Catalytic processes for CO2 conversion into Synthetic Methane

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Abstract

According to the Intergovernmental Panel on Climate Change (IPCC), human activity is responsible for climate change mainly due to the emission of greenhouse gasses from fossil fuel usage. After the Kyoto protocol commitment, many climate change mitigation policies have been promulgated to reduce anthropogenic greenhouse gas emissions in the EU and incentives were given to install renewable power plants (e.g. wind or solar) to reduce the dependency on fossil fuels. Renewable energy sources (RES) have a fluctuating and intermittent characteristic (daily or seasonal) with peak production generally not matching the demand. As adoption of RES grows in the electricity power source scenario, balancing of the electric grid without modulating the RES power plant is needed. Different technologies are available and under study for this purpose: flywheels, supercapacitors, batteries, compressed air storage, pumped hydroelectric storage, power-to-fuels (gas or liquid).

Power to Gas (PtG) appears to be a promising solution in converting renewable electricity in an energy carrier. Water electrolysis is used to convert electricity into hydrogen, which unfortunately presents some drawbacks as low energy density, steel embrittlement and challenges in storage/transportation. On the other hand, natural gas has a well-developed distribution grid and mature applications. Therefore, the most feasible solution is to further convert hydrogen in a substitute natural gas (SNG) compliant with the natural gas grid specifications. SNG can be produced by mixing hydrogen with carbon dioxide to carry out the Sabatier reaction.

The objective of this thesis was firstly to perform the process modelling of a power to liquefied methane system. The main units of the plant are the electrolyser, CO_2 capture from air, methanation unit, gas separation unit and the liquefaction unit. In this part the sizing and design of the separation system and liquefaction system was carried out in detail. Furthermore, the energetic analysis of the system was carried. An efficacy of 46% $_{(HHV\ basis)}$ could be reached with a mild heat integration between the methanation unit and the CO_2 capturing unit. The main energy losses/consumptions are due to the direct air capture (20%), the electrolyser (19%) and the methanation unit (8%). The liquefaction process, a well now energy intensive process, has an energetic impact of less than 2 % in this case.

The aging of a commercial nickel-based catalyst was studied in process relevant conditions in terms of temperature, pressure and feed gas composition. The feed gas composition was determined through the process modelling of the gas separation system that contains recycle streams. It was determined through 100h long tests that catalyst ages at temperature above 350 °C with a slow and gradual loss of activity. The cause of the catalyst activity decay was individuated by performing different catalyst characterisation techniques. Through temperature programmed combustion it was excluded carbon deposition as a possible cause of deactivation. Using X-ray diffractometry phase change of the nickel active metal was excluded as a possible cause of aging. The surface area analysis revealed a huge total area decrease that can be caused by the alumina support sintering. A kinetic analysis was performed on a fresh and aged sample. The activation energy does not change between

the samples meaning that there is no change in the reaction mechanism. Furthermore, a very good correlation was found between the ratio of the surface areas of the fresh and aged samples and the preexponential factor of the rate equation. To complete the kinetic description of the catalyst the intrinsic kinetics was determined and a LHHW model was fitted to the experimental data.

Finally, a multitube methanation reactor was developed in order to understand the effects of the operating conditions (temperature, pressure, space velocity) and the geometry on the temperature profiles and performance. An aging law was used in the model in order to consider the aging effect on the conversion rate. It was determined that to manage the declining performance caused by aging it is enough to adjust the operating temperature and pressure of the system to restore the initial conversion rates.