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Effect of the atomic active metal ratio in Al/Fe-, Al/Cu- and Al/(Fe–Cu)-intercalating solutions on the physicochemical properties and catalytic activity of pillared clays in the CWPO of methyl orange

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ABSTRACT

The effect of the composition of the intercalating solutions in the catalytic performance of the derived pillared clays has been studied. A Colombian bentonite was treated with Al/Fe-, Al/Cu- and Al/(Fe–Cu)-solutions, and the resulting pillared solids were used in the catalytic wet peroxide oxidation (CWPO) of the azo dye methyl orange (MO) in aqueous solutions. The active metal ratio (AMR), here defined as the atomic percent ratio between the active metals (Fe and Cu) and the total content of metals (Al, Fe and/or Cu) in the intercalating solutions, was found to be a key factor for the properties of the pillared solids. Low AMR values, between 0 and 10%, were considered, and the efficiency for the incorporation of the active metals into the layered structure was followed by chemical analyses and cationic-exchange capacity measurements. Further characterization studies were carried out by X-ray diffraction, H_2 temperature-programmed reduction, scanning electron microscopy/energy dispersive X-ray analysis, nitrogen adsorption at −196 °C and thermal analysis. Considering the physicochemical properties together with the catalytic performance, it is proposed that isomorphic incorporation of the active metals into the Al_{13}-like polycations may take place. The obtained pillared solids exhibited better catalytic performance as the AMR values were lowered in the corresponding intercalating solutions, displaying also high stability to chemical leaching into the strongly oxidizing environment of the catalytic reaction, especially in the binary Al/Fe- and Al/Cu-systems. The Al/Fe-pillared clays attained most of their maximal removal of the azo dye in solution after only 1 h of reaction at very mild experimental conditions (room temperature and atmospheric pressure of 18 °C and 0.7 atm).

1. Introduction

The catalytic abatement of toxic organic compounds in wastewaters has been extensively studied in the last years; from this kind of compounds, phenols and azo dyes have received much attention [1–7]. The last group comes mainly from the textile industry, providing toxic and highly coloured water streams wherein the penetration of solar radiation is significantly restricted, decreasing seriously the photosynthetic activity of biological agents in the aquatic environments affected [8]. Advanced oxidation processes (AOPs) have been widely proposed for elimination of these hazardous compounds, particularly when they are in low concentrated effluents. AOPs are a set of catalytic, photocatalytic, photolytic, etc. technologies, addressed towards a continuous generation of hydroxyl radicals ($HO^{\bullet}$), which are able to deplete a wide range of organic substances otherwise difficult to biodegrade [9–12]. Thus, although the well known Fenton-like activated peroxide elimination of organic compounds, carried out by cations of metals like Fe or Cu in homogeneous phase would fulfil the general requirements for AOPs, strong efforts have lately been made in order to develop solid catalysts able to perform the same activation of peroxide under heterogeneous conditions, then avoiding the expensive and difficult recovery of the metal from the effluent at the end of the treatment. AOP operated with this kind of active solids under very mild conditions of atmospheric pressure and room temperature has been referred to by some authors as Catalytic Wet Peroxide Oxidation (CWPO) [13–16]. Several solid materials have been claimed as being active to catalyse the Fenton-like reaction, among them: iron-containing zeolites, polymer-supported metal complexes, carbon-supported metal oxides, iron mesoporous materials, etc. [10,17–21]. However, the high performance displayed by Fe,Cu-modified pillared clays (Fe,Cu-PILCs) in this reaction is remarkable, achieving high rates of elimination of several model toxic compounds in terms of both, simple contaminant depletion as well as

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total organic carbon (TOC)/chemical oxygen demand (COD) elimination. Moreover, these catalysts can be obtained from inexpensive raw materials by means of very simple water-based chemical operations [1–4,14,22,23].

Several studies have pointed out that smectites pillared with Al-based polycations containing iron or copper are materials that show high performance catalysing the CWPO reaction [3,13,14,23–25]. Recently, Timofeeva et al. have reported the effect of some synthesis variables, like hydrolysis ratio of the pillaring solution (OH/(Al + Fe)) and temperature of calcination in the preparation of Fe/Al-PILCs [3], as well as the effect of the atomic ratio Fe/Cu in Fe,Cu,Al-clays on the catalytic properties of the resulting materials in the CWPO reaction [4]. It is worth noting here that the presence of Cu or Fe isolated species in this kind of materials should be ascribed to their intercalation by means of truly mixed Al/M-polycations. Although, despite the variety of experimental techniques displayed in many previous works [2,3,14,22,26–34], it is not absolutely and widely accepted that iron or copper could substitute aluminium in the Keggin-like polycation network. Although a close correlation between catalytic activity and concentration of isolated Fe species has been repeatedly claimed in these systems, not enough work has been carried out in order to establish the optimum conditions of preparation under which the catalytic response of Al/Fe-, Al/Cu- and Al/(Fe–Cu)-pillared clays in the CWPO reaction is improved in terms of catalytic activity and chemical stability of the active metals to leaching.

Therefore, this work is devoted to establish if a relationship takes place between the atomic metal ratio of the active metals (Fe and/or Cu), as an important synthesis variable in Al-based mixed intercalating solutions, and the physicochemical properties and catalytic behaviour of the obtained pillared clays in the CWPO elimination of the hazardous organic, azo dye methyl orange in aqueous solutions. Besides, the study will allow a correlation between the key properties of the materials, allowing proposing about the nature of the true metal species of Fe and Cu that are stabilized by mixed pillaring of smectites with Al and their possible catalytic role in the CWPO reaction.

2. Experimental

2.1. Materials

The starting material was a natural bentonite mined by Bentocol S.A. from the Valle del Cauca region, Colombia. The mineral was used in two commercial forms:

(i) The solid received as mined and then particle size refined at lab scale by separation of the ≤2 μm fraction (denoted BV). This fraction was mainly composed of montmorillonite; it had the chemical composition 60.5% SiO_2, 24.7% Al_2O_3, 10.2% Fe_2O_3, 0.05% MnO, 3.07% MgO, 0.64% CaO, 0.20% Na_2O, 0.58% K_2O; and its Cation Exchange Capacity (CEC), was 89 mequiv./100 g.

(ii) The mined solid submitted to homoionization with sodium as preferential compensating cation (process carried out by Bentocol at its own industrial plant), and followed by lab extraction of the ≤2 μm fraction (denoted NaBV). Its CEC was 87 mequiv./100 g.

For the experiments of intercalation and pillaring, $AlCl_3{\cdot}6H_2O$ (99%), $Fe(NO_3)_3{\cdot}9H_2O$ (99.99%) and $CuCl_2{\cdot}2H_2O$ (99.999%), all from Sigma–Aldrich, were employed as received. For the catalytic runs, methyl orange (MO), ACS reagent (>85%) from Sigma–Aldrich ($C_{14}H_{14}N_3NaO_3S$) and hydrogen peroxide (30%, w/w, A.R. from Panreac) were also used as received.

2.2. Preparation of pillared clays

The preparation of the pillared clays was carried out following a conventional procedure described in detail by Barrault et al. [13]. The corresponding starting clay was stirred (2 wt.% suspension) in distilled water for 24 h at room temperature. In each series, the starting clays were pillared with single Al hydrolysed solution (samples NaAl and BVAl, respectively). For the mixed systems, the Al/Fe-, Al/Cu- or Al/(Fe–Cu)-intercalating solutions were prepared by mixing various volumes of 0.2 M $AlCl_3{\cdot}6H_2O$, 0.02 M $Fe(NO_3)_3{\cdot}9H_2O$ and/or 0.02 M $CuCl_2{\cdot}2H_2O$, to reach AMR values below 10%. When both Fe and Cu were added together into the intercalating solutions, their mole ratio was always kept constant in 1.0. Thereafter, a 0.2 M NaOH solution was slowly added at 70 °C in enough amount to get hydrolysis ratio (OH/(Al + M)) of 2.0 (M = Fe, Cu or (Fe + Cu)). The resulting solution was then aged at the same temperature for 2 h, left to reach room temperature and slowly dropped (1.5 mL/min) to the clay suspension, under strong shaking. The resulting mixture was stored 24 h at the same temperature. The intercalated clay was filtered by suction, repeatedly washed with distilled water, dried at 60 °C and calcined at 500 °C for 2 h. The designation of the samples denotes the form of the clay employed as starting material (BV or NaBV), the pillaring metals (Al, Fe and/or Cu), finishing with the AMR value (see Table 1).

The AMR value is defined as the atomic percent ratio between the active metals (Fe and/or Cu) and the total content of metals (Al, Fe and/or Cu). For instance, AMR values for the system Al/Fe can be calculated as follows:

$$\mathrm{AMR}\quad(\%) = \left(\frac{\text{mmol Fe}}{\text{mmol Fe} + \text{mmol Al}}\right) \times 100$$

where “mmol” of every metal corresponds with the true amount of that metal present in the final intercalating solution added on the clay suspension.

2.3. Physicochemical characterization

Elemental chemical analyses of the solids were carried out by Activation Laboratories Ltd., Ancaster – Ontario, Canada, using inductively coupled plasma spectroscopy (ICPS). The monitoring for concentration of Fe and/or Cu leached in the effluent after the catalytic tests was made by atomic absorption spectroscopy (AAS) in a Perkin Elmer 2380 spectrometer.

The cationic-exchange capacity (CEC) of the materials was determined by saturation with 1 M ammonium acetate solution under reflux, followed by repeated washing with distilled water and centrifugation to eliminate excess of ammonium ions. The retained ammonium ions were then determined by the micro-Kjeldahl method.

X-ray diffraction (XRD) patterns of the solids were recorded over powder solids or oriented films by using a Siemens D-500 diffractometer, working at 40 kV and 30 mA with a scanning speed of 2°/min, employing Cu Kα filtered radiation ($\lambda = 1.5418$ Å).

Textural properties were determined from nitrogen (Air Liquide, 99.999%) adsorption data, obtained at −196 °C with a Micromeritics Gemini 2375 apparatus. Specific surface areas were obtained from the BET method; external surface areas and micropore volumes by means of the *t*-method, and the total pore volume from the nitrogen adsorbed at a relative pressure of 0.95.

Thermal analyses were performed on a SDT Q600 TA analyser, for simultaneous gravimetric and DSC analyses. All measurements were carried out at a heating rate of 10 °C/min under a flow of 20 mL/min of oxygen (Air Liquide, 99.999%) up to 1000 °C.

Hydrogen temperature-programmed reduction analyses (H_2-TPR) were carried out in a Micromeritics TPR/TPD 2900 instrument. Around 40 mg of sample were heated from room temperature to