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Mg–Al hydrotalcite-like compounds containing iron-phthalocyanine complex: effect of aluminum substitution on the complex adsorption features and catalytic activity

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Abstract

Mg–Al hydrotalcite-like materials ($Mg_{(1-x)}Al_x(OH)_2(CO_3)_{x/2} \cdot nH_2O$ with x=0.33, 0.25 and 0.20) were used as supports for the immobilization of Fe(III) tetrasulfonated phthalocyanine (FePcTs). Electron paramagnetic resonance (EPR) and X-ray absorption (XANES) spectroscopies were used to characterize the solids after FePcTs adsorption on the hydrotalcite-like materials (HTs). An adsorption study was carried out by monitoring in situ the FePcTs UV/visible electronic spectra during its addition to suspensions of HTs. The results showed that the HT composition controls the nature of adsorbed species: for HTs with higher Al^{3+} contents (x=0.33 and 0.25), the FePcTs was adsorbed mainly in the μ-oxo complex form whereas for HT with x=0.20, non-oxo-bridged FePcTs dimeric species prevailed. The heterogeneous catalytic studies of the HT-FePcTs materials in the oxidation of catechol, using hydrogen peroxide as oxidant, showed an enhanced catalytic activity and longevity, compared to the homogeneous counterpart. The catechol conversion was 63%, 73% and 88% for the materials containing HTs with x=0.20, 0.25 and 0.33, respectively. Therefore, the reactivity of HT-FePcTs materials was improved when the Al^{3+} content in the HTs increases. These catalytic tests associated to the adsorption studies showed that the μ-oxo complex of the FePcTs, mainly adsorbed on the HTs with x=0.25 and 0.33, seems to be the active species in catechol oxidation. These findings suggest that a cooperative effect take place in the HT-FePcTs materials, showing that HTs do not act as an inert support.

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1. Introduction

Layered double hydroxides (LDHs), also known as anionic clays or hydrotalcite-like compounds (HTs), are a class of inorganic layered materials represented by

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the general formula $[M^{II}_{(1-x)}M^{III}_{x}(OH)_2](A^{n-})_{x/n}\cdot zH_2O$. The bi-dimensional structure is composed of positively charged brucite-like layers of divalent and trivalent metals whose excess of positive charge is compensated by anions present in the interlayer region. The capability to accommodate a variety of anionic species between the layers and metallic cations in the layer composition make HTs interesting materials for applications such as catalysts, catalyst supports or precursors, anion exchangers, and sorbents (Cavani et al., 1991; Trifirò and Vaccari, 1996).

Many researches on HT derivatives have been devoted to the development of new catalytic materials (Sels et al., 2001). Several studies about the synthesis, characterization and catalytic applications of HTs containing anionic metal complexes have been reported (Rives and Ulibarri, 1999). Particularly interesting is the immobilization of macrocyclic ligand-containing complexes as metallophthalocyanines in HTs. Co(II) phthalocyanine, for example, is a well-known catalyst in the Merox industrial process for oxidation of mercaptans in petroleum distillates, under caustic conditions. The use of HTs to design redox-base heterogeneous catalysts through the immobilization of Co(II) phthalocyanine in calcined HTs showed to be an efficient strategy for mercaptan oxidation (Alcaraz et al., 1998; Liu et al., 2000). In addition to the high conversion rate, such approach leads to an environmentally friendly chemical process, avoiding caustic wastes and facilitating the catalyst recovery and recycle.

Fe(III) tetrasulfonated phthalocyanine (FePcTs) is an efficient homogeneous catalyst in the oxidation of aromatic pollutants (Meunier and Sorokin, 1997; Sorokin and Meunier, 1998). Different approaches have been used to immobilize the FePcTs for the heterogenization of the catalyst such as entrapment in sol–gel materials (Sorokin et al., 2001), covalent graft in mesoporous MCM-41 silica and organic polymers (Sorokin and Tuel, 1999; Sanchez et al., 2001), and supporting on ion-exchange resins (Tao et al., 2003). Although the cited materials show interesting results as heterogeneous catalysts in the oxidation of aromatic pollutants, the role of the host was not evaluated and seems to play minor influence in the catalytic activity.

The use of HTs as host materials is motivating once they can be used as solid base catalysts (Fraile et al., 2001; Weitkamp et al., 2001). Isolation of a hybrid material through immobilization of FePcTs in HTs could lead to a bifunctional catalyst which possesses both redox and basic sites suitable for catalytic reactions. So far, we have not found accounts examining the physico-chemical and catalytic properties of HTs containing FePcTs, as we previously reported for copper phthalocyanine (Barbosa et al., 2002).

In this paper, we report the synthesis of magnesium–aluminum hydrotalcite-like compounds with different Mg^{2+}/Al^{3+} ratios and the adsorption of Fe(III) tetrasulfonated phthalocyanine on the surface of these HTs. Attention is given to the adsorption phenomena in HT-FePcTs materials, through the observation in situ of the FePcTs UV/visible spectra during its addition to suspensions of HTs. The HT-FePcTs materials are evaluated as heterogeneous catalysts in the oxidation of catechol, using hydrogen peroxide as oxidant. An attempt is made to explain the relation between the features observed in the spectroscopic studies and the catalytic reactivity of the HT-FePcTs materials.

2. Experimental

2.1. Preparation

The hydrotalcite-like compounds of composition $[Mg_{(1-x)}Al_x(OH)_2](CO_3^{2-})_{x/2}\cdot zH_2O$ with x=0.33, 0.25 and 0.20 were prepared by coprecipitation procedure as previously described (Miyata, 1980). Chemical analysis (C, H, N) and water content measured by thermogravimetric analysis, resulted in the following compositions: $[Mg_{2.0}Al(OH)_{6.0}](CO_3)_{0.5}\cdot 2.2H_2O$, $[Mg_{3.0}Al(OH)_{8.0}](CO_3)_{0.5}\cdot 3.2H_2O$, $[Mg_{4.2}Al(OH)_{10.4}](CO_3)_{0.5}\cdot 3.7H_2O$. Specific surface area data of the prepared HTs are 42, 86 and 109 m^2/g, respectively. The HTs are designated as Mg_2Al, Mg_3Al, and Mg_4Al, respectively.

Fe(III) tetrasulfonated phthalocyanine (FePcTs, tetrasodium salt, Mid Century) was used as received and characterized by elemental and thermogravimetric analysis (Found: C, 30.9%; H, 3.0%; N, 8.7%; H_2O, 13.3%), indicating that the sample contains about 80% of FePcTs and 13% of water.

FePcTs was supported on the external surface of the HTs by suspending 1 g of the HT in 50 ml of 0.6 mM FePcTs

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