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Versatile heterogeneous dipicolinate complexes grafted into kaolinite: Catalytic oxidation of hydrocarbons and degradation of dyes

Francielle R. Araújo[a], Joel G. Baptista[a], Liziane Marçal[a], Katia J. Ciuffi[a], Eduardo J. Nassar[a], Paulo S. Calefi[a], Miguel A. Vicente[b], Raquel Trujillano[b], Vicente Rives[b], Antonio Gil[c], Sophia Korili[c], Emerson H. de Faria[a,*]

[a] Sol-Gel Group, University of Franca, Av. Dr. Armando Salles Oliveira, Parque Universitário, 201, 14404-600, Franca, SP, Brazil
[b] GIR QUESCAT, Departamento de Química Inorgánica, Universidad de Salamanca, Plaza de la Merced, S/N, 37008 Salamanca, Spain
[c] Departamento de Química Aplicada, Universidad Pública de Navarra, 31006 Pamplona, Spain

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ABSTRACT

New heterogeneous catalysts were prepared by immobilization of Me(II)-dipicolinate complexes (Me = Co, Mn or Ni) on kaolinite (Ka). The precursor material was kaolinite grafted with dipicolinic acid (dpa) obtained via melting of the acid. The catalysts were prepared by suspending the Ka-dpa precursors (lamellar or exfoliated) in Me^{2+} solutions with a cation/ligand ratio of 1:3. The grafted complexes were characterized by thermal analyses, X-ray diffraction, UV/Vis and infrared spectroscopies, and transmission electron microscopy. The catalysts were tested in three reactions: (i) epoxidation of *cis*-cyclooctene to *cis*-cyclooctenoxide reaching 55% yield, with total selectivity to cyclooctenoxide; (ii) oxidation of cyclohexane, reaching 22% yield, with total selectivity towards cyclohexanone; and (iii) Fenton-like decolorization of the dyes metanil yellow, methylene blue and green light, reaching 70–100% decolorization, the maximum effectiveness being observed for methylene blue degradation. The high conversion in the oxidation reactions and the high levels of decolorization of dyes confirmed the versatility of these heterogeneous catalysts based on kaolinite.

1. Introduction

The need to develop effective methods and catalysts for oxidation reactions is becoming ever more important to be commonly applied to synthesis of pharmaceuticals, agrochemicals, and flavours or fragrances, among others. From an industrial point of view, homogeneous catalysis methods remain unpractical, particularly due to the high cost of the catalysts and the difficulty of their recovery and reuse [1]. Thus, from an economic, environmental and technical point of view, heterogeneous supported catalysis is preferred because of the handling, separation and recycling abilities. The functionalization of clay minerals, such as kaolinite, with organic units renders the possibility of heterogeneization of active sites and promotes the reuse. Recently, our research group has reported the functionalization of natural kaolinite with pyridinecarboxylic acids, alkoxides, and ironporphyrins by the soft-guest displacement method [2,3].

In recent years, much interest has been given to hybrid materials based on clays. These materials are produced by several reactions and can lead to intercalation compounds with various applications, depending on the type of interaction between the inorganic matrix and the intercalated species. Transition metal complexes show high catalytic activity and selectivity in hydrocarbon oxidations in homogeneous media, but they have high difficulty to be recovered and reused. An alternative for applications requiring high temperature during the process, and more catalytic cycles with high conversion and selectivity, is based on the use of these complexes immobilized on/into inorganic matrices. A “heterogeneization” is made in this method, as the complexes are immobilized in inorganic matrices such as kaolinite, able to modify the kinetics and mechanism of the reactions. Hybrid materials have been explored for this purpose and, among them, the kaolinite-based materials stand out due to the high thermal stability of the hybrids obtained.

The search for efficient and environmentally friendly oxidation systems that could be used in green processes for several oxidation reactions has been recently intensified [4,5]. Transition metals are used in a large variety of catalytic processes. Bergamaschi et al. [6] used transition metals supported on zirconia in reactions of steam reforming of ethanol to obtain hydrogen. Thomas et al. [7]

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* Corresponding author.
E-mail address: eh.defaria@unifran.br (E.H. de Faria).

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reported the use of manganese and cobalt catalysts in the oxidation of toluene by hydrogen peroxide. Sen et al. [8] and Gupta et al. [9] demonstrated the effectiveness of nickel and manganese heterogeneous catalysts in oxidation reactions. Previous studies from our group [2,10] have demonstrated the efficient use of kaolinite as a support for metalloporphyrin and iron(III)-picolinate and dipicolinate complexes to obtain catalytic systems with good performance and high selectivity in cis-cyclooctene, cyclohexane and Baeyer-Villiger oxidation.

The transfer of oxygen atoms to carbon substrates, to understand or to mimic enzymatic porphyrin systems, has been previously reported [11], as well as the study of non-heme enzymatic model systems, such as metal complexes, to catalyze these reactions. In particular, Schiff base complexes are potentially applicable as catalysts in several oxidation reactions, including alkene epoxidation and hydrocarbon oxidation [9,12].

Industrial processes normally involve oxidation reactions in the presence of a metal complex as a catalyst, together with acids and permanganate as oxidant, in an homogeneous medium. However, these processes involve serious problems, namely, difficulty to recover the catalyst from the reaction medium, corrosion, and the need for expensive, hazardous, non-selective oxidants [9,12]. One strategy to overcome these drawbacks, is to heterogeneize the metal complex by immobilizing it on a polymer or an inorganic matrix and to accomplish the reaction using cleaner oxidants like hydrogen peroxide or molecular oxygen, which generates water as the only byproduct. However, many efforts are still necessary to develop heterogeneous catalysts that do not undergo deactivation during the catalytic process [9,12,13].

About 15% of the total world production of dyes is lost during the dyeing process and is released to the textile effluents, and this release of these colored waste waters in the ecosystem is a dramatic source of non-aesthetic pollution, eutrophication and perturbations in the aquatic life [14]. As international environmental standards are becoming more severe, new methods for the removal of organic pollutants, such as industrial dyes, have been very much studied by various groups. Among them, physical methods (as adsorption) [15], biological methods (as biodegradation) [16], and chemical methods (as chlorination or ozonation) [17], are the most frequently used ones. In this context, many studies have demonstrated the applicability of heterogeneous catalytic technologies in "Fenton-like" systems, advanced oxidation processes that use hydrogen peroxide (H_2O_2) and metallic species for the treatment of hazardous organic and inorganic pollutants existing in aqueous media. The Fenton-type processes are very promising since they are easy to operate and maintain, they offer a cost effective source of hydroxyl radicals, and achieve high conversions. The conventional production of $HO^\bullet$ radicals by the Fenton mechanism occurs by means of addition of H_2O_2 to Fe^{2+} according to the reaction: $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^\bullet + HO^-$ [18]. Recently, some other metals have been used to generate $HO^\bullet$ radicals [19,20].

On the other hand, dyes have been extensively used as model compounds for the evaluation of new catalysts, among other factors by the simplicity for following their reactions, especially decolorization. New research in the preparation of innovative Fenton-like reactions has been motivated by two main issues, namely, the improvement of the efficiency in the use of green oxidants, and the immobilization of the active sites into inert supports to facilitate the separation of the catalysts when the reaction has finished.

This work reports the catalytic study of Me(II)-dipicolinate complexes (Me = Co, Mn or Ni) immobilized into kaolinite. The grafted complexes were used as heterogeneous environmental-friendly catalysts in the epoxidation of *cis*-cyclooctene to cyclooctenoxide, in the oxidation of cyclohexane to cyclohexanol and cyclohexanone, and in the degradation of three dyes (metanil yellow, methylene blue and green light).

2. Experimental

2.1. Catalyst preparation

2.1.1. São Simão' kaolinite purification

The kaolinite used in this work came from the municipality of São Simão in the State of São Paulo, Brazil, and was kindly supplied by the mining company Darcy R. O. Silva & Cia. It belongs to the ball-clay type, known for its fine granulometry and for being rich in hexagonal kaolinite. Kaolinite was purified by dispersion in water, followed by sedimentation, according to Stock's law and using the procedure previously described [4,21–23]. The structural formula of purified kaolinite is $Si_{2.0}Al_{1.96}Fe_{0.03}Mg_{0.01}K_{0.02}Ti_{0.03}O_{7.06}$ [3].

2.1.2. Kaolinite intercalation with dimethylsulfoxide

To obtain the precursor intercalated with dimethylsulfoxide (Ka-DMSO), the method described by Detellier et al. was followed [8,9]. A portion of 20 g of the purified kaolinite was suspended in a mixture of 180 cm^3 of DMSO and 20 cm^3 of H_2O, which was maintained at 60 °C under agitation for 10 days. The material was centrifuged at 2000 rpm, washed with ethanol and oven-dried at 60 °C. The resulting complex, designated as Ka-DMSO, has the stoichiometry $Ka(DMSO)_{0.45}$.

2.1.3. Kaolinite grafting with dipicolinic acid

The hybrid organic-inorganic material was obtained by keeping a mass of the precursor (Ka-DMSO) in the presence of the melted dipicolinic acid for 48 h. The dipicolinic acid/kaolinite DMSO complex molar ratio was 5:1. The temperature for grafting H_2dpa acid was 190 °C. The resulting materials were washed several times with isopropanol or water and oven-dried at 80 °C. The first sample was washed several times with isopropanol, the second washed with water, and the third with isopropanol and suspended in an ultrasonic bath for 8 h to promote the exfoliation of the hybrid precursor; finally, all these samples were oven-dried at 80 °C and designated as Ka-dpa-IP, Ka-dpa-wt and Ka-dpa-exf, respectively.

2.1.4. Synthesis of the complexes immobilized into kaolinite

To obtain the metal-containing catalysts, Ka-dpa solids were suspended in a 0.1 mol/dm^3 Me^{2+} chloride solution ($Me^{2+} = Co^{2+}$, Mn^{2+} and Ni^{2+}), using the volume needed to reach a cation/ligand ratio of 1:2, and the mixture was stirred at 80 °C for 3 h. The suspensions were then centrifuged, and the resulting solids were washed with ethanol five times. The catalysts obtained were designated as Me(Ka-dpa)-IP, Me(Ka-dpa)-wt and Me(Ka-dpa)-exf, making reference to the active metal and the method of preparation of the hybrid precursor.

2.2. Characterization techniques

The powder X-ray diffractograms of the solids were acquired on a Siemens D-500 diffractometer operating at 40 kV and 30 mA (1200 W), using filtered Cu Kα radiation. All the analyses were processed at a scan speed of 2° per minute.

Infrared absorption spectra were obtained on a Perkin-Elmer 1739 spectrophotometer with Fourier transform, using the KBr pellet technique.

UV-Vis spectra were recorded in the 200–800 nm range on a HP 8453 Diode Array Spectrophotometer. The spectra of the solid samples were recorded in a quartz cell with 0.1 cm path length, in ethanol suspension.