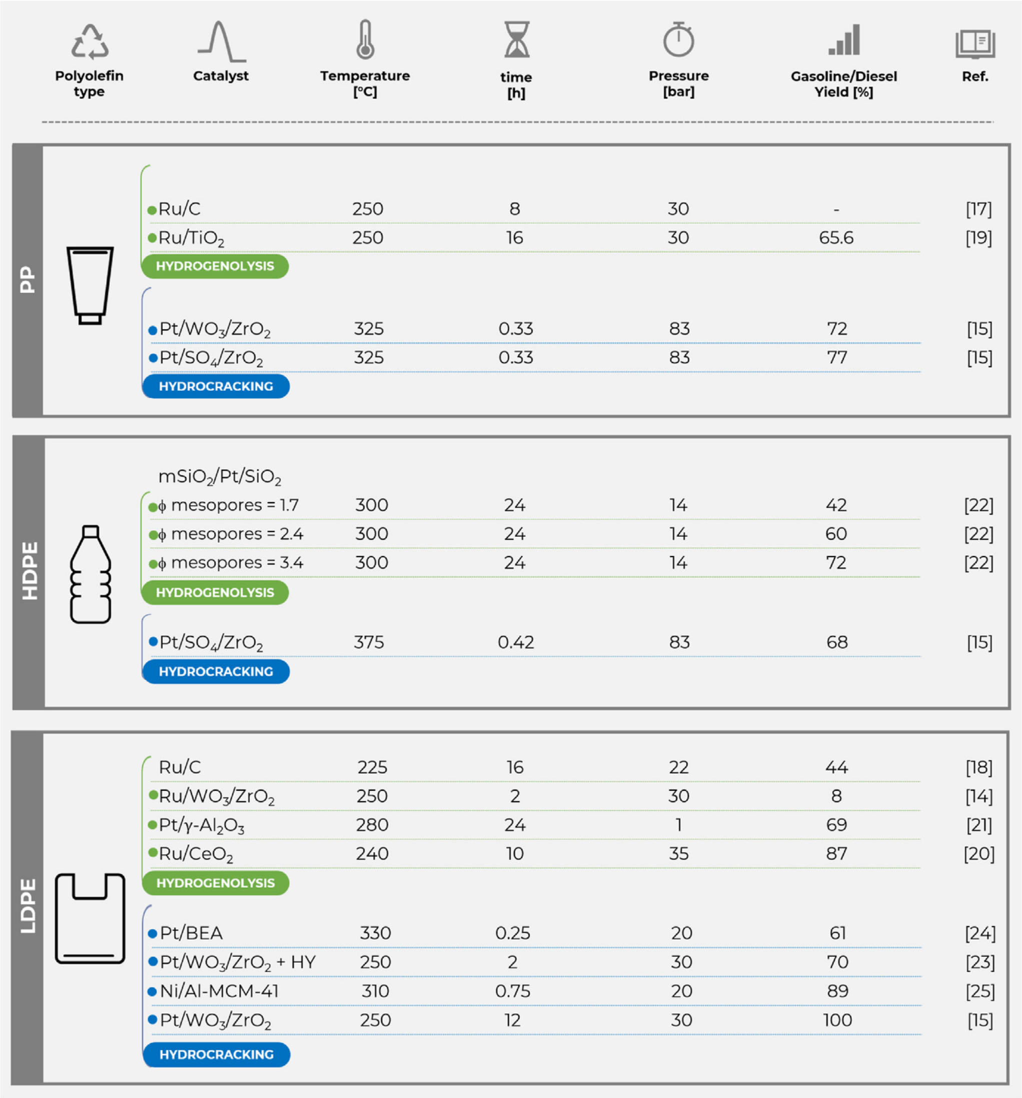
Hydrogenolysis processes are carried out in the temperature range 180–300 °C with prolonged reaction times that can exceed 15 h. Heterogeneous catalysts based on Ru are by far the most investigated system with an enhanced activity in the production of diesel [7]. When higher temperatures are adopted a poor efficiency in liquid products is registered as result of an extensive gas products formation.

With respect to other catalysts (Rh, Pt, Ni, Pd, Cu, Ag, Au), Ru is the most active metal centre in the hydrogenolysis of Polyolefins as a consequence of its relatively low free-energy barrier for C–C bond cleavage (the rate-determining step in reductive depolymerization).

Commercial Ru/C was found to be an efficient heterogeneous recyclable catalyst for the conversion of PP and LDPE into C5–C32 alkanes under mild conditions (200–250 °C, 20–50 bar H_2) in absence of solvent. Moreover, the same catalyst was found to be also active in the depolymerization of streams of mixed real postconsumer plastic polyolefin waste into liquid alkanes [17,18].

A high yield (66–80%) in lubricant-range hydrocarbons was obtained when TiO_2 was used as support for ruthenium: the hydrogenolysis of PP over the Ru/TiO_2 catalyst was proved to occur with a dynamic adsorption/desorption mechanism with the concurrent internal C–C bond breaking that lowers the production of gaseous products [19].

Also ZrO_2- and CeO_2-supported Ru (Ru/ZrO_2 and Ru/CeO_2) can be effective and reusable heterogeneous catalysts in the hydrogenolysis of various POs LDPE, HDPE and PP into valuable chemicals (liquid fuels and waxes) in high yields (83–90%) without isomerization or aromatization, which enabled high yield of the target valuable chemicals. The high selectivity towards liquid alkanes and lubricants over Ru/CeO_2 and Ru/



Polyolefin type	Catalyst	Temperature [°C]	time [h]	Pressure [bar]	Gasoline/Diesel Yield [%]	Ref.
PP	● Ru/C	250	8	30	-	[17]
	● Ru/TiO_2	250	16	30	65.6	[19]
	HYDROGENOLYSIS					
	● Pt/WO_3/ZrO_2	325	0.33	83	72	[15]
	● Pt/SO_4/ZrO_2	325	0.33	83	77	[15]
	HYDROCRACKING					
HDPE	mSiO_2/Pt/SiO_2					
	● ϕ mesopores = 1.7	300	24	14	42	[22]
	● ϕ mesopores = 2.4	300	24	14	60	[22]
	● ϕ mesopores = 3.4	300	24	14	72	[22]
	HYDROGENOLYSIS					
	● Pt/SO_4/ZrO_2	375	0.42	83	68	[15]
	HYDROCRACKING					
LDPE	Ru/C	225	16	22	44	[18]
	● Ru/WO_3/ZrO_2	250	2	30	8	[14]
	● Pt/γ-Al_2O_3	280	24	1	69	[21]
	● Ru/CeO_2	240	10	35	87	[20]
	HYDROGENOLYSIS					
	● Pt/BEA	330	0.25	20	61	[24]
	● Pt/WO_3/ZrO_2 + HY	250	2	30	70	[23]
	● Ni/Al-MCM-41	310	0.75	20	89	[25]
	● Pt/WO_3/ZrO_2	250	12	30	100	[15]
	HYDROCRACKING					

Fig. 5. Selected hydrogenolysis and hydrocracking catalytic processes for the reductive upcycling of PP, HDPE and LDPE.

ZrO_2 systems is attributed to the small and well dispersed Ru particles: CeO_2 and ZrO_2 are characterized as strong Lewis base sites that allow formation of smaller Ru particles [20].

At the same time, the presence of highly dispersed WO_x clusters in Ru-WZrO_x systems allows the storage of hydrogen by a reverse-spillover mechanism on the catalytic surface promoting the hydrogenolysis of LDPE into higher molecular weight fuels and lubricants oils suppressing methane formation [14].

Pt catalysts have been proved to be a valid alternative to Ru systems. The catalytic hydrogenolysis of various polyethylene grades promoted by Pt/γ-Al_2O_3 permits to obtain low molecular-weight liquid/wax products (long-chain alkylaromatics and alkylnaphthenes) in high yields even in absence of molecular hydrogen, with little production of gases. The Pt/γ-Al_2O_3 can be used for three consecutive 6-h recycling tests without any significative performance loss. Interestingly, it was demonstrated that direct conversion of PE into aromatics requires milder reaction conditions if compared to those generally used for making BTX from n-alkanes [21].

mSiO_2/Pt/SiO_2 systems were found to be very active in the hydrogenolysis of post-consumer HDPE, tuning the liquid yield by modifying the dimension of the mesopores in the external mSiO_2 shell [22].

On the contrary, hydrocracking processes generally operate at higher temperatures (250–400 °C) and shorter reaction times, allowing the production of gasoline in higher yield compared to hydrogenolysis derivates. Catalysts based on Pt or Ni metals coupled with a large variety of acid supports (e.g., WO_3/ZrO_2, SO_4/ZrO_2, SiO_2–Al_2O_3, Al-SBA-15, Al-MCM-41) are generally adopted [7].

Platinum is by far the most adopted system in the hydrocracking conversion of POs. Indeed, the bifunctional Pt/WO_3/ZrO_2 catalyst converts LDPE into branched fuel- and lubricant-ranged alkanes with an adhesive isomerization mechanism between the Pt and Brønsted acid sites in parallel with the polymer C–C bond cracking. the catalyst metal-to-acid site molar ratio (MAB) shifts the product distribution to larger cracked products and increases the isomerization degree in the residual polymer [15].

The same authors presented a mixture of mechanically blending of Pt/WO_3/ZrO_2 and FAU-type zeolite (HY) system for the hydrocracking of LDPE into a mixture of gasoline, diesel, and jet-range hydrocarbons in mild conditions (250 °C, 30 bar H_2, 2 h). The polymer undergoes hydrocracking over Pt/WO_3/ZrO_2 into relatively large olefins- or alkanes-based intermediates that diffuse into HY zeolite acid sites that promote further C–C bond cracking into C5–7 alkenes [23].

Platinum on zeolite beta exhibits marked selectivity toward C4 hydrocarbons starting from LDPE in a fixed-bed continuous flow reactor. The catalyst efficacy was attributed to its acidic and structural properties with a depolymerization mechanism that proceeds via tertiary carbenium ions and backbiting reactions. Hydrogen ensures the reductive state of platinum, prevents the coke formation on the catalyst surface and allows the hydrogenating of the LDPE as well as its cracking products [24].

Ni-based catalysts have found limited applications requiring harsher reaction conditions with temperature generally higher than 300 °C [25, 26].

5. Conclusions and future challenges

There is no doubt that the reductive upcycling of polyolefins has opened the door for converting plastic wastes into fuels, lubricants, and waxes. While several experimental studies have been carried out for the decomposition of model polyolefins and/or clean single-use PO products, a lot of efforts from the scientific and industrial communities are still needed to clarify some key points, including:

- a better fundamental understanding of catalysts properties (support acidity and porosity, metal dispersion, dimension, and reductive state) in driving the different C–C bonds cleavage;
- the role of solvent in both hydrogenolysis and hydrocracking processes in terms of (i) mass transfer facilitation, (ii) faster kinetics of the process and (iii) higher product selectivity;
- the preparation of cheap and robust catalytic system with high productivity (especially in terms of amount of produced liquid per a given amount of catalyst in a certain time) and stability (a time-consuming and costly cleaning step would be necessary in the case of metal leaching);
- the effect of possible impurities and/or additives on the catalyst performances;
- the use of indirect H_2 source in order to make catalytic processes safer (with respect to the use of pressurized gas), according to the green chemistry principles;
- scale-up of most promising catalytic processes from laboratory to industrial scale, paying also attention to the catalyst recovery and recycling in particular in the presence of unconverted plastic (that can "trap" other solid particles at temperatures below POs melting point thus drastically reducing the catalyst's recyclability).

In conclusions, in this graphical review, a comprehensive overview of the actual state-of-the-art concerning the hydrogenolysis and the hydrocracking of polyolefins with the aim to increase the scientific and industrial awareness on the high potentiality of reductive catalytic upcycling of POs waste is reported with the aim to increase relative research opportunities.

CRediT authorship contribution statement

Alessandro Piovano: Conceptualization, Writing – original draft, Writing – review & editing. **Emilia Paone:** Conceptualization, Writing – original draft, Writing – review & editing.

Declaration of competing interest

Authors declare no conflict of interests.

Data availability

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

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This paper is dedicated in memoriam of Emeritus Professor Rosario Pietropaolo that unexpectedly passed away on July 1st, 2022. Rector of Università degli Studi Mediterranea di Reggio Calabria, first Dean of the Faculty of Engineering as well as a visionary of science, master of ethics, integrity and dedication and inspiration for many colleagues and students.

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