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Preparation of Al/Fe-Pillared Clays: Effect of the Starting Mineral

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Abstract: Four natural clays were modified with mixed polyoxocations of Al/Fe for evaluating the effect of the physicochemical properties of the starting materials (chemical composition, abundance of expandable clay phases, cationic exchange capacity and textural properties) on final physicochemical and catalytic properties of Al/Fe-PILCs. The aluminosilicate denoted C2 exhibited the highest potential as starting material in the preparation of Al/Fe-PILC catalysts, mainly due to its starting cationic exchange capacity (192 meq/100 g) and the dioctahedral nature of the smectite phase. These characteristics favored the intercalation of the mixed $(Al_{13-x}/Fe_x)^{7+}$ Keggin-type polyoxocations, stabilizing a basal spacing of 17.4 Å and high increase of the BET surface (194 m²/g), mainly represented in microporous content. According to H₂-TPR analyses, catalytic performance of the incorporated Fe in the Catalytic Wet Peroxide Oxidation (CWPO) reaction strongly depends on the level of location in mixed Al/Fe pillars. Altogether, such physicochemical characteristics promoted high performance in CWPO catalytic degradation of methyl orange in aqueous medium at very mild reaction temperatures (25.0 ± 1.0 °C) and pressure (76 kPa), achieving TOC removal of 52% and 70% of azo-dye decolourization in only 75 min of reaction under very low concentration of clay catalyst (0.05 g/L).

Keywords: smectite; pillared clay; keggin-like mixed Al/Fe polyoxocation; mineralogical composition; catalytic wet peroxide oxidation

1. Introduction

Clays are products of rock erosion and are found widely distributed in nature. Their chemical and textural composition varies from one place to another, depending on their geological origin and the presence of organic and inorganic impurities [1]. Bentonite clays consist mainly of phases of the smectite group, which belong to type 2:1 materials (layers of phyllosilicates formed by two tetrahedral sheets, plus one octahedral, T:O:T) condensed in a layer, and exhibit a net neutral or negative electric structure that can vary significantly between illite, smectites, vermiculites, micas, etc. [2]. Smectites exhibit many interesting properties, especially for their application in adsorption and heterogeneous catalysis, originating in their peculiar physical, chemical and crystalline character. Among these properties, their cationic exchange capacity (CEC) and ability to swell in polar media make clays interesting as raw materials for modification through soft chemistry and intercalation methods. Pillaring has been

no excess of H₂O₂). It was proved that the catalytic performance exhibited by the material was not due to either Fe being present in the starting mineral, simple adsorption of the dye on the catalyst's surface or direct oxidizing effect of the molecular hydrogen peroxide, without previous catalytic effect.

Supplementary Materials: The following are available online at www.mdpi.com/1996-1944/10/12/1364/s1, Figure S1: X-ray diffraction patterns of raw minerals in oriented films: (a) C1, (b) C3 and (c) BV, under following conditions: (1) untreated, (2) Ca²⁺-homoionized, (3) saturated with ethylene glycol and (4) calcined at 400 °C/2 h, Figure S2: Nitrogen adsorption-desorption isotherms of refined and pillared forms of C1 and C3 clays, Figure S3: Hydrogen-temperature programmed reduction (H₂-TPR) diagrams of refined (R) and pillared forms of clays C1 and BV.

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Conflicts of Interest: The authors declare no conflicts of interest.

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