IDENTIFY THE CATALYSTS THAT ARE REDUCING THE CARBON FOOTPRINTS OF THE PROCESS INDUSTRIES

TCGR's report, '***Catalysts and Catalyst Manufacturing Methods for Decarbonization***,' provides innovation in catalysis and catalysis manufacturing for decarbonization and greenhouse gas (GHG) emission reduction. The report includes:

- Recent achievements in decarbonization of the chemical industry to produce commodities and new energy vectors
- Analysis of more robust, durable, and cheaper heterogeneous catalysts for the intensification of challenging industrial processes under milder experimental conditions
- Examples of catalysts for the conversion of renewable and energy-rich wastes into hydrocarbon fuels, hydrogen, refining products of the chemical and petrochemical industry and those for the power-to-X (PtX)
- Insights on catalyst manufacturing methods, including methodologies using waste or novel materials that increase circularity in catalyst manufacture or methodologies utilizing renewable energy.
- Existing regulatory landscape for CO_2 reduction and potential opportunities and greener solutions for the catalyst industry and catalyst manufacturers.

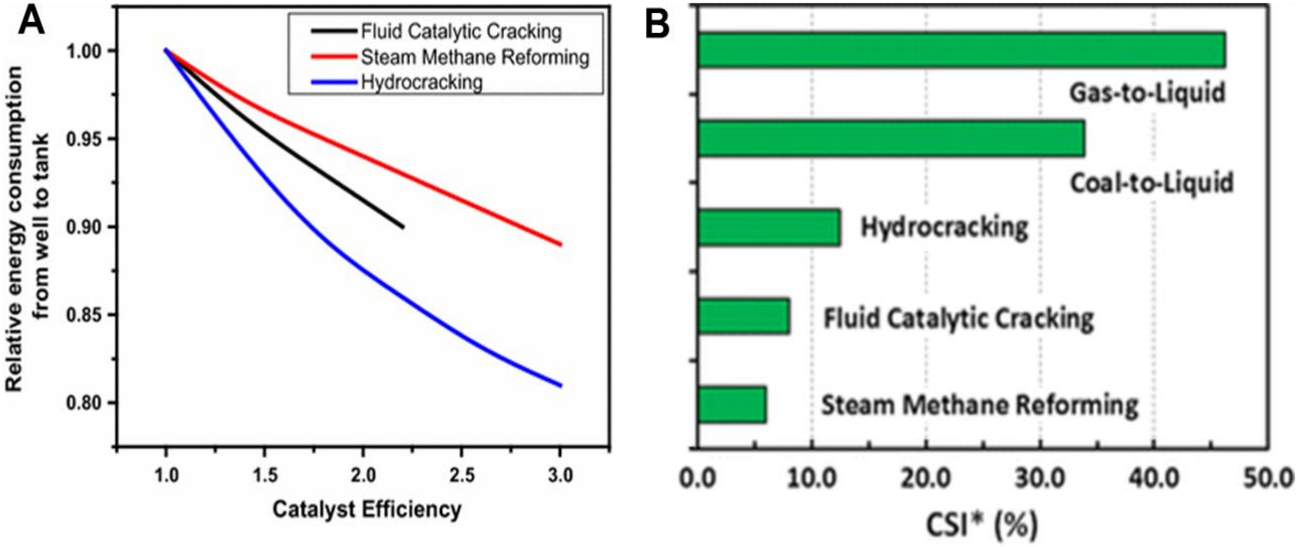

Figure 1: (A) Relative energy consumption vs Catalyst Efficiency (CE) for three catalytic processes; (B) Catalyst Selectivity Index (CSI) for various catalytic processes. Source: Xiao, et al., 2020

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CATALYSTS AND CATALYST MANUFACTURING METHODS FOR DECARBONIZATION

A technical investigation commissioned by the members of the Catalytic Advances Program (CAP)

Report Completed: July 2023

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NEED FOR THE STUDY

- Managing carbon emissions is undoubtfully a grand challenge in chemistry and engineering. Catalysis is essential in decarbonization by increasing energy efficiency and enabling the transition to clean energy sources. It plays an essential role in addressing this global challenge by increasing energy efficiency, reducing carbon emissions, capturing carbon dioxide, displacing carbon-intensive feedstocks and products, and utilizing clean energy sources to displace fossil fuels.
- Several recent advances in catalyst development enable better industrial process efficiency and utilization of clean energy sources. At the same time, advances are often scientific and/or technological without putting them in the right context of the alternative possibilities and the evolving scenario related to the energy transition. Thus, it may often be unclear to understand their effective possible impact, pros/cons, and thus whether they will be a scientific advance only or a key element to building a framework of innovation for the new future production.
- This TCGR report aims to provide an overall picture of the recent (mainly last few years) developments of catalysts and catalyst manufacturing methods for decarbonization while at the same time providing indications of how these results related to the ongoing transition and the possible future scenario, also taking in consideration that short, medium and long terms solutions must be developed at the same time.
- Two main driving factors in the current model of petrochemical production have been identified: (i) the use of fossil fuels and (ii) the scale economy. The energy transition will determine a change in the dominant use of fossil fuels and the scale economy. Distributed productions, and thus technologies for this production model which use local resources must be developed. Often, literature reviews analyze only specific scientific or technological advances. However, without putting them in the right context and discussing alternative possibilities, they cannot correctly determine emerging trends, new possibilities and perspectives beyond state of the art.

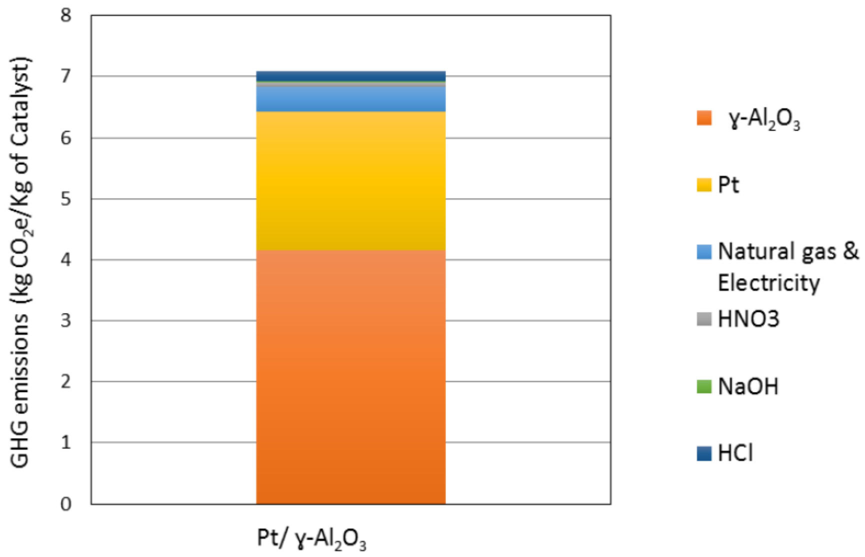

Figure 2: Cradle-to-gate GHG emissions for Pt/ γ-alumina catalyst. Source: Adapted from Pahola Thathiana Benavides et al., 2017.

This TCGR study provides, together with an analysis of the recent developments, the elements to identify how the scientific/technological advances can be related to the future carbon-zero production and economy.

SCOPE OF REPORT

- The scope of this report is to provide an update on recent developments in the field of catalysts and catalyst manufacturing methods for decarbonization, with an eye on the transformation context and the needs for the future technologies commented on above. It includes an analysis of catalyst developments that lead to lower CO_2 emissions (for example, by lowering heat requirements or improving yields) and methods of catalyst manufacture or regeneration that lower CO_2 emissions in catalyst manufacturing processes. The report also considers regulatory progress for CO_2 reduction, such as the recent Inflation Reduction Act (IRA) in the US, that leads to opportunities for catalysis.

- A special emphasis is put on innovative and greener solutions suitable to meet with the urgent legislation requirements in terms of process intensification, reduction costs, catalyst durability, recycling policy and, in particular, GHG emissions. The search for alternative decarbonization solutions in catalysis is analyzed through a series of waste materials for the new catalysts manufacturing. This catalysis decarbonization approach represents a cost-effective and environmentally benign solution for a second and greener life to waste materials, alternative to their costly landfill disposal.

- Section 1 provides a general introduction to the topic of catalysts and catalyst manufacturing methods for decarbonization.

- Section 2 dedicated to catalysts for decarbonization. It is structured into five main sub-sections: (i) catalysts to lower CO_2 emissions and carbon footprint, (ii) catalysts for decarbonized products, (iii) catalysts for reducing GHG, (iv) catalysts to lower the carbon footprint of CO_2 capture, and (v) current industrial applications and future commercial prospects.

- Section 3 describes catalysts manufacturing methods, offering a different perspective to the decarbonization of chemical industry, emphasizing the waste-to-wealth concept within the catalysis chain (and the catalysts manufacturing in particular), for a real zero-landfill and zero-waste policy.

- Section 4 provides a regulatory overview and framework for the aspects discussed in Sections 2 and 3. It covers the existing and anticipated regulatory landscape for CO_2 reduction (and decarbonization), what this means for catalyst manufacturers and potential opportunities.

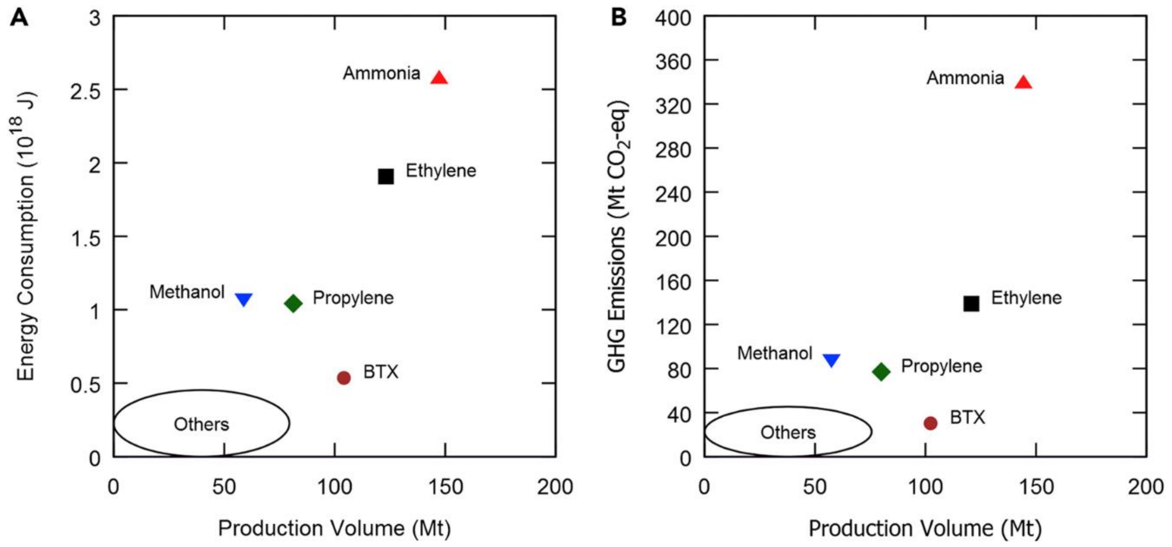

Figure 3: Energy consumption and carbon footprint of high-volume commodity chemicals: (A) energy consumption and (B) GHG emissions versus production volume for top chemicals by volume in 2010. "Others" shows approximately where the next 13 largest contributors fall. Source Schiffer & Manthiram, 2017.

CATALYSTS TO LOWER CO_2 EMISSIONS AND CARBON FOOTPRINT

- Decarbonization of industrial sectors is indicated as the next frontier because it accounts for about a third of the GHG emissions but requires breakthrough technologies and an in-depth shift in the current technologies and approaches to meet the targets. Around 45% of CO_2 emissions in the industrial sector result from feedstocks that cannot be decreased by a change in fuels, only by changes to processes. About 35% of emissions come from burning fossil fuels to generate high-temperature heat. Abatement of these emissions requires switching to alternatives, such as zero-carbon electricity or low-carbon fuels.

- The report identifes three possible strategies to lower the carbon footprint in catalytic technologies:
  1. **Increase the selectivity by minimizing CO_2 formation:** this is the general objective of catalysis, but the expected progress in meeting political targets for deep decarbonization is low. However, there are two advantages: (i) the applicability to in-operation processes and (ii) a direct beneficial economic return due to increased productivity. We can distinguish two targets: (i) introducing more selective catalysts in the processes and (ii) improving catalyst lifetime and developing anti-coking catalysts.
  2. **Develop new catalytic paths for near-room temperature:** Operating at ambient temperatures minimizes external energy supply, and costs of energy recovery, thus, capital expenditure. It reduces risks and allows better control of side reactions. Ambient temperature catalysis is possible for homogeneous catalysis and, in limited cases, for heterogeneous catalysis, particularly hydrogenation reactions. Using (nonthermal) plasma (NTP) to activate the reactants, it is possible to perform catalytic reactions under very mild conditions, even if they occur at typically much higher temperatures. This approach must overcome, in exothermal reversible reactions, the trade-off between high temperatures for kinetic reasons and low temperatures for equilibrium (thermodynamic) reasons.
  3. **Process heat electrification**, e.g., using renewable energy to provide the heat necessary in chemical processes. Over half of the GHG emissions in energy-intensive processes are associated with furnaces, mainly realized using fossil fuels. Thus, using electrical heating with renewable electrical energy can substantially decrease the process's carbon footprint. In decarbonization technologies, there is an increasing interest in electrified chemical reactors, although mainly limited to endothermic processes, because they are the most obvious case example. The relevance for catalysis is that this change from fired to electrically-heated reactors also opens new possibilities for redesigning catalysis and realizing process intensification. The possibility of reduction of the carbon footprint using this strategy is over 40%, but it can be higher if the novel opportunities offered can be exploited.

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CATALYSTS FOR DECARBONIZED PRODUCTS: HYDROGEN FOR FUELS OR AMMONIA

- Decarbonization of the production of fuels, both carbon-based, derived from CO_2 but often also from biomass and not based on carbon (ammonia, in particular), requires the availability of large amounts of green (ultra-low carbon) hydrogen.
- Given the many environmental issues in both blue hydrogen and the new aqua hydrogen route and their limited practical degree of carbon footprint decrease in producing H_2, the perspective of large implementation of these routes is little. On the other hand, producing H_2 by electrolysis is an energy-intensive operation, requiring the readiness of large amounts of renewable electricity, which are hardly available, at least in a future scenario up to 2050.
- Thus, alternative paths to produce ultra-low-carbon would be necessary. The most obvious solution is to produce hydrogen by photocatalysis, but notwithstanding the large scientific efforts on the particulate photocatalytic hydrogen production system, the solar-to-H_2 efficiencies are quite low, below 1%, even if stability and low-cost production in a 100 m^2 panel demo plant was shown. In this approach, H_2 and O_2 are co-produced, and thus besides safety issues, the separation between H_2 and O_2 should be realized, with additional costs and problems in the quality of the H_2 produced.
- An alternative is a photoelectrochemical approach where a more complex device is necessary, but there is an intrinsic separation of the H_2 and O_2 produced. Significantly higher solar-to-hydrogen (STH) efficiencies (ηSTH) are possible, over 20%, even if the systems' reliability and stability have not always been proven. To obtain high ηSTH, expensive photovoltaic modules and electrode materials have been used. In addition, these results should be integrated with current density values because often high ηSTH were obtained at negligible values of current density, e.g., productivity.
- Values of ηSTH above 10% could be obtained in systems not using expensive materials or costly PV modules. The PV/EC approach is currently the more robust to get high performances, even if demo units with a large surface area of the panels, comparable with the 100 m^2 for the particulate photocatalysts (PP) approach, are not yet available.
- An extension of this approach is to integrate into the unit also the intermediate storage of H_2 to allow continuous production of H2 or on demand. This possibility was demonstrated in a recent paper where the coproduction of formic acid and H2 from CO2 and H2O in a combination of a photovoltaic module with an integrated electrocatalytic cell (PV/EC) module with high solar-to-fuel efficiency (10%) was demonstrated using only earth-abundant materials, proposing at the same time the concept drawn to use the results for a device with integrated storage of H_2 in the form of formic acid which may be decomposed catalytically during the night or when higher productivity in H_2 is required.
- Although productivities are low, it is possible to consider the feasibility of developing artificial trees for the distributed production of H_2, which overcome several limits in costs and availability of sufficient renewable electrical energy for all the planned uses.
- By changing the cathode, the same PV/EC module could produce in a single step either fuels or chemicals from CO_2 (for example, methanol, ethylene, methane, etc.) or ammonia from N_2. Productivities are still far from the application needs, but fast progress in the area may be expected.

METHODOLOGIES WHICH INCORPORATE OR WILL INCORPORATE RENEWABLE ENERGY IN CATALYST MANUFACTURING

- With respect to the large volume high surface area (HSA) catalysts that have been the focus of consideration, prioritization for applications of renewable energy in processing, particularly Scope 1 emissions for which the manufacturer has the most control, is a focus.
- Whether one looks at zeolite production, fluid catalytic cracking (FCC) catalyst production, or hydroprocessing catalyst production, two common energy consumption steps are at the forefront. The removal of synthesis water via drying steps and calcination at elevated temperatures to assure physical integrity and desired porous microstructure, in current manufacturing schemes consume significant amounts of fossil fuels, predominantly natural gas. This, then, leads to energy choices that impact Scope 2 emissions.
- Drying operations involve spray dryers, tray dryers, belt dryers, and rotary dryers. Calcination operations typically involve rotary kiln calciners that operate at much higher temperatures than rotary dryers which are somewhat similar. In all cases, there are three opportunities to mitigate the GHG emissions:
    - Address formulations that inherently require less process water, reducing the drying load
    - Select energy options that use more or exclusively renewable sources
    - Apply carbon capture and sequestration (CCS) processing to capture CO_2 generated

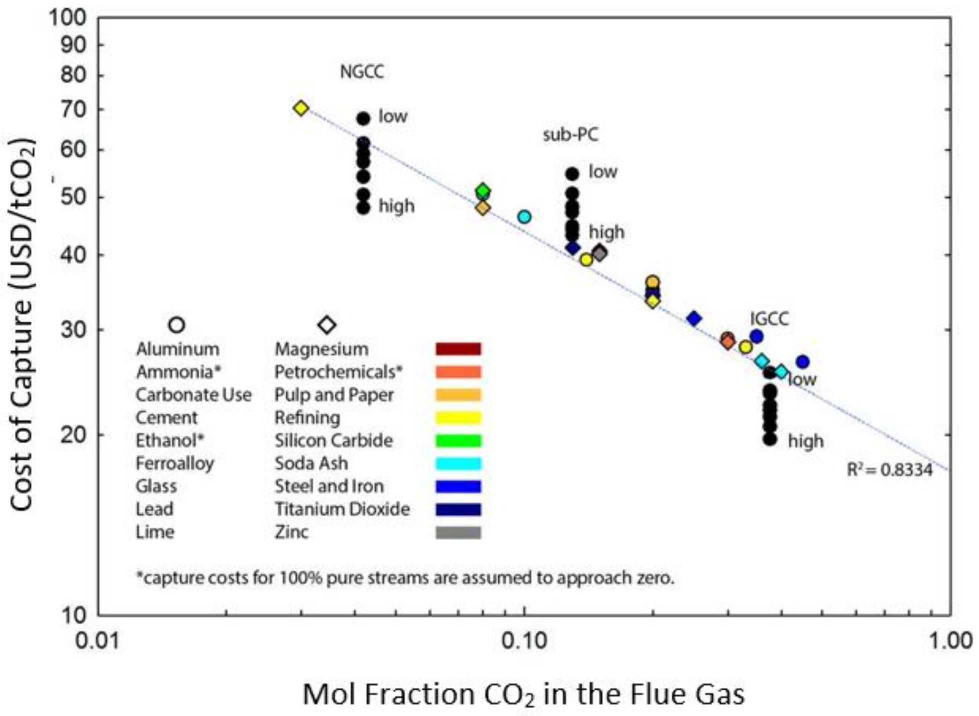

Figure 4: Capture cost vs. CO_2. Source: Psarras et al., 2017

RECYCLING OF SPENT CATALYST MATERIALS AND RECYCLING OF CATALYST MANUFACTURING WASTE STREAMS

- The recycling of spent catalyst materials as well as recycling of catalyst manufacturing waste streams has been practiced with varying degrees based firstly on economics and secondly on the prevailing regulatory environment. Owing to the competitive nature of the catalyst manufacturing businesses, recycling wastes in high volume catalyst segments has a history of several decades. As pressures for circularity in all businesses grow, and regulatory fiat or incentives evolve, catalyst manufacturers will respond as options become even more economically favorable.

- Recycling of PGM-containing catalysts focusses on the PGMs themselves and covers a span of applications, ranging from automotive catalytic converters, the largest, to petroleum and chemical catalysts. Platinum and palladium make up the bulk of PGM demand and consequently are a large portion of the recycling pool. Catalytic converters dominate, with it comprising 40% of the demand for platinum and 84% of the demand for palladium in 2021. Chemicals and petroleum catalysts account for 11% of the platinum and 6% of the palladium demand.

- The extremely high value of the PGMs in HSA catalysts have economically mandated that they be recycled just as is the case for catalytic converters. The increased use of PEM electrolyzers to produce green hydrogen will add to the growth and need for PGM recycling, particularly for platinum and iridium PGMs.

- Various methods such as pyrometallurgical, hydrometallurgical, biological, and physical separation are employed for the efficient and economic recovery of PGMs from waste catalysts. The selection of recovery methods largely depends on the PGM concentration, carrier materials, and presence of other constituents. However, hydrometallurgical and pyrometallurgical methods are the dominant commercial processes.

- Key players in PGM catalyst recycling are Johnson Matthey, Hereaus, BASF, Sabin, and Umicore. Johnson Matthey uses smelting, leaching, and refining to recover the PGMs and other associated metals from waste catalysts. Sabin is exclusively pyrometallurgical in their processing.

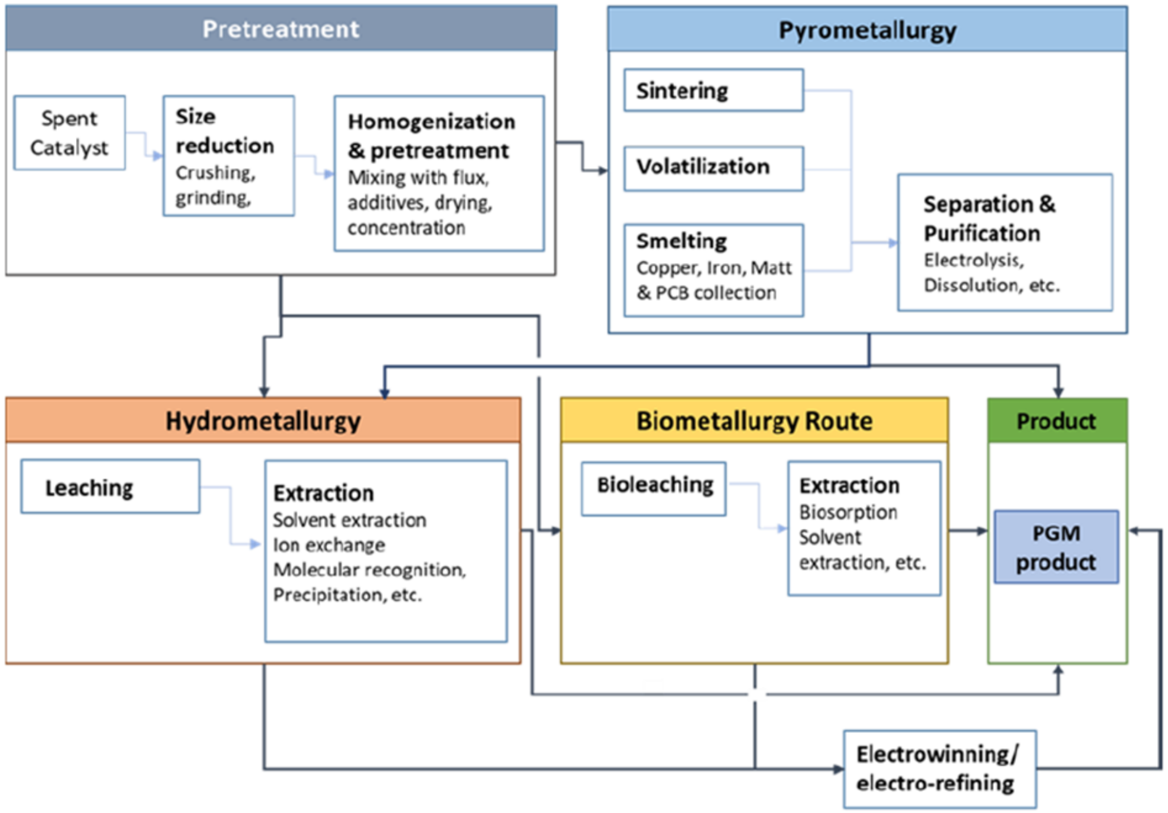

Figure 5: Process paths for PGM catalyst recovery. Source: Smith et al., 2022

REGULATORY TRENDS IN DECARBONIZING ENERGY, PETROLEUM, AND CHEMICAL INDUSTRY TECHNOLOGIES

- The production, processing, and supply of energy and by-products of hydrocarbons such as coal, oil, and natural gas (NG) are essential in key sectors of the economy including petrochemicals, agriculture, manufacturing, etc. Given the growing drive to curtail the greenhouse gas (GHG) emissions, especially carbon dioxide and methane, attributable to energy industry operations, this chapter reviews the existing and anticipated regulatory landscape for decarbonization, and what the emerging trends mean for the production and investment in catalysts and catalytic processes.
- In reviewing the trends and uncertainties surrounding the unfolding energy industry transition and decarbonization efforts, the BP Energy Outlook (2023 edition) notes that the use of modern bioenergy, such as solid biomass, biofuels, and biomethane, could play a key role in decarbonizing hard-to-abate sectors and processes, while electrification, developing low-carbon hydrogen, hydrogen derivatives, carbon capture, utilization, and storage (CCUS), and carbon removal technologies would presumably be essential 30 years from now considering various energy policy scenarios.
- Going forward, catalysts can play a key role in the pathways to fostering efficient GHG emissions reduction and net-zero technologies for industrial, manufacturing, and energy-related processes. Recent experiences show that oil and gas companies are becoming engaged in developing alternative energy and fueling systems. For instance, Shell's CANSOLV CO_2 Capture System is expected to be used in capturing CO_2 emissions from processed flue gas and a combined cycle gas turbine (CCGT) power plant.
- A recent interview shows how the company engages in research and development and the application of catalysts in developing technologies such as methane oxidation catalysts. Heavy industries and refiners can produce blue hydrogen from natural gas with carbon capture and storage (CCS). Although green hydrogen produced using electrolysis and renewable power is likely to be a long-term solution, analysts suggest it may not achieve cost parity with blue hydrogen until about 2045.

SUMMARY

- The topic of catalysts and catalyst manufacturing methods for decarbonization is at the heart of strategies for transforming production in the energy and chemistry sectors. However, it is quite complex to address because it involves a deep transformation of the economic, industrial and societal reference system. For this reason, the evaluation of the techno-scientific advances also is not sufficient without putting them in the evolving framework context to determine which of the alternatives has better chances of success but at the same time to determine the crucial aspects on which to focus the attention.
- The main challenges and hurdles, at the same time, in catalysts for decarbonization are thus to create the right vision of the ongoing transformation, which allows going beyond the scientific or technological development to determine how they contribute to creating the new paths, the pros/cons from this perspective, and the right balance necessary between short-, medium and long-term activities and innovative technologies.
- Improvements in the catalysts and related processes to decrease the carbon footprint and GHG emissions in the chemical industry and energy production are relevant objectives to meet the targets toward a net-zero emission future.
- Using catalysts leads to faster, more energy-efficient chemical reactions, and advancements in the development and use of catalysts have led to innovations in carbon capture and reduction technologies, petrochemicals, manufacturing of biodegradable plastics, new pharmaceuticals, and environmentally safer fuels and fertilizers, etc.
- In a commercial sense, such opportunities seem to be on the rise considering the highlighted incentives and policy support mechanisms in countries like the US, EU, UK, Japan, India, etc. Nevertheless, from a regulatory standpoint, both operators and decision-makers in the energy sector will be concerned about issues such as the implications of the regulatory measures on the affordability and costs of supplying energy and by-products of processing and refining energy resources as well as reliability and security of supply. If the costs and implications are reasonably manageable, there could be considerable potential for developing catalysts and catalytic processes.

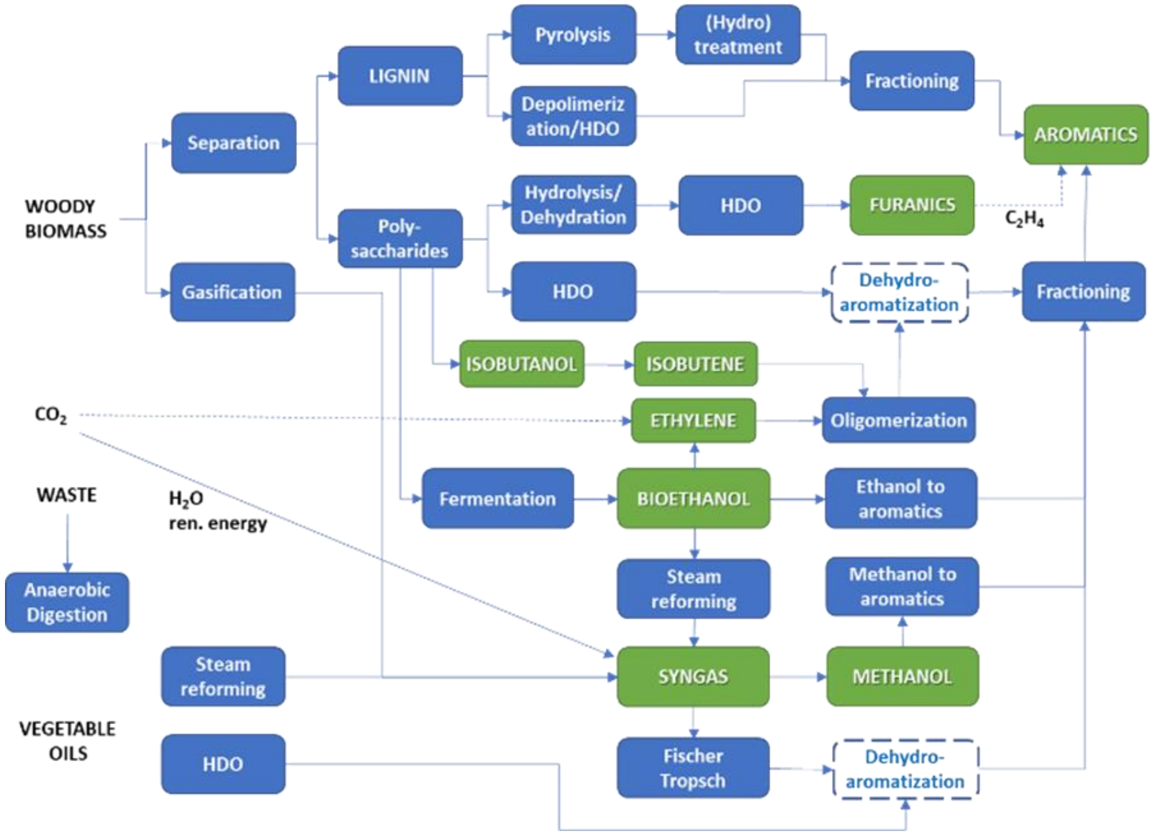

Figure 6: Overview of different possible routes to produce FFs-free aromatics as raw materials for the chemical industry. Surrounded by a broken line indicates technologies still to be developed. HDO indicates hydrodeoxygenation. Source: Centi & Perathoner, 2022.

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