Applied Catalysis B: Environmental 104 (2011) 252–260

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Strategies for immobilization of manganese on expanded natural clays: Catalytic activity in the CWPO of methyl orange

Luis Alejandro Galeano[a,c,*], Antonio Gil[b], Miguel Angel Vicente[c,**]

[a] *Grupo de Investigación en Materiales Funcionales y Catálisis GIMFC, Departamento de Química, Universidad de Nariño, Calle 18, Cra 50 Campus Torobajo, Pasto, Colombia*
[b] *Departamento de Química Aplicada, Universidad Pública de Navarra, Edificio Los Acebos, Campus de Arrosadía, 31006 Pamplona, Spain*
[c] *Departamento de Química Inorgánica, Facultad de Ciencias Químicas, Universidad de Salamanca, Plaza de la Merced, s/n, 37008 Salamanca, Spain*

ARTICLE INFO

Article history:
Received 19 January 2011
Received in revised form 13 March 2011
Accepted 16 March 2011
Available online 12 April 2011

Keywords:
Al/Mn-pillared clay
MnS cluster
Azo-dye methyl orange
CWPO

ABSTRACT

The efficiency of the immobilization of manganese on natural bentonite has been studied by the comparison of three methods: (i) pillaring with Al_{13} followed by wet impregnation with aqueous manganese nitrate, (ii) pillaring with a mixed Al/Mn oligomeric solution and thermal treatment, and (iii) Mn^{2+}-homoionization of the starting clay and subsequent in situ generation of MnS clusters by H_2S gas treatment. The resulting solids were characterized by atomic absorption spectroscopy (AAS), cationic exchange capacity (CEC), powder X-ray diffraction (XRD), scanning electron microscopy/energy dispersive X-ray analysis (SEM-EDX), nitrogen adsorption at −196 °C and thermal analysis (DSC/TGA). Catalytic assessment of the materials was made in the Wet Peroxide Oxidation (CWPO) of the azo-dye methyl orange in aqueous solution at room temperature and atmospheric pressure. The in situ generation of the intercalated MnS clusters was shown to be the most efficient method for the metal incorporation in the interlayer of the hosting aluminosilicate. The solids obtained by this method resulted to be stable against the chemical leaching of the metal as well as the most active to catalyze the CWPO reaction under very mild conditions of temperature, pressure and pH (18 °C, 0.7 atm and 7.5).

1. Introduction

Manganese is one of the most versatile metals playing a central catalytic role in environment. For instance, there are several literature reports devoted to realize the mechanism of water oxidation by the oxygen-releasing complex of the photosystem II (PSII), where a tetra-nuclear manganese complex of the type oxo-Mn_4Ca cluster seems to play an important catalytic role [1,2]. PSII is a complex system that involves the binding of two water molecules, the removal of four electrons and four protons from the Mn-complex/substrate–water entity, O–O bond formation, and final dioxygen release [2]. Preparation of synthetic metal complexes able to mimic the catalytic redox reactions driven by such a photosystem, of huge interest in order to develop a kind of artificial photosynthetic system, has been also studied [3,4]. Meanwhile, a rapid redox cycle Mn(II) ↔ Mn(III,IV) into certain environments has been also reported, with direct impact on biogeochemistry studies [5]. For some Mn cluster species, water results essential in order to stabilize the higher oxidation states of the metal [4]. It has been also found that Mn(III,IV) oxides and hydroxides can be reductively dissolved by a variety of aromatic and nonaromatic compounds, whose reaction can be further accelerated by light [6,7]. A number of studies have also pointed out the high catalytic activity of Mn–Schiff base complexes with various oxidation states of the metal for reactions of olefin epoxidation by several oxidizing agents [8], as well as in oxidation reactions of other organic compounds [8,9]. These diverse topics briefly summarized here show the high potential that manganese may take as active metal to efficiently carry out a lot of catalytic reactions involving redox transformations.

The cumulative contamination suffered by aquatic resources with bio-refractory organic compounds like azo-dyes, mainly from the textile industry [10], constitutes a critical environmental problem that under low to middle toxic loadings (Chemical Oxygen Demand, COD ≤ 5000 mg/L) may be efficiently destroyed through catalytic oxidation [11]. Some technologies like Catalytic Wet Peroxide Oxidation (CWPO) can achieve the complete abatement of such refractory compounds and most of their oxidation by-products [12,13]. Many references report iron and copper as very active catalytic agents in the oxidation of refractory organic compounds with peroxide, based on the Fenton mechanism [14–16]. However, as long as we know very few references [17,18] report manganese and its compounds as active catalysts in the elimination

---

* Corresponding author at: Grupo de Investigación en Materiales Funcionales y Catálisis GIMFC, Departamento de Química, Universidad de Nariño, Calle 18, Cra 50 Campus Torobajo, Pasto, Colombia. Tel.:/fax: +57 2 7313106.
** Corresponding author. Tel.: +34 923 2944489; fax: +34 923 294574.
E-mail addresses: alejandrogaleano@udenar.edu.co (L.A. Galeano), andoni@unavarra.es (A. Gil), mavicente@usal.es (M.A. Vicente).

0926-3373/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcatb.2011.03.023

of toxic organic compounds present in water by peroxide-derived radical species. Several years ago, a couple of studies pointed out a high activity of manganese sulfides that catalytically decompose H_2O_2 in the absence of organic substrates [19,20]. Later, the catalytic activity of some metal sulfides confined in zeolite-like structures, including manganese, was also reported in the high-temperature oxidation of chlorobenzene [21].

On the other hand, in the past few years the clay minerals have been one of the most studied nanostructured solids employed as catalytic supports, mainly in their expanded pillared form stabilized by treatment with several metal oligocations [22–24]. Despite the very interesting catalytic properties of manganese oxides and hydroxides to activate redox reactions, the studies devoted to the development of methods other than impregnation for the preparation of natural clays modified with Mn have been rather scarcely documented. Mishra et al. reported the intercalation/pillaring of natural and acid-activated montmorillonites with a tri-nuclear Mn-acetato complex [25,26]. The resulting solids were expanded and stable up to 500 °C, mainly when submitted to multi-step exchange, but offered rather low performance when evaluated in the catalytic nitration of chlorobenzene [26]. Gandía et al. [27] reported the modification of a montmorillonite with mixed pillaring Al_{13} and Mn citrate solutions aged together. The authors found a negative effect of the Mn addition on conventional intercalation of the clay with Al-based Keggin polycations, leading to significantly lower specific surface and volume of micropores in the final materials. Accordingly, it is very interesting to explore alternative strategies to achieve the specific incorporation of manganese into the interlayer of the aluminosilicate, with simultaneous high stability under the aggressive redox environment, typical of many catalytic reactions. Thus, although targeting various applications like the development of semiconductor and optoelectronic materials, a couple of works have recently investigated the stabilization of Mn into the pore structure of zeolite-like materials by growing MnS clusters generated in situ, applying a procedure that involved extensive cationic exchange with the metal followed by streaming with hydrogen sulfide under thermal treatment [28,29]. Another approach aimed at growing the same kind of clusters in the interlayer of a natural montmorillonite by solid–solid reactions, although demanding very long times of reaction [30,31]. The novel synthetic route applied on zeolites would be properly adapted in order to incorporate manganese into the interlayer region of natural clays; indeed, it is one of the strategies studied in the present investigation. More recently, other metal sulfides, CdS and ZnS, have been prepared at nanoparticle size level onto a bentonite by a soft wet method and the final solids were applied in the UV/photocatalytic degradation of eosin B, with promising results [32].

Therefore, the efficiency of the incorporation and stabilization of manganese into the structure of a bentonite by three methods is compared in the present work. The strategies have been evaluated in terms of their ability to provide expanded materials being at the same time highly active and stable in the CWPO elimination of the azo-dye methyl orange, dissolved in water. Azo-dyes are widely used in textile industry and their concentration in waste streams typically varies from 10 to 50 mg/L [33]. Besides, such a kind of compounds displays high toxicity and low biodegradability even at low concentrations.

2. Experimental

2.1. Materials and methods

A Colombian bentonite from Valle del Cauca region, with chemical composition (mass%): 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 cationic exchange capacity (CEC) of 89 meq/100 g, has been employed as starting material. Physicochemical and mineralogical characterization of this aluminosilicate has been reported in a previous work [34], which classifies the smectite fraction as a montmorillonite. The raw mineral was homoionized with sodium as preferential compensating cation (NaBV) in a process carried out by the mining company Bentocol S.A., then employed without further refining as starting material for the chemical treatments. The modification experiments were carried out with $AlCl_3·6H_2O$ (99%, Sigma–Aldrich), $Na_2S·9H_2O$ (98.5%, Sigma–Aldrich), and $Mn(NO_3)_2·4H_2O$ (98.5%, Merck), which were used as received. For the catalytic runs, methyl orange (MO) ACS reagent (>85%, 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 modified materials

In the method A, the starting material NaBV previously intercalated with aluminum polycations was doped by wet impregnation with Mn. The clay was intercalated with 18 $meq_{Al^{3+}}/g_{clay}$ of an Al_{13} pillaring precursor prepared by controlled base-hydrolysis of $AlCl_3·6H_2O$ solution (hydrolysis ratio $OH^-/Al^{3+} = 2.0$), according to a procedure adapted from Barrault et al. [35]. The material was then separated by centrifugation and thoroughly washed with distilled water to remove the excess of adsorbed ions, dried at 60 °C and heated at 400 °C for 2 h under air atmosphere, obtaining the solid AlP-NaBV. Thereafter, this alumina-pillared material was impregnated with 1.0% $Mn(NO_3)_2·4H_2O$ aqueous solution in amount enough to get a final ratio of 2.0 g of Mn/100 g of AlP-NaBV, dried at 60 °C and heated at 400 °C for 2 h as before (solid Mn,AlP-NaBV(A)).

The method B consisted in the intercalation of the clay with a mixed co-hydrolyzed Al–Mn oligomeric pillaring solution; Mn was incorporated into the intercalating solution before the hydrolysis step. The loading of aluminum was the same as in method A (18 $meq_{Al^{3+}}/g_{clay}$), besides adding 2.0 $meq_{Mn^{2+}}/g_{clay}$ from $Mn(NO_3)_2·4H_2O$. Thus, the total added metals to clay ratio was 20 meq/g_{NaBV}, and Mn atomic percentage was 14.29% of the total added metals. Such dissolution was then hydrolyzed as before with 0.2 M NaOH for final hydrolysis ratio OH^-/Met of 2.0 (Met = Al + Mn), value commonly employed in the efficient intercalation of clays with mixed pillaring systems based on aluminum [35,36]. The dissolution was heated at 70 °C for 2 h, then left to get to room temperature and slowly dropped on the clay aqueous suspension (2.0 $g_{NaBV}/100\ cm^3$ suspension) under continuous stirring. The material obtained was washed, dried and heated as in method A, generating the solid Mn,Al-P-NaBV(B).

The method C laid on the in situ growing of MnS clusters from previously interlayered Mn^{2+} ions; the procedure applied was adapted from that proposed by Iacomi et al. [28] to develop such clusters into zeolite structures. In the first step, the starting clay was Mn-homoionized by repetitive treatment with 1.0 mol/dm^3 $Mn(NO_3)_2·4H_2O$ aqueous solution at room temperature, thoroughly washed with distilled water and dried at 60 °C. Portions of this Mn-form of the clay (MnBV) were exposed to H_2S at 77 °C or 100 °C for 12 h. The continuous flow of hydrogen sulfide was evolved from a fastened flask by constant and slow dropping of concentrated HCl (37%) over Na_2S saturated solution, passing through a $CaCl_2$ column trap in order to retire any moisture before the gas stream reached the solid. A fraction of each sample was then treated under air atmosphere at 200 °C for 2 h and another fraction at 400 °C for 2 h to assess for the effect of the temperature of the thermal treatment. The resulting materials are here referred to as MnS77-NaBV/200, MnS77-NaBV/400, MnS100-NaBV/200 and MnS100-NaBV/400, the numbers accounting for the temperatures of chemical and subsequent thermal treatments, respectively.