

Attachment A Brief description of the training project

Title of the Training Project:

NO₂ adsorption enhancement in liquid phase

Description of the scientific and educational objective: *(min 1.000 characters - MAX 5.000 characters)*

The stage of NO₂ adsorption is a critical and costly stage in the overall process of production of nitric acid and fertilizers. Understanding and improving this stage, which is associated with the stage of NO to NO₂ oxidation, leads thus to a reduction of the energetic costs of the process, and a process intensification with economic benefits. At the same time, understanding how to improve this step is also critical to developing new alternative technologies to produce directly fertilizers using renewable energy sources, such as by non-thermal plasma or by anodic electrocatalytic conversion of N₂.

The PhD work will thus investigate how to improve the adsorption of NO₂ in liquid phase to intensify the process in which the NO₂ is transformed in nitric acid. In parallel it will be investigated the low-temperature oxidation of NO to NO₂ using novel catalysts, and how the reaction rate correlates with catalyst design characteristics such as the lattice dynamic. In parallel, will be also studied how other catalyst design characteristics, such as performing the oxidation in confined environments, by using zeolites, MOF or carbon-materials, could help in overcoming thermodynamic limitations in the reversible exothermic oxidation of NO to NO₂.

In addition to these aspects, the PhD will also study the possibility to develop alternative processes to produce nitrate solutions based on the direct use of renewable energy sources, such as based on catalytic-assisted non-thermal plasma or electrocatalytic direct conversion of N₂.

(of greenhouse gases) for 2050.

The topic addressed will therefore allow the creation of a highly qualified figure, on the issues of i) development of innovative processes to produce fertilizers, ii) process intensification of the production of nitric acid and fertilizers, iii) preparation and testing of catalysts, iv) mechanisms of reactions and structure-activity relationships, v) advanced characterization of the catalytic materials, vi) devices and cells for the study of renewable-energy driven processes and their engineering.

The study provides for the multidisciplinary integration of various skills, focused on industrial chemistry, but which extends from the study of the physics and chemistry of materials and their characterization to the engineering of devices and industrial development. The proposed study is therefore perfectly consistent with the themes of the ACCESS PhD which is centered on the development of innovative solutions for industries that use renewable energy to convert molecules such as N₂ and the development of innovative low-carbon chemical technologies.

The proposed research is fully consistent with the needs of the country, in terms of i) reduction of dependence on fossil fuels and ii) greenhouse gas emissions, iii) promotion of the use of renewable energy, iv) increase of the innovative capacity and the competitiveness of industry, v) promotion of human capital. It is also fully consistent with the territories involved in the program (Sicily), as there is a) the promotion of human capital, b) the development of the renewable energy chain, c) the reduction of greenhouse gas emissions and d) the development of innovative solutions for closing the carbon cycle in energy-intensive industries.

The technologies developed will allow an increase in the resilience of the territory and represent new innovative possibilities for the development of sustainable and integrated chemistry with the territory, which also represents an industrial recovery plan for the crisis areas present in the region following the closure of many production lines in the chemical area.

Company Supervisor: Dr. Pierdomenico Biasi (CASALE SA)

Methods of carrying out training and research activities:

The training and research activities will be integrated into the context of the ACCESS International and Industrial Doctorate which provides for a series of training and educational activities, which are

coherently integrated with the proposed research activity. The interaction with other PhD students, the possibility of interaction and collaboration with other national and international PhD students, the training activities (from seminars to schools and meetings) and the additional skills that are provided (from training to work in the industrial sector, to aspects of confidentiality and patents, to the increase of computer and linguistic skills, as well as to work in teams) are an added value compared to the typical training in Doctorates. The additional added value is represented by a period, from 6 to 12 months, at Casale SA to further increase the ability to operate in the field of industrial development.

The research activity, apart from the period at Casale SA, will be carried out at the CASPE Laboratory (Catalysis for Sustainable Production and Energy) of the University of Messina which has over twenty years of experience in the issues of catalysis and oxidation. In addition, the lab has the staff and equipment that allow the PhD student to operate with maximum efficiency in achieving the aims of the project.

The study will address the various elements necessary for complete training of the PhD student, from the preparation of the catalysts and other necessary materials to their characterization using a combination of experimental techniques, to the study of their behaviour, and to the development of the reactors and devices necessary for the study, including aspects of scale-up and industrial development, depending on the results obtained.

Effects and expected results with particular emphasis on promoting economic development and the production system:

The study combines both fundamental and applicative aspects, as the goal is the development of technology applicable from an industrial point of view, with therefore considerable attention to all aspects that allow a quick transition from laboratory results to industrial application.

The expected results are the development of knowledge for a new technology for process intensification in NO to NO₂ and NO₂ absorption in nitric acid/fertilizers production as well as in the development of alternative technologies based on the direct use of renewable energy and starting from N₂ rather than NH₃. The results will allow the evaluation of the development of a new process that replaces the current one, after the further necessary stages of study at higher TRL.

The results, therefore, represent the first element in the development of a new intensified process technology or of a novel technology based on renewable energy, which therefore allows reaching the mitigation objectives. climate change and innovation at the basis of the PNRR and economic development and the production system.

The company CASALE SA will host the PhD student beneficiary of the scholarship financed on the resources of the Ministerial Decree 352/2022 for no. 6 months in the course of the doctorate.