

DIATOMACEOUS EARTH AS EFFICIENT SUPPORT FOR HETEROGENEOUS IRONPORPHYRIN CATALYSTS

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Synthetic metalloporphyrins have been successfully used as biomimetic catalysts in many oxidation reactions. However, their high cost and the difficulties inherent to homogeneous catalysis have prevented their large-scale application. Catalyst heterogenization aims to overcome these drawbacks in addition to mimicking enzyme site isolation, thereby improving reaction selectivity. The search for new matrixes is essential to reach this target. Diatoms are unicellular algae that present porous silica cells, named frustules, with distinct 3-D architectures. When aquatic diatoms die, they sink and collect on ocean and lake floors to form a material known as Diatomaceous Earth (DE). High surface area, high permeability, low density, non-toxicity, and possible chemical functionalization are characteristics that make diatoms very promising supports for metalloporphyrins. Here we report on new multifunctional hybrid materials consisting of a DE functionalized with amine groups by using aminopropyltriethoxysilane (DE-APTES), followed by grafting with Fe(III)-mesotetrakis(carboxyphenyl)porphyrin (DE-APTES-FeTCPP). The materials were characterized by PXRD, UV-Vis and FTIR spectroscopies, thermal analyses, scanning electron microscopy, and nitrogen adsorption. The infrared spectrum of DE-APTES-FeTCPP displayed the characteristic band of amine groups (1570 cm^{-1}), confirming that FeTCPP was grafted into DE-APTES via the amine groups. Weakening of the band due to hydroxyl groups (3653 cm^{-1}) showed FeTCPP also interacted with OH groups. The yellow–brown color of DE-APTES-FeTCPP indicated that FeTCPP was actually immobilized in the matrix (DE-APTES is white pink)—the UV–vis spectrum of the material exhibited the typical profile of the spectrum of FeTCPP with Soret band at 422 nm, which is characteristic of an ironporphyrin located in a confined space. Comparison between leaching of FeTCPP adsorbed onto DE and DE-APTES confirmed that the ironporphyrin was entrapped and not just adsorbed on the silicate surface. XRD analysis revealed DE displayed crystalline phases typical of quartz and cristobalite phase. The intensity of its characteristic reflection at $2\Theta = 22^\circ$ decreased in the presence of FeTCPP, confirming that the ironporphyrin influenced the organization of the material. The results obtained herein show that diatoms are promising natural supports for ironporphyrin catalysts via functionalization.

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