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BOOK OF FULL ABSTRACTS

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Czech-Italian-Spanish (CIS) Conference
Italian Interdivisional Catalysis Group (GIC)

XVI National Congress of Zeolites Science and Technology

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XXI National Congress of Catalysis

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MESOPOROUS ZSM-5 LOADED WITH AMINO ACIDS: DOES SECONDARY MESOPOROSITY AFFECT SORPTION CAPACITY AND THERMAL REGENERATION?

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Zeolites are microporous materials characterized by high surface area, high sorption capacity and selectivity as well as excellent resistance to chemical, biological, mechanical and thermal stress. These properties make zeolite effective sorbent materials for biochemical molecules from aqueous solutions, such as amino acids. However, sometimes micropores can induce confinement effects and diffusion limitations due to the blocking of pores mouth caused by undesired side products formation, which leads to the early catalyst deactivation. Compared to microporous zeolites, the so-called hierarchically organized zeolites (HOZs), built on a multilevel pore network,[1] are characterized by higher specific external area, which determines improved selectivity for target molecules, higher reaction rates for diffusion-limited reactions and higher thermal stability in catalysts regeneration processes.[2] These properties are a fundamental prerequisite for the development of superior polyfunctional biocatalysts. Based on this, mesoporous zeolites can be thought as promising amino acids catalysts in form of well ordered-layers. Amino acids, which represent the primary structural unit of proteins, belong to an important class of biochemical compounds principally exploited in pharmaceutical and biomedical fields for oligopeptides and biopolymers production.[3-4] Although a lot of information are reported in literature about biocatalysis on zeolites, most of them are approached from a chemical or theoretical point of views.[5,6] Hence, a lack of crystallographic and structural informations has been observed, even if it is well known that to fully optimize biocatalysts design, a deep knowledge of interactions between entrapped amino acids and sorbent materials is mandatory. Based on the previous remarks, in this work, hierarchical ZMS-5 zeolites have been selected to study adsorption and desorption processes of two essential amino acids in humans, leucine ($C_6H_{13}NO_2$) and l-lysine ($C_6H_{14}N_2O_2$), through Synchrotron X-ray powder diffraction. ZMS-5 zeolites used in this project were synthesized and provided by the Environmental and Chemical Engineering Dept. of the University of Calabria (Rende, CS,). Mesoporosity was induced through post-synthesis desilication. The parent H^+-form ZSM-5 (MFI, Si/Al ratio=100) was treated in 0.2M NaOH solution (30 $^{ml}/_{g\ zeolite}$) under stirring at 65 °C for 15 and 30 minutes (*i.e.*, samples were labelled 776_D15 and 776_D30, respectively) to induce desilication. The solid was recovered by

filtration, washed with D_2O until neutral pH and finally dried overnight. N_2 adsorption data confirmed the presence of induced secondary mesoporosity in both 776_D15 and 776_D30 ZSM-5. Firstly, the thermal stability of both bare mesoporous ZSM-5 was tested through *in situ* Synchrotron X-ray powder diffraction analysis (data collection at the MCX beamline of the Elettra Synchrotron, each 100 °C, from 25 to 600 °C, heating rate=5 °C/min). Powder patterns refinement confirmed that no loss of crystallinity occurred. Once proved the thermal resistance, both samples were loaded with l-lysine and leucine as single compounds (pH loading=5.5) by using the batch method. Capillary electrophoresis confirmed that both amino acids were entrapped within hierarchical ZSM-5 channels: almost equal concentrations of l-lysine and leucine were adsorbed on 776_D15 sample, while 776_D30 appears more selective toward l-lysine. All loaded samples were then analyzed through *in situ* X-ray powder diffraction analysis at the MCX Beamline of the Elettra Synchrotron, according to the following heat treatment profile: heating ramp from 25, to selected temperature of 50, 100, 200, 300, 400 and 500 °C (5 °C/min heating rate). Diffraction data were processed through Rietveld structural refinements (GSAS software)[7] to extract the evolution of both zeolite crystal structure upon heating and amino acids/water molecules sorption/desorption processes, focusing the attention on the influence of zeolite pore size and structure on amino acid selectivity and sorption capacity. Specifically, powder X-ray diffraction data allowed to: 1) characterize ZSM-5 zeolites structure after l-lysine and leucine adsorption; 2) probe host-guest interactions 3) establish the zeolites regeneration temperature; 3) determine the occurrence of temperature-dependent framework geometry variations. All the informations obtained about mesoporous ZSM-5 sorption capacity and thermal regenerability lead to confirm that the hierarchical zeolite might be suitable as amino acids biocatalyst.

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