SYNTHESIS, FUNCTIONALIZATION AND CHARACTERIZATION OF FOAMED ZEOLITE MONOLITHS FOR ENVIRONMENTAL AND ENERGY APPLICATION

Carlo Gravino – Advisor: Prof. Domenico Caputo

Curriculum: Ingegneria dei Materiali e delle Strutture

Pollutants in wastewater and waste gas streams cause environmental pollution and can adversely affect human and animal health. Active materials, where the pollutants can reversibly adsorb on, are often used to limit their dispersion in the environment. An ideal adsorbent material should have a high adsorption capacity, be easy to handle, selective towards the pollutant, regenerable by physical or chemical processes and sustainable throughout its life cycle. The adsorbent materials widely used (zeolites, activated carbon, MOF) are obtained in the form of fine powders, which are difficult to handle and process; moreover, they show a considerable pressure drop and possible channeling phenomena. Although the use of a binder phase can help overcome these critical issues, it can partially obstruct the zeolite's active sites.

My studies, therefore, initially focused on the production, functionalization, and characterization of zeolite rich foams, produced by inducing the in-situ conversion of a geopolymer precursor through appropriate hydrothermal treatment, whose main parameters of hydrothermal treatment are solution concentration, temperature and time of treatment. It is possible to tune the porosity (closed or open) of the product by adding a suitable foaming agent to the geopolymer slurry. Closed porosity is useful for insulating materials, while open porosity improves exchange properties increasing the contact surface between the fluid and the adsorbent material itself. Moreover, the morphology and size distribution of the pores can be varied using suitable surfactants. By means of this synthesis methodology, a porous monolith based on zeolites is obtained without incurring the disadvantages of using a binder to shape the zeolite powder. These materials could therefore be effectively used in environmental and energy applications, like zeolites.

My current PhD research activity is concentrated on the production of such monoliths, with a focus on the choice of foaming agent (silicon powder, aluminium powder and hydrogen peroxide), surfactant (HDTMA-Br and a natural surfactant) and their content in the mixture. This resulted in a series of samples characterized by highly dispersed porosity, density and compressive strength values. X-ray analysis, water adsorption, cation exchange analysis (to assess both cation exchange capacity and possible selectivity), gas adsorption (such as N_2 for evaluation of specific surface area S_{BET} or CO_2 for evaluation of adsorption capacity towards this gas and possible use in CCS), SEM analysis, evaluation of pore size distribution by mercury porosimetry will also be carried out. In parallel with all these analyses, mixtures with different Si/Al ratios will be evaluated to promote the nucleation of other zeolitic phases of industrial interest such as chabazite or ZSM-5.

For example, using Metakaolin as silica and alumina source, Si as foaming agent and a 10M NaOH solution as alkaline activating agent, a multimodal porous monolith, containing macro-, meso- and micropores and two distinct zeolites, Na-A [LTA] and Na-X [FAU], was achieved by an unconventional two-step method, which involves the production of a foamed geopolymer precursor and its subsequent conversion by a hydrothermal treatment (0.5 M NaOH solution at 60 °C for 20 days). In this way, multimodal porous monoliths, containing macro-, meso- and micropores and two distinct zeolites, Na-A [LTA] and Na-X [FAU], were obtained.

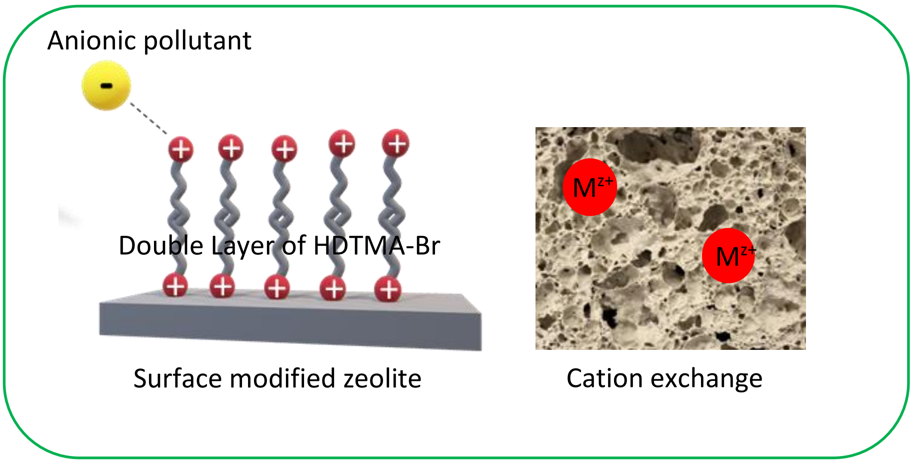
Several of these samples are currently undergoing cation exchange tests in a 0.1M LiCl solution; the samples thus functionalized will be used as a substrate for making catalysts. For the same purpose, impregnation with LiCl or different chemical species, such LiOH, is evaluated.

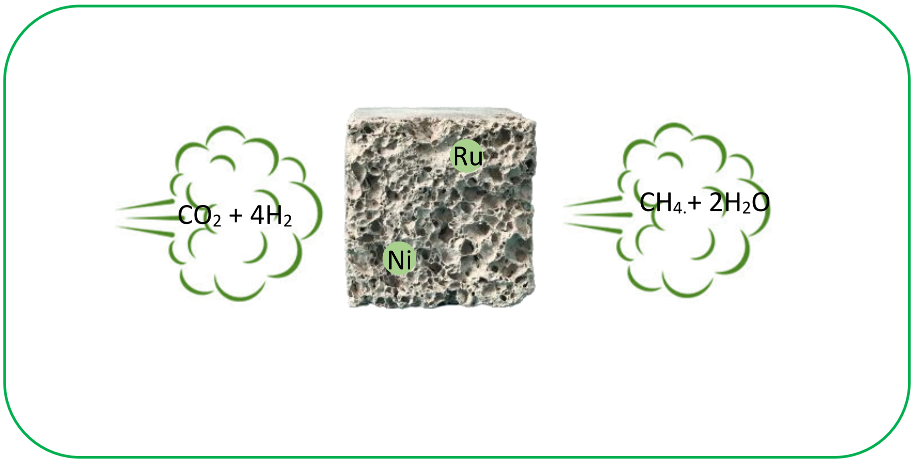
The next step of my research could involve evaluating the cation exchange capacity of these multimodal porous monoliths and their selectivity towards cationic pollutants such as heavy metals or dyes for their use in environmental applications (e.g., reactive permeable barriers), moreover it is possible to perform a surface modification to make the frameworks suitable for the adsorption of anionic pollutant species.

Simultaneously, their utilization as substrates for catalysts in energy applications such as syngas or methane production could be evaluated.

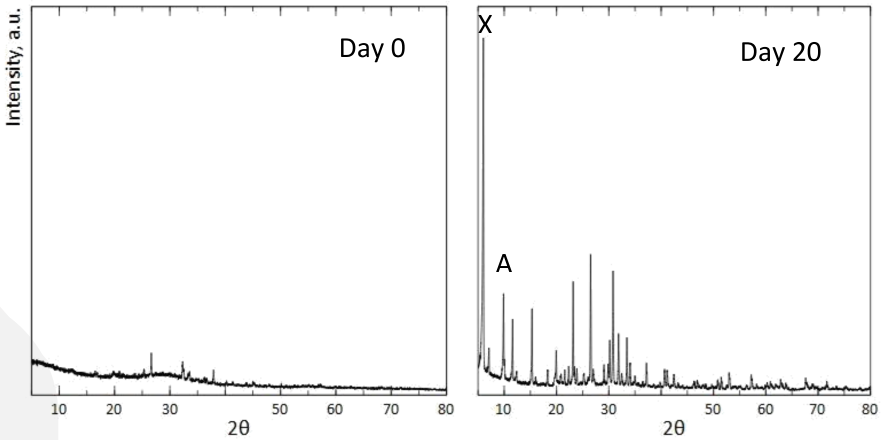
Multimodal Porous Monolith

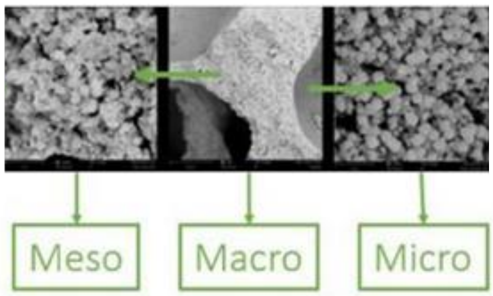
Environmental application

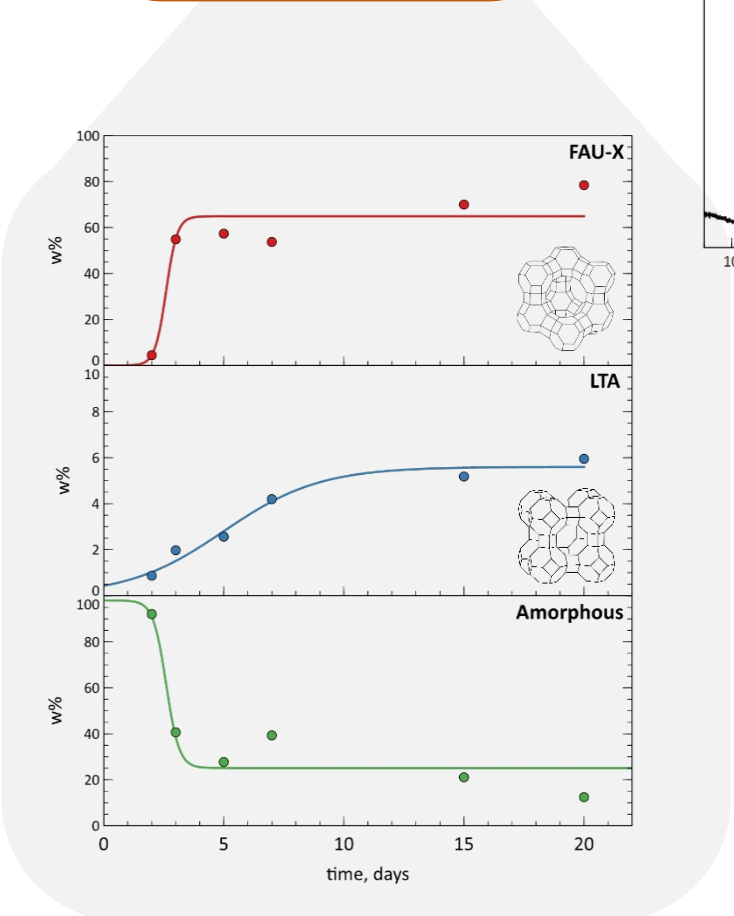




Energetic / catalytic application







Carlo Gravino, PhD student XXXVIII cycle, May 2023

carlo.gravino@unina.it