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Structure and properties of vanadium-doped α-MnO_2 and enhanced Pb^{2+} adsorption phenol/photocatalytic degradation

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HIGHLIGHTS

- Vanadium-doped cryptomelanes were synthesized by refluxing at atmosphere.
- V doping greatly modified the physicochemical properties of cryptomelane.
- These V-doped cryptomelanes have increased adsorption capacity for Pb^{2+}.
- ~1.43 wt.% V doped cryptomelane photocatalytically degraded phenol most effectively.

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ABSTRACT

Vanadium (V)-doped cryptomelane was synthesized and characterized by powder X-ray diffraction, electron microscopy, N_2 adsorption, diffuse reflectance spectroscopy, X-ray photoelectron spectroscopy and X-ray absorption spectroscopy. Vanadium doping does not change the basic crystal structure but slightly decreases the lattice parameters (a, b, c, β and cell volume) and increases the coherent scattering domain (CSD) sizes (16–19 nm). These V-doped cryptomelane materials are granular particles with increased specific surface areas (149–183 $m^2\ g^{-1}$) and increased concentrations of hydroxyl groups on the surfaces with increasing V doping. Both V $2p_{3/2}$ spectra and V K-edge X-ray absorption near edge spectroscopy indicates that V exists in +5. Substitution of V^{5+} for Mn^{4+} in cryptomelane framework results in reduction in Mn average oxidation state and increase in bond lengths of Mn-O in [MnO_6] unit, edge- and corner-sharing Mn-Mn(V) pairs. These V-doped materials have greatly increased adsorption capacities for Pb^{2+} (937–1146 mmol kg^{-1}). Doping ~1.4 wt.% V can significantly enhance cryptomelane optical absorption properties and thus photocatalytic degradation of phenol, i.e., with a TOC removal rate of ~77%. These results can facilitate the modification and application of environmental friendly Mn oxide materials in pollution control and remediation.

1. Introduction

Nowadays environment pollution (e.g. heavy metals and organic contaminates) is becoming one of the greatest concerns around the world. Lead, one of the most common toxic heavy metal pollutants in soils and waters, was discharged into the environments mainly through various anthropogenic activities, including smelting and mining, acid battery recycling, pesticides, power plants, etc. It can insert into human body through digestive and respiratory tract, resulting in gastrointestinal disorders and destructive effect to nervous system [1–3]. Industrial wastewaters from coking, petroleum refining, metallurgy, coal gasification, pesticides, pharmacy and phenolic resin production usually contain high concentrations of phenolic pollutants. Being regarded as mutagens and carcinogens, phenol can cause serious damages to animals and

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microorganisms in water bodies. Owing to its high toxicity and long persistence, it is included in the blacklist of precedence-controlled pollutant in water, and is often used as a model organic pollutant [4,5]. Various techniques are being explored to remove the pollutants from wastewaters before discharging them into nature water bodies. Among them, adsorption is an effective method to remove heavy metal pollutants from water systems while photocatalytic degradation is the real decomposition process for the organic contaminates such as phenol in wastewaters. Among various inorganic oxide materials applied into wastewater treatment, manganese (Mn) oxide materials gain much interests due to their large specific surface areas (SSA), highly reactivity, and being widely involved in a series of adsorption, redox and photocatalytic degradation reactions of various contaminants [5–9].

Out of several tens of Mn oxide materials, cryptomelane attracts special concerns. Natural cryptomelane minerals can be found in the supergene oxidation zones of Mn deposits and lateritic weathered profiles formed by authigenic precipitation [10,11]. It can also be the transformation products from birnessite-like precursors [12–15]. Some cryptomelane minerals are also found in ferromanganese nodules and fine silt in soils, weathered ultramafic rocks, volcanic ash, and so on [16–18]. For example, cryptomelane is the majority of Mn oxide minerals in the Xiangtan manganese deposit, China [19,20]. However, natural cryptomelane usually co-exists with other minerals, has complex compositions and occurs as aggregates [19,20], and its synthetic analogues are usually used in various studies [21–23].

Cryptomelane is one kind of manganese oxide mineral with 2×2 tunnel structure ($0.46\ \mathrm{nm} \times 0.46\ \mathrm{nm}$) formed by regular linkage of $[MnO_6]$ unit by corner- and edge-sharing [22]. Recent research suggests that its structure might also contain some 1×1 [23] and 3×2 [15] tunnels. The framework of cryptomelane is composed of Mn^{4+} and Mn^{3+}, which can be replaced by other cations such as Co^{3+}, Fe^{3+} and V^{5+} [9,14,21,23–28]. Other ions, H^+, K^+, Li^+, Na^+, Rb^+, Cs^+ and NH_4^+ often exit in the tunnel structure [29–31]. The tunnel structure can also host heavy metals such as Cd^{2+} [33], Fe^{3+} [9] etc. It was reported that cryptomelane owns the strongest photocatalytic reactivity towards organic contaminates [5], and has the second highest adsorption capacity for Pb^{2+} [6] among several typical manganese oxides.

Introducing transition metals (TM) into the structure of cryptomelane will significantly change its microstructure and physicochemical properties. By doping single TM cation (Co, Ni, Cu, Cr, Fe, V, W) [21,24,25,28,33,34], two cations (Co + Ni) [8] and multiple cations (Cu + Fe + V + Mo) [23], the physicochemical properties of cryptomelane materials (such as particle size, morphologies, Mn average oxidation state (AOS) and thermal stability) can be tailored, and thus the chemical activities in a series of reactions (adsorption, sensing and photocatalysis) can also be adjusted. Under different reaction conditions, i.e. temperatures, the structure and properties of doped cryptomelane are different. For example, hydrothermally synthetic (600–800 °C) Fe-doped cryptomelane had rod-like morphology, and the dopant Fe replaced framework Mn [28]. But synthetic Fe-doped cryptomelane by reflux under ambient pressure were granular particles, and a part of Fe was located in framework while the rest Fe was absorbed in tunnel [9].

Though several studies have reported on V-doped cryptomelanes [24–27,35], these V-doped cryptomelanes were synthesized at relatively high temperatures, i.e. > 160 °C. In the present study, a series of V^{5+}-doped crypromelane with different V contents were synthesized by refluxing at 100 °C at ambient pressure. The obtained samples were characterized by powder X-ray diffraction (XRD) and Rietveld structure refinement, field emission scanning electron microscope (FESEM), N_2 physical absorption, X-ray photoelectron spectroscopy (XPS) and diffuse reflection spectroscopy (DRS) to explore their basic microstructure and physicochemical properties. Synchrotron-based X-ray absorption spectra (XAS) is applied to study local coordination environments of Mn and V in the mineral structure. Based on information of the structure and basic physicochemical properties of these minerals, their reactivity towards Pb^{2+} adsorption or photocatalytic degradation of phenol from wastewater was further investigated.

2. Material and methods

2.1. Syntheses of V-doped cryptomelanes

Vanadium-doped cryptomelane samples were synthesized following the same method of McKenzie [36] and Feng et al. [6]. After heating 80 mL of $0.4375\ \mathrm{mol\ L^{-1}}$ $KMnO_4$ solution to 60 °C, it was quickly poured into a mixture of 100 mL of $0.5\ \mathrm{mol\ L^{-1}}$ $MnSO_4$ and a certain amount of Na_3VO_4 and $2\ \mathrm{mol\ L^{-1}}$ CH_3COOH solution (which was also pre-heated to 60 °C). Then the mixture was refluxed at 100 °C for 20 min. A suitable amount of $2\ \mathrm{mol\ L^{-1}}$ CH_3COOH solution was added to make up the volatilized CH_3COOH during the reaction. The obtained solids were washed with deionized water thoroughly, and then dried in oven at 60 °C for several days. After ground in an agate mortar to particle sizes below 100 mesh (154 µm), the products were stored in closed polyethylene plastic tubes at room temperature. Based on the initial molar ratios of V/Mn, the products were named as Cry0, V2, V4 and V5, respectively.

2.2. Basic physicochemical properties

Powder XRD analysis of these samples were conducted on a Bruker D8 Advance diffractometer using a Cu Kα source ($\lambda = 0.15418\ \mathrm{nm}$). The diffractometer was operated at a tube voltage of 40 kV and a current of 40 mA with 1.2 s counting time per 0.02° 2θ step. Micromorphologies of the samples were probed by field emission scanning electron microscopy (Jeol JSM-6700F microscope) after being coated with a gold evaporated film. The chemical composition, specific surface area and pore analysis, X-ray photoelectron spectroscopy (XPS) and diffuse reflection spectroscopy (DRS) of these samples were analyzed as described in Refs. [5,37].

2.3. X-ray absorption spectroscopy

The XAS spectra of these V-doped cryptomelane samples were collected at beamline 4-3 at the Stanford Synchrotron Radiation Lightsource (SSRL) [38]. V K-edge spectra were collected in fluorescence model over a range of 5265–6217 eV. Mn K-edge spectra were collected in the transmission model over a range of 6339–7291 eV. The EXAFS spectra of Mn and V metal foils were collected simultaneously with a reference ion chamber to calibrate the monochromator energy position.

IFEFFIT/Athena was used to do the spectra processing [39]. Parameters used for background removal of V K-edge spectra were: $E_0 = 5483$ eV, $R_{bkg} = 1.0$ Å and k-weight = 2. Those for Mn K-edge spectra were: $E_0 = 6553$ eV, $R_{bkg} = 1.0$ Å and k-weight = 2. The Mn K-edge EXAFS spectra were fitted over a k range of 3.3–11.2 Å^{-1} and an R range of 1–4 Å using several single scattering paths. Phase and amplitude functions for single-scattering paths were calculated based on cryptomelane structure using FEFF7 [40]. An amplitude reduction factor (S_0^2) of 0.973 for Mn was adopted from a previous study [41]. In all fits, the number of independent variables used was less than the number of variables that the data points allowed. During Fourier transformation and EXAFS data fitting, the Hanning window was used.