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Regular Article

Selective oxidation catalysts obtained by immobilization of iron(III) porphyrins on thiosalicylic acid-modified Mg-Al layered double hydroxides

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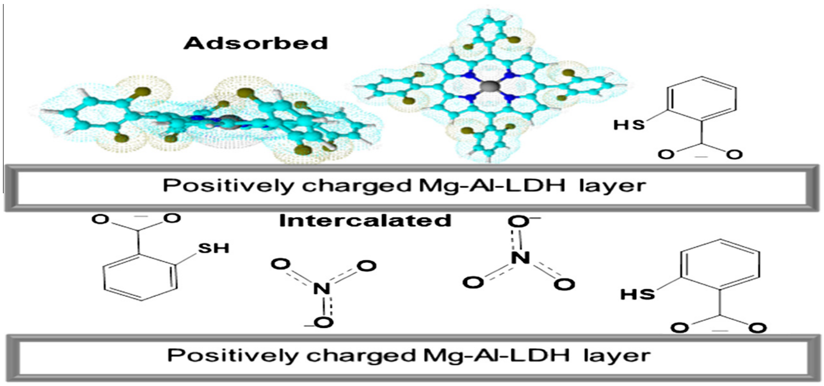
GRAPHICAL ABSTRACT

Nitrate-intercalated Mg-Al layered double hydroxides were exfoliated in formamide. Reaction of the single layer suspension with thiosalicylic acid under different conditions afforded different solids that were used as supports to immobilize neutral and anionic iron(III) porphyrins and used as catalyst for oxidation reactions.



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ABSTRACT

Nitrate-intercalated Mg-Al layered double hydroxides (LDHs) were synthesized and exfoliated in formamide. Reaction of the single layer suspension with thiosalicylic acid under different conditions afforded two types of solids: LDHA**1**, in which the outer surface was modified with the anion thiosalicylate, and LDHA**2**, which contained the anion thiosalicylate intercalated between the LDH layers. LDHA**1** and LDHA**2** were used as supports to immobilize neutral (FeP**1** and FeP**2**) and anionic (FeP**3**) iron(III) porphyrins. For comparison purposes, the iron(III) porphyrins (FePs) were also immobilized on LDH intercalated with nitrate anions obtained by the co-precipitation method. Chemical modification of LDH facilitated immobilization of the FePs through interaction of the functionalizing groups in LDH with the peripheral substituents on the porphyrin ring. The resulting FePx-LDHAy solids were characterized by

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Heterogeneous catalysis
Oxidation

X-ray diffraction (powder) and UV–Vis and EPR spectroscopies and were investigated as catalysts in the oxidation of cyclooctene and cyclohexane. The immobilized neutral FePs and their homogeneous counterparts gave similar product yields in the oxidation of cyclooctene, suggesting that immobilization of the FePs on the thiosalicylate-modified LDHs only supported the catalyst species without interfering in the catalytic outcome. On the other hand, in the oxidation of cyclohexane, the thiosalicylate anions on the outer surface of LDHA**1** or intercalated between the LDHA**2** layers influenced the catalytic activity of FePx-LDHAy, leading to different efficiency and selectivity results. FeP**1**-LDHA**2** performed the best (29.6% alcohol yield) due to changes in the polarity of the surface of the support and the presence of FeP**1**. Interestingly, FeP**1** also performed better in solution as compared to the other FePs. Finally, it was possible to recycle FeP**1**-LDHA**2** at least three times.

1. Introduction

Since the first report on the use of synthetic metalloporphyrins (MPs) as catalysts for the hydroxylation and epoxidation of substrates by iodosylbenzene (as oxygen donor) [1], many studies have helped researchers to understand and explore the ability of MPs to participate in redox catalysis under mild conditions [2–6]. This important property has pointed to the possible application of MPs in the remediation of contaminated groundwater and industrial effluents [7].

Initial studies on the use of iron(III) porphyrins (FePs) as bioinspired catalysts in homogeneous oxidation reactions led to promising results [1,8–11]. However, some problems arose, mainly issues associated with the homogeneous catalytic system-reactions in solution generated catalytically inactive species, which culminated in low catalytic efficiency. Additionally, recycling of the catalyst, usually a very expensive molecule was impossible. Over the past 20 years, synthetic advances in the preparation of novel resistant, stable, efficient, and selective molecular structures [16–19] have minimized inactivation of the catalyst by self-destructive processes [3,12,13] and have diminished formation of other inactive species [6,14,15] in solution. Despite these advances and the amazing catalytic results provided by this family of oxidation catalysts (for which some patents have been deposited [20–22], difficult catalyst recovery and reuse still prevent implementation of new technologies to produce different compounds based on MPs in solution.

Heterogeneous catalysis constitutes an alternative to MPs in homogeneous solution. Catalyst heterogenization has gained importance in relevant industrial processes because it furnishes efficient and selective catalysts [23–25]. Many solid catalysts have been obtained by supporting MPs on a variety of solid supports. These heterogenized catalysts have been investigated in countless catalytic processes, including the oxidation of organic substrates [3,4,26–30]. Inorganic solids, such as silicas, zeolites, clay minerals, layered double hydroxides (LDHs), and others, have been evaluated as supports to immobilize MPs, giving rise to solid systems that offer at least one more advantage easy recovery from the reaction mixture [31,32].

Among possible catalyst supports, LDHs are interesting solids: they are easy to synthesize and modify with different organic groups, which in turn facilitate interaction of LDH with the catalyst. The formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2][A^{n-}]_{x/n}\cdot mH_2O$ represents the structure of LDH, where M^{2+} and M^{3+} are divalent and trivalent metal cations, respectively, and A is an exchangeable gallery anion [33,34]. Generation of controllable excess positive charges in the stacked LDH layers provides this class of solids with an important property anion-exchange capacity. This is especially promising for further modifications to the structure of the support [35], which could improve interaction of the support with complex molecules [36,37]. Besides that, LDHs are environmentally benign and non-toxic.

Different molecules and methodologies have been used to modify LDHs for the immobilization of MPs. For example, Wypych *et al.* [38] intercalated glycinate anions into Mg-Al-LDH layers after exfoliation and immobilized an ionic FeP on the resulting support. Characterization revealed that the glycinate anions remained intercalated between the LDH layers, and that the FeP anions adsorbed on the surface of the LDH crystals.

Based on the work of Wypych *et al.* [38], Nakagaki and coworkers [39] prepared two composites consisting of Mg-Al-LDH containing glycinate ions. The latter authors immobilized different FePs on the composites and evaluated the performance of the resulting solids in the catalytic oxidation of two diagnostic substrates, cyclohexene and cyclooctene. In the oxidation of cyclohexane, the composites containing FePs showed high selectivity for the alcohol, one of the two possible products. However, yields were not high and remained between 4 and 20 wt%. The catalytic activity of the immobilized FePs depended on the accessibility of the substrate to the catalytic centers. Accessibility should be easier in the case of the FeP system that adsorbed on the surface of the support, indicating that the type of immobilization was crucial to catalyst performance.

More recently, Nakagaki *et al.* [32] studied how triethanolamine, a neutral molecule intercalated between LDH layers containing a neutral FeP, influenced the catalytic oxidation of cyclohexane and cyclooctene. Once again, yields were not high. Despite the high catalytic efficiency for the oxidation of cyclooctene (98 wt%), the composite containing triethanolamine and the FeP afforded 26 wt% of alcohol and 2.2 wt% of ketone during the oxidation of cyclohexane. Although this was an average result, it pointed to new approaches toward a better understanding of the role of the molecular modifier and the FeP in the oxidation process. In other words, this result helped to find out whether superior product yields were obtained when the modifier and the MP were intercalated between the LDH layers or adsorbed on the surface of LDH and whether the MP charge affected process efficiency and selectivity.

Nakagaki *et al.* [31] also investigated the use of different FePs intercalated between LDH layers as catalysts in oxidation reactions. The anion intercalated into previously synthesized LDH was substituted with a FeP by using dodecyl sulfate followed by exfoliation and immobilization of the FeP. Such immobilized FePs displayed different efficiency and selectivity as compared to the corresponding homogeneous catalysts because chemical modification of LDH with suitable organic groups may have provided the catalyst-support assembly with greater stability [33,40].

This work reports on the immobilization of two neutral FePs (FeP**1** and FeP**2**) and an anionic FeP (FeP**3**) (Fig. 1) on LDH in which the outer surface was modified with the anion thiosalicylate (LDHA**1**) or on LDH containing thiosalicylate intercalated between the LDH layers (LDHA**2**). The aim of this work was to verify whether the way the modifier attached to LDH impacted the