



Mechanochemical transformation of an organic ligand on mineral surfaces: The efficiency of birnessite in catechol degradation

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ARTICLE INFO

Article history:

Received 5 September 2011

Received in revised form

15 November 2011

Accepted 16 November 2011

Available online 25 November 2011

Keywords:

Birnessite

Catechol

Mechanochemistry

Abiotic degradation

ABSTRACT

The aim of this work is to investigate the efficiency of the phylломanganate birnessite in degrading catechol after mechanochemical treatments. A synthesized birnessite and the organic molecule were grounded together in a high energy mill and the xenobiotic-mineral surface reactions induced by the grinding treatment have been investigated by means of X-ray powder diffraction, X-ray fluorescence, thermal analysis and spectroscopic techniques as well as high-performance liquid chromatography and voltammetric techniques.

If compared to the simple contact between the birnessite and the organic molecule, mechanochemical treatments have revealed to be highly efficient in degrading catechol molecules, in terms both of time and extent. Due to the two phenolic groups of catechol and the small steric hindrance of the molecule, the extent of the mechanochemically induced degradation of catechol onto birnessite surfaces is quite high. The degradation mechanism mainly occurs via a redox reaction. It implies the formation of a surface bidentate inner-sphere complex between the phenolic group of the organic molecules and the Mn(IV) from the birnessite structure. Structural changes occur on the MnO₆ layers of birnessite as due to the mechanically induced surface reactions: reduction of Mn(IV), consequent formation of Mn(III) and new vacancies, and free Mn²⁺ ions production.

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1. Introduction

The mechanochemical method, based on grinding reactants in solid phase, has recently aroused interest for its capability to degrade both organic [1–3] and inorganic [4] pollutants. When compared with other techniques, the mechanochemical method offers advantages for simple operations on a large amount of toxic compounds [3,5,6] by eliminating the use of organic solvent and facilitating the estimation of overall kinetic and thermodynamic parameters in the degradation processes. The direct contact between the mineral surface and the xenobiotic is indeed a crucial aspect of the mechanochemical interactions. In fact, it exerts a profound effect on the pathways and rates of chemical changes in organic pollutants and plays a primary role in activating surface reactions responsible for the abiotic degradation of organic pollutants without the presence of a solvent phase [3,6]. In order to

fully exploit the potentials of the mechanochemical technique in remediating contaminated sites, a fundamental understanding at a molecular scale of organic molecule transformations onto mineral surfaces (i.e. individuation of the pathways of reactions) is still needed.

In the present study the capability of birnessite (δ -MnO₂) surfaces to mechanically degrade catechol has been investigated and the degradative mechanisms of the ligand onto the phylломanganate has been hypothesized. To this purpose a synthesized birnessite and the organic ligand catechol were continuously grounded in a zirconia ball mill using different experimental setups. The phylломanganate, its ground mixtures with the organic molecule, and their organic and aqueous extracts have been analyzed through several techniques.

The choice of birnessite as a substrate for mechanically induced degradation of the organic molecule catechol lies in the fact that the mineral possesses unique crystal-chemical characteristics [7–10] which confer it extensive redox and sorption properties. Besides, birnessite plays an important role in the fate of organic pollutants in soils because it is one of the most commonly identified Mn oxide

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minerals in soils and geochemical environments [11]. Birnessite is a layered phyllosulfate, i.e. a manganese oxide constituted by bidimensional layers of edge-sharing MnO_6 octahedra, with cations (K, Na, Li) in the interlayers and water molecules. These cations balance the negative charge arising from the layers as a consequence of the presence of Mn ions with an oxidation number lower than +4.

The organic molecule catechol, an ortho-diphenol, was chosen because it is commonly found in soils as an organic matter constituent (plant polyphenol), as an intermediate of microbial metabolism of xenobiotics, and is often used in laboratory experiments to model degradation of xenobiotics [12]. Further, ortho-type semiquinones are common intermediates in pesticide degradation pathways and are involved in oxidative coupling reactions leading to the formation of soil humic substances [13].

2. Materials and methods

2.1. Sample preparation and treatments

Catechol (hereafter CAT) was purchased from Aldrich Chemical Company (Milwaukee, WI, USA, 99% of purity) and used without a further purification. The phyllosulfate K-birnessite (*KBi*) was synthesized starting from KMnO_4 and HCl according to the method described by McKenzie [11].

CAT was mixed with synthesized *KBi* and 6.3 g of these mixtures (0.3 g of organic molecule + 6 g of phyllosulfate, 1/20 weight ratio) were grounded in a planetary ball mill. In the used mechanochemical reactor (Pulverisette-7, Frisch, Germany) – consisting of two zirconia pots with an inner volume of 45 cm^3 situated on a rotating disk – 14 zirconia balls (10 mm diameter) were arranged. The mill was operated applying a high rotation speed (700 rpm) for different milling times (4 steps of 15 min followed by 15 min cooling periods to prevent an excess of heating). Afterwards, ground mixtures were incubated at 30°C in capped porcelain cups for periods ranging from 24 h to 7 d.

2.2. Solid phase analyses

Thermogravimetry (TG) and differential thermal analysis (DTA) curves were simultaneously recorded for the synthesized *KBi* using a thermal apparatus (SEIKO Instrument, UK), $10^5 \mu\text{V}$ DTA sensitivity, $10^7 \mu\text{g}$ TG sensitivity, under the following operating conditions: 20–25 mg sample weight, Al_2O_3 as a reference material, 20– 1050°C temperature range, $20^\circ\text{C}/\text{min}$ heating rate, nitrogen flow.

X-ray powder diffractometry (XRPD) was performed both on untreated birnessite and birnessite/CAT mixtures grounded for 60 min using a Philips PW1710 diffractometer with a conventional Bragg-Brentano parafocusing vertical geometry and a CuK_α radiation source, at the following operational conditions: 40 kV, 20 mA, 0.02° step scan, 10 s acquisition time per step.

X-ray photoelectron spectra (XPS) of untreated *KBi* and birnessite/catechol mixtures were collected using Theta Probe spectrometer (Thermo Electron Corporation), with a monochromatized AlK_α X-ray source, 400 μm spot size, 100 eV pass energy, under vacuum condition of 2×10^{-7} Pa in the analytical room. The sample was prepared as pressed pellets. The neutralization of sample charging was obtained using low energy electrons combined with Ar^+ ions and the binding energy scale was corrected using the signal of adventitious carbon ($\text{C}1s = 284.8 \text{ eV}$).

Fourier transform infrared (FT-IR) spectra of untreated birnessite – at room temperature and heated for 1 h at 120 and 250°C – and of 60-min ground birnessite/CAT mixtures have been acquired with a Nicolet 5 PC FT-infrared spectrometer using KBr pellets on a

spectral range of $400\text{--}4000 \text{ cm}^{-1}$. Nominal resolution was 4 cm^{-1} and final spectra are the average of 128 scans.

Electron paramagnetic resonance (EPR) spectroscopy measurements have been performed at room temperature using a spectrometer (ER 200D-SRC, Bruker, Germany) operating at X-band (about 9.5 GHz). The g -values were determined using DPPH radical [2,2-di(4-tert-octyl-phenyl)-1-picrylhydrazyl, $g = 2.0037$] as an external standard. The measurements have been carried out on powdered samples of synthetic birnessite and birnessite/xenobiotic mixtures put in Teflon bags to avoid spurious effects from magnetic alignment phenomena and kept into amorphous silica capillaries. EPR parameters have been refined by means of spectral simulations.

X-ray fluorescence (XRF) analysis has been executed with an automatic spectrometer (PHILIPS PW1480, USA). The untreated birnessite was treated with elvacite solution (acetone 16%, w/v) and subsequently transformed in a pellet through a hydraulic press using a pressure of 10 tons. The loss of ignition (L.O.I.) was determined after heating the sample at 950°C overnight.

2.3. Solvent extracts analyses

After each milling step and each incubation time, two aliquots of the milled and non-milled mixtures (50 mg) were extracted with 5 mL of aqueous solution and stirred at room temperature for 20 min. All the suspensions were centrifuged ($2880 \times g$) at 4°C for 10 min. Then, the supernatants were filtered through $0.2 \mu\text{m}$ regenerated cellulose filters to determine (i) by high-performance liquid chromatography with diode-array detector (HPLC-DAD) the amount of un-reacted CAT and (ii) by anodic stripping voltammetry (ASV) the amount of Mn^{2+} ions possibly released as a consequence of the surface reactions of CAT with birnessite.

The HPLC analyses were performed with an apparatus from Perkin Elmer (Mod. 410, Monza, Italy) operating with a flow rate of 1 mL min^{-1} , a $3.9 \times 150 \text{ mm}$ C-18 column and the detector sets at 280 nm. The mobile phase, used in an isocratic elution, was composed of acidified water (0.05% phosphoric acid) and acetonitrile at a ratio of 20/80 (v/v). Standard solutions CAT were used as controls and all the experiments were performed in triplicate.

The concentration of manganese ions in solution was defined in alkaline aqueous solution ($\text{Na}_2\text{B}_4\text{O}_7 + \text{NaOH}$, pH 9.5–10) through ASV (Metrohm 693, Origgio, Italy) using the procedure Application Bulletin 123/3 (Metrohm Italiana). The metal reduction was obtained upon the hanging mercury drop electrode (HMDE). All the analytical determinations were repeated three times.

3. Results

The K and Mn concentrations in the synthesized birnessite have been measured from XRF analysis ($\text{K} = 1.27 \text{ wt.}\%$ and $\text{Mn} = 62.67 \text{ wt.}\%$), whereas the water content has been estimated from the weight loss measured between 120°C and 210°C . The main features of DTA curve of the synthesized birnessite are represented by four endothermic peaks at about 100, 150, 790 and 830°C and one exothermic peak at about 500°C (Fig. 1). The two endothermic peaks at low temperature correspond to the loss of adsorbed and interlayer water, respectively. From the weight loss measured between 120°C and 210°C in TG curve [9] about a 7.39 wt.% of interlayer water has been deduced in the synthesized *KBi*. The exothermic peak at 500°C corresponds to the transformation of the dehydrated birnessite to cryptomelane, whereas the endotherms at higher temperatures correspond to transformation into $\delta\text{-Mn}_2\text{O}_3$ phase ($\sim 790^\circ\text{C}$) and $\delta\text{-Mn}_2\text{O}_3$ melting ($\sim 830^\circ\text{C}$) [3].

The X-ray powder diffraction pattern of the *KBi* consists of a small number of broad lines (Fig. 2a), due to the low crystallinity of

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