Structure and properties of Co-doped cryptomelane and its enhanced removal of Pb^{2+} and Cr^{3+} from wastewater

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ABSTRACT

Cryptomelane is a reactive Mn oxide and has been used in removal of heavy metal from wastewaters. Co-doped cryptomelane was synthesized by refluxing at ambient pressure and characterized by powder X-ray diffraction, scanning electron microscopy, X-ray photoelectron spectroscopy and extended X-ray absorption fine structure spectroscopy, and its performances for removal of Pb^{2+} and Cr^{3+} from aqueous solutions were investigated. Co doping has a negligible effect on the structure and morphology of cryptomelane but increases the specific surface area and Mn average oxidation state. Mn and Co K-edge extended X-ray absorption fine structure spectroscopy (EXAFS) analysis shows that Co barely affects the atomic coordination environments of Mn, and distances of edge- and corner-sharing Co–Me (Me=Co, Mn) pairs are shorter than those of the corresponding Mn–Me pairs, implying the replacement of framework Mn(III) by Co(III). These Co-doped cryptomelanes can quickly oxidize Cr^{3+} to be $HCrO_4^-$ and remove 45%–66% of the total Cr in the reaction systems by adsorption and fixation, and they have enhanced Pb^{2+} adsorption capacities. Thus these materials are promising adsorbents for heavy metal remediation. The results demonstrate the design and modification of environmental friendly Mn oxide materials and can help us understand the interaction mechanisms of transition metals with Mn oxides.

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Introduction

Heavy metal contamination is a current worldwide environmental problem, especially in water and soil. As heavy metals are not degradable and exposure even at trace level is believed to be a risk for human beings, they create huge hazards for human beings and ecosystems (Hua et al., 2012; Bolan et al., 2014; Chung et al., 2014). Pb^{2+}, Zn^{2+}, As, Cr^{3+}, and Cu^{2+} are common contaminants in water. Among numerous methods proposed for heavy metal removal from waters, adsorption by various adsorbents has been widely used due to its selectivity,

simplicity and ease of application, and it is the most common and efficient method of heavy metal treatment in aqueous systems (Mishra et al., 1996; Pan et al., 2009; Sharma and Sohn, 2009). Owing to the small particle size, structure defects and thus negative charges, and the mixed valence of Mn, Mn oxides play a more important role in the adsorption and oxidation of heavy metals in natural environments than other metal oxide adsorbents (Feng et al., 2007; Yin et al., 2011; Hua et al., 2012).

Cryptomelane is a tectomanganate, also called α-MnO$_2$ or octahedral molecular sieve (OMS-2). Its framework consists of

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edge- and corner-shared [MnO$_6$] octahedra forming a 2 × 2 tunnel structure, and the tunnel cavity is filled by cations, such as K$^+$ and H$^+$ (Suib, 2008a,b). Cryptomelane has been widely investigated in the fields of adsorption (Randall et al., 1998; Feng et al., 2007), oxidation (Feng et al., 2007), and catalytic activities (Chen et al., 2007; Lee et al., 2007; Tang et al., 2010; Sun et al., 2011; Zhang et al., 2011; Hou et al., 2013).

Incorporation of cations into the cryptomelane framework likely induces changes in its structure and physicochemical properties. Various cation-doped (Ni^{2+}, Cu^{2+}, Fe^{3+}, Co^{2+}, Mg^{2+}) todorokite and cryptomelane have different conversion rates and selectivity during oxydehydrogenation of ethanol, with Co-doped todorokite showing the highest reactivity (Zhou et al., 1998). Doped cryptomelanes have increased specific surface area (SSA) and pore volume but decreased thermal stability (Chen et al., 2002). Co doping improves the cryptomelane catalytic activity with respect to olefin oxidation as well as significantly affects its electrode performance (Lee et al., 2007). Incorporation of W into the cryptomelane framework creates vacancies and modifies the crystallinity, thermal stability and resistivity (Calvert et al., 2008). Doping V(V) substitutes for Mn(III) in the cryptomelane framework, decreasing Mn AOS and greatly increasing resistivity (Polverejan et al., 2004). More V exists on the cryptomelane surfaces, resulting in more defect surface sites and greatly enhanced catalytic activities in low-temperature complete oxidation of formaldehyde at 140°C and in complete oxidation of methane at 450°C (Tang et al., 2010; Sun et al., 2011). Multiple framework substitution of Mo, V, Cu and Fe into cryptomelane provides a ready way to control the particle size, morphology, and the SSA. Multiple doping also greatly increases the catalytic activity towards the oxidation of diphenylmethanol compared to the undoped cryptomelane materials (King'ondu et al., 2011). Previous studies mainly focused on hydrothermally synthesized cryptomelanes in terms of their reactivities in the catalytic oxidation of organic pollutants and electrochemical applications, while few studies tested the structure and properties of cryptomelanes synthesized at mild conditions and their performance for removing heavy metal pollutants.

In this work, Co-doped cryptomelanes were synthesized at ambient pressure, and their structure and physicochemical properties were characterized by powder X-ray diffraction (XRD), Rietveld structure refinement, wet chemical analysis, scanning electron microscopy (SEM), N$_2$ adsorption, X-ray photoelectron spectroscopy (XPS) and Co K-edge and Mn K-edge extended X-ray absorption fine structure spectroscopy (EXAFS) analysis. These Co-doped cryptomelanes were further used to remove heavy metals (Pb^{2+} and Cr^{3+}) from simulated aqueous solutions. The results will increase understanding into the modification of Mn oxide materials and their applications in remediation of polluted environmental systems. They also provide insight into the interaction mechanisms of transition metals (TMs) with Mn oxide minerals in nature.

1. Materials and methods

1.1. Sample preparation

Co-doped cryptomelanes were synthesized through reflux process at ambient pressure (McKenzie, 1971; Feng et al.,

2007). 80 mL 0.4375 mol/L KMnO$_4$ solution was heated to 60°C and poured into 100 mL solution of 0.5 mol/L CoSO$_4$ + MnSO$_4$ solutions (in which the molar ratio of Co/Mn is 0, 0.05 or 0.10) and 2 mol/L acetic acid at 60°C. The mixture was heated and kept boiling under stirring for 20 min. A suitable amount of 2 mol/L acetic acid was added to make up the volatilized CH$_3$COOH during the reaction. After cooling to room temperature naturally, the obtained slurries were washed with deionized water thoroughly, and then dried in oven at 60°C for several days. After samples were ground in an agate mortar and passed through a 100 mesh sieve, they were stored in closed polyethylene plastic tubes at room temperature. Based on the initial molar ratios of Co/Mn, the products were named Cry, Cry5 and Cry10.

1.2. Physicochemical characterization of Co-doped cryptomelanes

Powder X-ray diffraction analysis of Co-doped cryptomelanes was carried out on a Bruker D8 Advance diffractometer using Ni-filtered, Cu Kα radiation (λ = 0.15418 nm). The diffractometer was operated at a tube voltage of 40 kV and a current of 40 mA with 1.2 sec counting time per 0.02° 2θ step. Sample chemical compositions were determined by atomic absorption spectroscopy 240FS (Varian, Palo Alto, USA) and flame spectrometry Model 410 (Sherwood, Cambridge, UK) after complete dissolution with a mixture of NH$_2$OH·HCl and H$_2$SO$_4$ solutions. Mn AOS was determined by the oxalate reduction-permanganate back titration method (Kijima et al., 2001). Micromorphologies of the samples were probed by scanning electron microscopy JSM-6390LV (NTC, Tokyo, Japan) after being coated with a gold evaporated film. The SSAs of samples were calculated using the BET model based on data measured by N$_2$ adsorption using a standard physical adsorption analyzer Autosorb-1 (Quantachrome, Florida, USA) after degassing 0.1000–0.2000 g samples at 110°C for 3 hr under vacuum. XPS characterization was carried out as described in details in our previous publication (Yin et al., 2012). The charge effect was corrected by adjusting the binding energy of adventitious C (1 s) to 284.80 eV. A Shirley-type background was used.

1.3. EXAFS spectroscopy

EXAFS spectra of Co-doped cryptomelanes were measured at room temperature on the 1W1B beamline at the Beijing Synchrotron Radiation Facility. Co K-edge EXAFS spectra were obtained in fluorescence mode over 7570–8507 eV. The monochromator energy was calibrated to the first derivative of Co-metal (E$_0$ = 7709 eV) prior to measuring each sample. Mn K-edge EXAFS data were collected in transmission mode over the energy range of 6421–7336 eV. A Mn metal foil reference was used (E$_0$ = 6539 eV) to calibrate the monochromator energy.

EXAFS spectra were processed using the program Ifeffit/Athena, including energy calibration, averaging, background removal, and normalization procedures (Ravel and Newville, 2005). Parameters used for background removal of Co K-edge spectra were: E$_0$ = 7726 eV, Rbkg = 1.0 Å and k-weight = 2. Then, the EXAFS spectra were converted into the k^3-weighted function, and Fourier transformed spectra (FTs) were calculated over a k range of 3.1–11.7 Å^{-1}. Mn K-edge spectra