CO_2 CATALYTIC HYDROGENATION TO METHANE

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In the last decades global warming has been recognized as an increasingly critical phenomenon of this era, and today this topic is central in the international debate. In this context, the European Green Deal, a set of political, economical and technical initiatives proposed by the European Commission, aims at reducing CO_2 emissions, so to achieve the climate neutrality in Europe by 2050. At the same time, global energy demand is expected to have a steep growth in the next years: it could be more than doubled by 2050 (from 12 to 30 TW) and more than tripled by the end of the century.

One of the biggest challenges for research and technological development is to efficiently combine the need to reduce CO_2 emissions, to contain global warming, and the satisfaction of ever-growing global energy demand, which is responsible of a large part of those emissions.

Atmospheric CO_2 concentration has increased from 280 to 410 ppm over the last 150 years, mainly due to the increasing use of fossil fuels from the XIX century. To reduce greenhouse gas levels in atmosphere, different approaches can be adopted, such as improving energy efficiency of the generating systems or replacing fossil fuels with renewable energy resources, possibly promoting the reuse of waste materials.

Within this context, hydrogen is expected to play an important role: in July 2020, the European Union approved the "Hydrogen Strategy for a climate-neutral Europe", which proposes this energy vector as a possible bridge between our fossil-based energy market and the fossil-free one which can hopefully be achieved in the future decades. To this end, massive incentivization of the so-called green hydrogen, i.e. hydrogen produced *via* water electrolysis powered by renewable energy sources, is expected in the coming years, with a short-medium term roadmap until 2030 and longer terms objectives to be fulfilled up to 2050.

Nevertheless, because of its low volumetric energy density and high volatility, hydrogen is poorly suited for certain applications, such as long term storage of renewable energy, which is an important issue to be addressed for an efficient implementation of fluctuating energy sources (such as solar and wind) in the existing energy infrastructure.

Power to Gas (PtG or P2G) processes aim to the conversion of green H_2 to methane, which would be a much better long term storage options for renewable energies, thanks to its higher volumetric energy density and its perfect compatibility with the gas grids; furthermore, based on the most recent projections, natural gas, which is primarily composed by methane, is expected to cover an increasing fraction of the energy demand in the coming decades, therefore methane market value will be steady, or even increase, for many years to come. Hydrogen can be converted to methane through the Sabatier reaction, which is strongly exothermic and involves its conversion alongside CO_2.

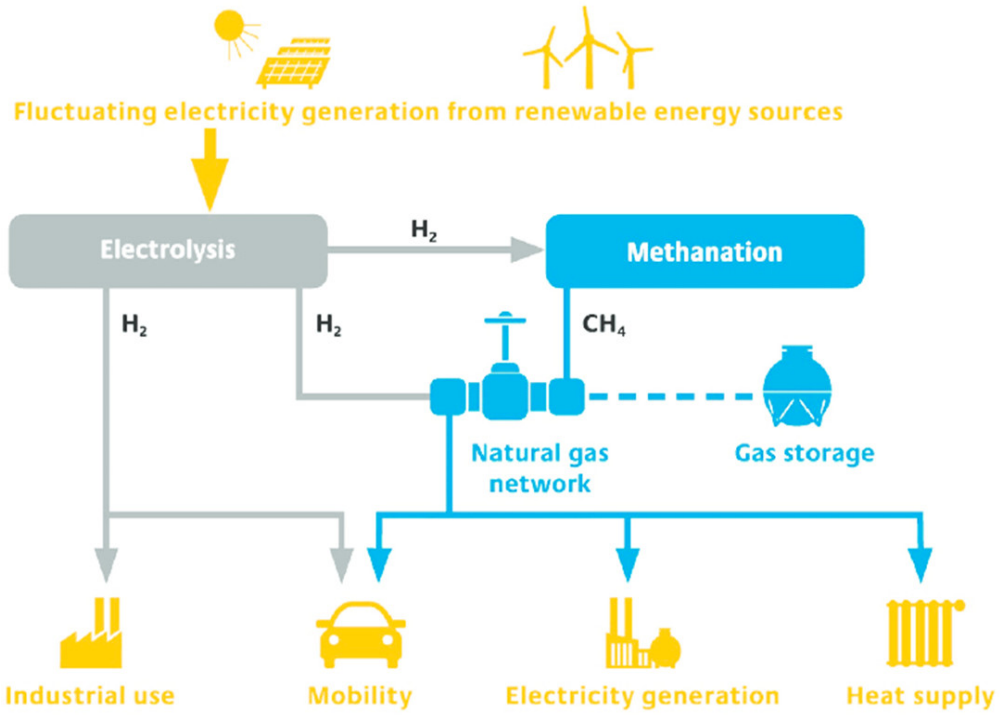
This process, therefore, can also be viewed as a sink for CO_2 captured from industrial emissions, effectively coupling the Carbon Capture and Utilization (CCU) strategy, pushed by the immediate decarbonization need, with the ever-increasing implementation of renewable energies in the market.

The Sabatier reaction has some serious kinetic limitations since it is promoted at low temperatures (above 400 °C the reverse water-gas shift reaction, producing CO, starts to be favored) and it involves the reduction of CO_2, the most oxidized form of carbon and an inherently very stable molecule. Therefore, this process requires the utilization of a proper catalyst, typically employing Ni as an active phase, and a reactor system providing optimal contact between the feed mixture and the supported catalyst and efficient heat management to avoid hot spots, which could lead to catalyst deactivation, and effectively dissipate, or possibly recover, the large amount of heat produced by the Sabatier reaction.

The most recent literature on the Sabatier process (which is often called as "methanation" of CO_2) highlights that, although many innovative catalysts and reactor geometries have been presented, very little studies are available on the catalyst/reactor system as a whole and the maximization of their synergy to achieve full process optimization.

Therefore, this PhD project aims to advance the technology readiness level (TRL) of the methanation process by simultaneously investigating novel catalyst materials (i.e. Ni supported on mesoporous materials) and reactor configurations (such as micro-reactors or three-phase reactors), to design an integrated system capable of maximizing their synergy to achieve peak performance, while also keeping in check the process economics.

The first year of the PhD is dedicated to a thorough literature research about the state of the art of methanation catalysts and reactors, and to the construction of a lab-scale plant to conduct all future experimental tests.
The second year shall be focused on the screening of advanced catalysts for the Sabatier reaction in a simple fixed bed reactor, employing Ni as an active phase on different mesoporous supports (i.e. nanostructured metal oxides, carbon nanotubes, mesoporous silica nanoparticles, etc.) and with the implementation of different promoters (Ce, Fe or metals). The goal of this experimental campaign will be to characterize these catalysts in terms of activity, selectivity and stability and to select the best performing one for more advanced reactor testing.
Lastly, in the third year, an advanced reactor (micro-reactor or three-phase reactor) shall be tailored on the previously selected catalyst to ensure the maximum synergy between them, while also providing an effective heat management system to optimize the thermal aspects of the Sabatier reaction. All the experimental data gathered shall be modelled, allowing for further and targeted optimization of the overall process.



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