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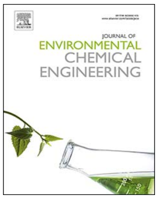

Research Paper

Spinel manganites synthesized by combustion method: Structural characterization and catalytic activity in the oxidative degradation of organic pollutants

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ABSTRACT

Two spinel-type oxides, $CuMn_2O_4$ and $CoMn_2O_4$ were synthesized by a simple combustion method. The oxides were characterized by X-ray Diffraction, infrared spectroscopy, scanning electron microscopy and atomic absorption spectroscopy. The structures of the obtained oxides were refined by the Rietveld method. The obtained samples were tested in the catalytic degradation of phenol and methyl orange. Two different oxidants were employed: potassium persulfate and peroxymonosulfate. The catalytic activity was tested, as well as the degradation efficiencies. The best results were obtained with the copper substituted oxides, using oxone as oxidant. With this system, mineralization of total organic carbon (TOC) reached more than 94% within 120 min of reaction. For cobalt mixed oxides, the TOC mineralization reached as much as 68% in the same condition. The activation mechanisms for the different systems studied in this work are discussed and two different pathways are proposed depending on the oxidant and/or the substitution metal.

1. Introduction

The contamination of toxic organic pollutants in subsurface soil and groundwater has been subject of concern in recent years. Water treatment plays an important role in the awareness of the environment preservation. Different industrial activities (petrochemical, pharmaceutical, chemical, textile, among others) discharge hazardous organic products in water bodies, causing damage to the human health.

Among the different processes to treat organic pollutants, such as biodegradation [1,2] and classical adsorption [3,4], advanced oxidation processes (AOPs) have gained attention lately as an attractive alternative due to its high efficiency [5–7]. These processes are based on the generation of hydroxyl radicals ($\cdot$OH), more effective oxidant species than the chemical reagents that are commonly employed for this purpose (ozone, H_2O_2, etc). Similar to OH radicals, sulfate radicals may react with organic compounds by electron transfer, hydrogen abstraction or addition mechanisms. These radicals can be produced through the activation of persulfate (PS) anion, $S_2O_8{}^{2-}$, or decomposition of peroxymonosulfate (PMS), $HSO_5{}^{-}$. The anions activation may be achieved by heat, chelated or not-chelated transition metals, hydrogen peroxide, and alkaline pH conditions. The efficiency, effectiveness and reaction products may vary among the different contaminants and activation methods.

Recently, manganese oxides [8,9] and metal transition mixed oxides [10–12] were tested as heterogeneous catalysts in the activation of PS and PMS for the degradation of pollutants as azo dyes and phenolic compounds. In the first case, it has been demonstrated that manganese oxides resulted in effective catalysts for generating sulfate radicals to degrade phenol, being their efficiency dependant on the oxidation state of manganese and on its redox potential. In the latter case, the spinel-type structures were used as successful catalysts for the degradation of Acid Orange II, through oxone activation at neutral pH. Co, Mn and Ni substitution improved the reactivity of the spinel oxide.

In order to gain more insight about the effect of metal substitution, in this study, two spinel-type oxides, $CuMn_2O_4$ and $CoMn_2O_4$ were synthesized by a simple combustion method and fully characterized. The structures of the obtained oxides were refined by the Rietveld method and the catalytic activity was evaluated in the degradation of two organic pollutants, methyl orange azo dye and phenol. The reactivity of the oxides in PS and PMS activation was also discussed.

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2. Experimental

2.1. Manganite oxides preparation

Two manganite oxides ($CuMn_2O_4$ and $CoMn_2O_4$) were synthesized following the technique reported by Arul Dhas et al. and Lazarraga et al. [13,14]. For each synthesis, both $Co(NO_3)_2{\cdot}6H_2O$ or $Cu(NO_3)_2{\cdot}3H_2O$ and $Mn(NO_3)_2{\cdot}4H_2O$ (Merck, A. R. grade), and the fuel (refined saccharose) were weighted in 1:2:1 molar proportions, taken in a Pyrex dish and dissolved in a minimum amount of distilled water. A heating plate was used to concentrate the solution until ignition took place and produced a foamy, black powder of low density. The as-produced sample was divided in two batches in order to calcine them at different temperatures (400 °C and 900 °C). The yield of the reaction was ca. 100%.

The stoichiometric reactions are:

$$Co(NO_3)_{2(aq)} + 2Mn(NO_3)_{2(aq)} + C_{12}H_{22}O_{11(aq)} + yO_{2(g)} \rightarrow CoMn_2O_4 + 2N_{2(g)} + 2NO_{x(g)} + 12CO_{2(g)} + 11H_2O_{(g)}$$

$$Cu(NO_3)_{2(aq)} + 2Mn(NO_3)_{2(aq)} + C_{12}H_{22}O_{11(aq)} + yO_{2(g)} \rightarrow CuMn_2O_4 + 2N_{2(g)} + 2NO_{x(g)} + 12CO_{2(g)} + 11H_2O_{(g)}$$

where $y = 5 + x$.

2.2. Solids characterization

The metal content in the samples was determined by atomic absorption spectrometry (AAS) from total dissolution of 30 mg of the solids in 6 M HCl, at 80 °C, using a GBC Model B-932 atomic absorption spectrometer. Chemical analyses were made in duplicate.

The IR spectra of the substances as KBr pellets were recorded in the 4000 to 400 cm^{-1} range on a Nicolet Nexus FTIR spectrometer.

The morphology of the particle aggregates and their qualitative compositions were characterized using scanning electron microscopy (SEM) coupled with energy-dispersive spectroscopy (EDS) using a JEOL 8230 electron microprobe, housed at LAMARX-UNC.

The specific surface area of the catalysts was calculated by the BET method from the nitrogen adsorption isotherms obtained at 77 K using a Micromeritics ASAP 2020 Plus apparatus.

Powder X-ray diffraction (XRD) experiments were performed with a PANAnalytical X'Pert Pro diffractometer (operated at 40 kV and 40 mA) with $CuK\alpha_{1+2}$ radiation, between 10° and 130° (2θ), with a step size of 0.02° (2θ) and counting time of 10 s/step. Rietveld structural refinements were performed using the FULLPROF program [15]. Peak profiles were fitted using a pseudo-Voigt function.

2.3. Catalytic activity

The two synthesized catalysts calcined at 400 °C were evaluated in the degradation of two pollutants, methyl orange and phenol. The efficiency of two oxidant agents, potassium persulfate ($K_2S_2O_8$) and Oxone® ($KHSO_5{\cdot}½KHSO_4{\cdot}½K_2SO_4$), was also tested. The UV–vis spectra of the degradation experiments were registered using a Cecil 2021 spectrophotometer.

2.3.1. Methyl orange (MO) degradation

The degradation reactions were performed in a glass reactor, containing 150 mL of MO solution (10 mg L^{-1}) at 30 °C. The pH was adjusted to 3 with H_2SO_4. In a typical procedure, the reaction was initiated by adding oxidant and 50 mg of the catalyst into the prepared reaction solution. The mass ratio dye:oxidant:catalyst was 1:20:33. The reaction was held under mechanical stirring. At designated sampling intervals, aliquots of solution were removed from the reaction vessel. Immediately, the sampling was filtered with a syringe through a Nuclepore membrane (pore size 0.22 μm) and tested by the UV–visible spectrophotometer. The MO concentration at different reaction times was determined by measuring the absorption intensity at λ_{max} = 506 nm. Prior to the measurement, a calibration curve was obtained using MO solutions with known concentrations. The degradation efficiency of methyl orange was defined as follows:

$$\text{Degradationefficiency} = \left(1 - \frac{C_t}{C_0}\right) \times 100$$

where C_0 (mg L^{-1}) is the initial concentration of methyl orange, and C_t (mg L^{-1}) is the concentration of methyl orange at reaction time, t (min).

2.3.2. Phenol degradation

100 mg of catalyst were equilibrated in a glass reactor, containing 150 mL of phenol solution (60 mg L^{-1}) at 30 °C. The initial pH of the solution was 5.4. After that, adequate quantities of oxidant were mixed with the oxide suspension. The initial mass ratio phenol:oxidant:catalyst was 1:55.5:11.2. Samples were taken out at regular intervals and filtered in the same way as described above. The supernatant was then used for the analysis through an UV–vis full wavelength scanning.

The degree of mineralization of both pollutants were evaluated by measurements of total organic carbon (TOC), using a TOC-LCPH/CPN analyzer (Shimadzu). The pH was monitored with an Orion 250Aplus pHmeter equipped with a pH electrode.

The leaching of Co, Cu and Mn ions in the solutions were also determined with a GBC Avanta B-932 Atomic Absorption Spectrometer.

For recycled catalyst tests, the oxides were collected by filtration after reaction, washed with water and dried overnight for reuse test, keeping constant the oxidant:pollutant:catalyst mass ratio.

Quenching experiments were performed in the same experimental conditions, being the only difference the addition of ethanol (mass ratio pollutant:alcohol 1:250).

3. Results and discussion

3.1. X-Ray diffraction and Rietveld refinement

XRD patterns of the two obtained solids calcined at 900 °C are presented in Fig. 1, together with the refined patterns and their differences.

For sample $CuMn_2O_4$, the product obtained by calcined at 400 °C corresponds to a cubic spinel phase (88 wt.%) with a lattice parameter a of 0.82853 nm (Table 1), in good agreement with values reported in the literature [16]. Additional peaks indicate the presence of hausmannite ($MnMn_2O_4$, tetragonal). The content of this second phase was 12 wt%, and may be interpreted as a segregation of a Mn-rich spinel. When the calcination temperature was raised to 900 °C, the product crystallinity seemed to be higher (as indicated by narrower and higher peaks) but the segregation effect was more pronounced, with 20 wt% $MnMn_2O_4$. The tetragonal phase is attributed to the presence of Mn^{3+} ions (produced by oxidation of reagent Mn^{2+}) in octahedral sites. The Mn^{3+} ions distort the cubic spinel structure by deforming the octahedra via Jahn-Teller interactions. For $CoMn_2O_4$, experimental runs yielded a single phase, regardless of calcination temperature. The lattice parameters (Table 3) are also in good agreement with the literature [17,18].

Cell parameters, agreement factors, refined atomic coordinates and calculated main interatomic distances and angles are summarized in Tables 1–6.

The vibrational spectra of $CoMn_2O_4$ and $CuMn_2O_4$ spinels can be seen in Fig. S1 (Supplementary material). In general, spinel type compounds present two main metal-oxygen bands. The spectrum of $CoMn_2O_4$ is typical for a Co-Mn spinel. The bands at around 608 cm^{-1} can be assigned to the vibrational bending modes of the atoms in the tetrahedral oxygen environment (mainly cobalt), while those around 502 cm^{-1} can be related to the vibration of the atoms in the octahedral