Addressing the challenges of the Power-to-Fuel technologies from a catalyst development and techno-economic point of view

Summary

The research focuses on the study of Power-to-Fuel technologies for producing renewable fuels or chemicals (i.e. methane, methanol and dimethyl-ether) from renewable energy sources and CO_2. Renewable energy sources (RES) exhibit an intermittent electric production and the electric energy has to be stored as an energy carrier such as hydrogen that could be produced through water electrolysis. CO_2 could be obtained by using carbon capture technologies in order to favour the closed carbon cycle and produce alternatives to fossil fuels.

Concerning Power-to-Gas technology, research has made significant progress and has been supported by many European projects (e.g. Store&Go and Helmeth). A model of a Power-to-Gas plant for the CO_2 hydrogenation to methane coupled to an intermittent electrical input from renewable energy sources was developed in Matlab® environment. In addition, a technical-economic analysis was carried out on the plant model, considering the possibility of managing the plant with both chemical and electrochemical storage tanks in order to decouple the production from the intermittent electric input. Subsequently, in collaboration with the Energy Department of the Politecnico di Torino and within the European project Store&Go, the coupling of Power-to-Gas plants with the medium voltage network was investigated in order to reduce electrical issues caused by the fluctuations of the electric production of RES. The techno-economic assessment revealed that the process is economically competitive in a future scenario in which the costs of the electrolyser and the electricity price will be lower than current prices. Furthermore, electrochemical storages are too expensive to be implemented, even if they allow the Power-to-Gas plant to be decoupled from the electric grid and to reduce the number of plant shutdowns. Furthermore, small and medium size Power-to-Gas plants allow electrical problems caused by RES fluctuations (i.e. overvoltages, overcurrents and reverse power flow) to be mitigated or solved.

Concerning the Power-to-Methanol technology, three aspects of the topic have been studied. Firstly, mixed copper-ceria catalysts were developed in the context of the Italian project Saturno for understanding in more detail the synergistic effect between the two phases. Secondly, the catalytic reactors for CO_2 hydrogenation to methanol were modelled in Matlab® environment for determining the presence of thermal issues, the best reactor configuration and the start-up time of the plant. Thirdly, a techno-economic

and environmental assessment of thermocatalytic and electrocatalytic Power-to-Methanol plants was performed for investigating the feasibility of both processes.

Regarding the development of copper-ceria catalysts, they have been synthesized by means of three different synthesis techniques (i.e. impregnation, solution combustion synthesis and gel-oxalate coprecipitation), characterized by N_2 physisorption, XRD, H_2-TPR, CO_2-TPD, ICP-MS, FE-SEM and EDS analyses. Furthermore, the catalysts were tested in an experimental test bench to evaluate and comparing their performance. These catalysts exhibited a synergistic effect between copper and ceria in CO_2 hydrogenation to methanol. In particular, the oxalate-gel coprecipitation technique favours the formation of small nanoparticles of both phases, the increase of the specific surface area and the interface between copper and ceria; therefore, the methanol productivity is significantly enhanced.

Concerning the reactor modelling, a pseudo-homogeneous one-dimensional model of the reactor was developed and another model that also includes the methanol separation section and the recirculation of unreacted gases. The purpose of the work was to evaluate the internal profiles of the reactor, evaluate the best reactor configuration to obtain the maximum performance of the plant and estimate the plant start-up time. The study has revealed that there are no crucial thermal issues the best reactor configuration is a double refrigerated fixed-bed reactor.

Lastly, the techno-economic and environmental assessments of the feasibility of Power-to-Methanol processes have required to study a scale-up of both processes starting from reliable laboratory data on a ternary catalyst (CuZnAl) for CO_2 hydrogenation to methanol in both reactor configurations. The assessments have revealed that the electrocatalytic technology could be further developed for achieving greater performances and that it could be economically competitive with the thermocatalytic process. Furthermore, the feasibility of even small-sized plants has been demonstrated if the allocation of the product on the market is considered.

Finally, in the field of dimethyl-ether production, the research is focused on the development of CuZnZr ferrierite-based hybrid catalysts for direct CO_2 hydrogenation to dimethyl-ether in a one-step process. The activity and stability of four hybrid catalysts supplied by CNR-ITAE of Messina and obtained by using different synthesis techniques (i.e. co-precipitation, impregnation and physical mixture) were investigated. The tests were carried out varying both the space velocity and the reaction temperature. Moreover, both calcined and aged catalysts were characterized by means of different techniques: N_2 physisorption, H_2-TPR, NH_3 pulse chemisorption, XRD, ICP-MS, FESEM, EDS, XPS and TEM measurements. The coprecipitated CuZnZr-ferrierite hybrid catalysts exhibited the best performances and a higher oxide/zeolite ratio favours the dimethyl-ether yield.