Structural and catalytic characteristics of a new layered compound involving cationic and anionic metalloporphyrins

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Layered compounds are structures formed by the stacking of bidimensional units (lamella) connected to each other by weak bonding forces. Metalloporphyrins (MP), which are typically soluble oxidation catalysts, are examples of molecules that can interact with layered materials[1]. This work presents a different synthesis strategy to obtain and to characterize lamellar solids involving Zn^{II} and Ti^{IV} and also studies involving two different metalloporphyrin immobilization ([Mn(TDFSPP)] (MnP)) – an anionic porphyrin and ([Fe(T4MPyP)] (FeP)) – a cationic porphyrin) into the prepared solids. All the prepared materials were characterized by techniques UVVIS, FTIR, ICP, XRD and subsequently tested as catalysts for cyclooctene and cycloexane oxidation. Three solids where synthesized and named by **A**, **B** and **C**, each of them with a different source of Ti^{IV} ions. The diffraction pattern obtained through XRD analysis, showed that the solids **A** and **C** were compatible with a layered material, and the solid **B** showed a TiO_2-like diffraction pattern[2,3]. Based on the amount of the obtained materials the studies were carried on only with the solid **C**. As this layered material family is known as good ion exchangers, an anionic porphyrin (MnP), and a cationic porphyrin (FeP), were immobilized in different sample of the solid **C.** Later, also both of them were immobilized in the same sample of **C**. The UVVIS spectroscopy analysis of these resultant solids confirmed the presence of the MPs in each solid by the presence of the characteristic Soret band of each MP (464 nm for MnP and 422 nm for FeP)[4]. The XRD of the solids containing the MPs show the same pattern as the solid without them, suggesting that the MPs are not immobilized between the layers of the material[5]. The quantification of the metals in the solid was carried through ICP in order to estimate the ratio between the amounts of zinc and titanium ions in the solid **C**. Beside that, all the techniques applied until this moment cannot differentiate how the titanium species are disposed in the prepared layered material (**C**). Preliminary catalytic tests were made using the prepared solid containing the MPs. The oxidation of the cyclooctene to epoxide and cyclohexane to the alcohol and ketone were investigated. The solids containing only one porphyrin (**C**-MnP or **C**-FeP) showed catalytic results comparable to their homogenous analogues (MnP or FeP in solution), while the solids containing both MPs (**C**-1MnP/2FeP) did not show great increase in their catalytic activity suggesting that no synergistic activity was achieved under the preliminary catalytic conditions used. In order to explore the known photoactivity of the titanium species photocatalytic tests are under development with the prepared solids.

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