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MODIFICATION AND CHARACTERIZATION OF CLINOPTILOLITE FOR THE CO-IMMOBILIZATION OF FORMATE DEHYDROGENASE AND GLYCEROL DEHYDROGENASE ENZYMES

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In the last decades there is a rising concern for the increasing concentration of carbon dioxide, considered the major responsible of Global Warming. A solution to this critical issue is the catalytic conversion of CO_2 into high value-added products. Among the different strategies that could be applied, the enzymatic process of CO_2 reduction to methanol, employing a sequence of three enzyme-catalyzed reactions[1], seems to be very promising. The simultaneous employment of formate dehydrogenase and glycerol dehydrogenase allows to reduce CO_2 to formic acid, the first of the sequential reactions, and at the same time regenerate the nicotinamide cofactor, that is very expensive. To reuse enzymes, with a consequential reduction of cost, and increased their stability, they can be immobilized on a proper support. In this context, porous materials, such as zeolites, present appropriate features to be suitable for enzymes immobilization. In particular, they are well suited for the covalent immobilization technique due to the fact that they can be functionalized with different functional groups[2]. Natural zeolites, like Clinoptilolite have the advantage to be low-cost materials largely diffused in different part of the world. Clinoptilolite was subjected to dealumination-desilication treatments to modify the zeolite's morphology, increasing its specific surface area. According to the literature, the dealumination procedure was done with sequential acid attacks using HCl solutions. Instead, for the subsequent desilication process NaOH solution is required[3]. The effects of desilication-dealumination treatments were investigated through complementary techniques such as N_2 physisorption at -196 °C, XRD and SEM. The analysis revealed that the Clinoptilolite specific surface area increased by 400% following the dealumination-desilication procedure; at the same time the XRD analysis shows that the processed Clinoptilolite has the same main peaks of the unmodified one. Finally, the retained activity and the stability of the immobilized enzymes were evaluated, the results show that these aspects were enhanced by the modification through acid-alkaline attacks of the Clinoptilolite.

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