Characterization of Co-doped birnessites and application for removal of lead and arsenite

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ABSTRACT

Nanostructured Co-doped birnessites were successfully synthesized, and their application for the removal of Pb^{2+} and As(III) from aquatic systems was investigated. Powder X-ray diffraction, chemical analysis, nitrogen physical adsorption, field emission scanning electron microscopy (FE-SEM) and X-ray photoelectron spectroscopy (XPS) were used to characterize the crystal structure, chemical composition, micromorphologies and surface properties of the birnessites. Doping cobalt into the layer of birnessite had little effect on its crystal structure and micromorphology. Both chemical and XPS analyses showed that the manganese average oxidation state (Mn AOS) decreased after cobalt doping. The Co dopant existed mainly in the form of Co(III)OOH in the birnessite structure. Part of the doped Co^{3+} substituted for Mn^{4+}, resulting in the gain of negative charge of the layer and an increase in the content of the hydroxyl group, which accounted for the improved Pb^{2+} adsorption capacity. The maximum capacity of Pb^{2+} adsorption on HB, CoB5, CoB10 and CoB20 was 2538 mmol kg^{-1}, 2798 mmol kg^{-1}, 2932 mmol kg^{-1} and 3146 mmol kg^{-1}, respectively. The total As(III) removal from solution was 94.30% for CoB5 and 100% for both CoB10 and CoB20, compared to 92.03% for undoped HB, by oxidation, adsorption and fixation, simultaneously.

1. Introduction

Manganese oxide octahedral molecular sieves (OMS) have been widely used in oxidation catalysts, absorbents, semiconductor and electrochemical materials due to their special layered or porous structure, mixed valence of manganese and specific physicochemical properties, among others [1–6].

Incorporation of various transition metal ions into the framework of manganese oxides by doping with cations is an effective route to enhance the properties of these materials. Zhou et al. successfully doped first row transition metal ions into the framework of todorokite (OMS-1) and cryptomelane (OMS-2). Both the conversion and selectivity of the oxidative dehydrogenation of ethanol over each individual OMS material are highly dependent on the nature of the dopants. The [Co]-OMS-1 materials possess the highest conversion and selectivity in the catalysis of acetaldehyde oxidation among all the materials [7]. The OMS-2 doped with various ions has a higher surface area and pore volume and lower thermal stability compared to undoped analogies [8]. The resistivity, thermal stability and crystallinity of Tungsten-doped OMS-2 are closely related with the amount of exotic ions [9]. The Co substitution for Mn in nanostructured birnessite and cryptomelane leads to the improvement of their catalytic activity with respect to olefin oxidation and significantly impacts their electrode performances [10]. Doping with Co in K-birnessite prepared by calcination and aqueous treatment improves the discharge–recharge capacity and capacity retention in an aprotic Li cell [11]. Bi^{3+} and Pb^{2+} modification facilitates a significantly longer cycle life for birnessite operating in alkaline cells [12,13]. However, these literatures are mainly focused on the fabrication and characterization of doped materials and their application to catalysts for organic oxidation, sensors and cathode fields. Few reports are on the application of modified manganese oxides in the adsorption and oxidation of toxic metal ions from polluted aquatic systems.

Birnessite possesses a layered structure of edge-sharing [MnO_6] octahedra alternating with water layers with either Na^+ or K^+ in the interlayer. Some of the octahedra are vacant, and H^+ and Mn^{3+}/Mn^{2+} are localized above and/or below these sites [14]. Here, birnessite was synthesized by the reaction of mixed, concentrated hydrochloride and cobalt chloride with potassium permanganate solutions at 100 °C at atmospheric pressure for no more than 1.5 h. Owing to their similar sizes and charges, cobalt can substitute for manganese in the layers. However, the electronegativity of cobalt in various crystallographic situations is different from those of manganese, and the Co^{3+}/Co^{2+} redox conjugate pair has a greater standard redox potential than those of $MnO_2/Mn^{3+}/Mn^{2+}$. Thus, the

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purpose of this paper is to investigate the effects of cobalt doping on the crystal structure, morphology, Mn AOS, layer charge and the abundance of hydroxyl groups in the birnessite, the resulting removal of Pb^{2+} and As(III) from aquatic systems, and to discuss the underlying mechanisms. It is helpful to further understand the interaction of manganese oxides with cobalt, the effects of cobalt on the reactivity of manganese oxides, and to synthesize novel environmentally friendly nanoscale manganese oxide materials doped with other transition metal ions in practice.

2. Materials and methods

2.1. Sample preparation

Nanocrystalline Co-doped birnessite was prepared according to McKenzie's method [15]. Mixtures of 45 mL of 6 mol L^{-1} HCl and CoCl$_2$ were added dropwise at a constant velocity of 0.7 mL min^{-1} into a boiling solution of 300 mL of 0.667 mol L^{-1} KMnO$_4$ with vigorous stirring. After boiling for a further 30 min, the suspension was cooled naturally and then aged at 60 °C overnight. The obtained powder was washed thoroughly with DDW and then dried at 40 °C.

Based on the initial molar ratios of Co/Mn, the products were named HB, CoB5, CoB10 and CoB20.

2.2. Lead adsorption experiments

The Pb^{2+} adsorption experiments were conducted at a constant supporting electrolyte concentration (NaNO$_3$, I_c = 0.1 mol L^{-1}). An aliquot of 0–10 mL of 15 mmol L^{-1} Pb(NO$_3$)$_2$ (pH = 5 ± 0.05) was pipetted into a series of 50-mL polyethylene tubes; then the NaNO$_3$ solution was added to fill the volume up to 10 mL. An aliquot of 5 mL of 5 g L^{-1} Co-doped birnessite suspension, which was pre-equilibrated to a pH level of 5, was added into each tube, followed by shaking at 250 r/min for 24 h at 25 °C. The pH of the reaction system was maintained at 5.00 ± 0.05 using a pH-stat technique. At the end of the reaction, the mixtures were centrifuged, and the supernatants were collected for Pb^{2+}, Mn^{2+}, Co^{2+} and K$^+$ analyses by atomic absorption spectrometry (AAS, Varian AAS 240FS) and flame spectrometry (Sherwood Model 410) [16].

2.3. As(III) transformation

The As(III) transformation was carried out at 25 °C while stirring. A quantity of 0.1250 g of birnessite was suspended in 150 mL of 0.1 mol L^{-1} NaNO$_3$ for 12 h to eliminate the effect of stirring and surface aquotization, and the pH was adjusted to 7. A volume of 100 mL of a 0.2 mmol L^{-1} NaAsO$_2$ solution (pH = 7, containing 0.1 mol L^{-1} NaNO$_3$) was quickly poured into the suspension to initiate the reaction. An aliquot of 10 mL of the mixtures was withdrawn and immediately filtered through a 0.45-µm membrane at intervals to investigate the kinetics of the oxidation. After reacting for 7 h, the spent mineral was immediately collected by centrifugation, washed with DDW and then dried at 60 °C overnight. One portion of the spent mineral was analyzed by X-ray diffraction and XPS. The other portion was extracted by 0.1 mol L^{-1} NaOH for 24 h [17]. The total As in solution was detected by hydride generation-atomic absorption spectrometry [18]. As(V) was measured using the colorimetric method described by Oscarson et al. [19].

2.4. Characterization

2.4.1. Powder X-ray diffraction

The crystal structures of the Co-doped manganese oxides were characterized by powder XRD measurements carried out on a Bruker D8 Advance diffractometer equipped with a LynxEye detector using Ni-filtered Cu Kα radiation (λ = 0.15406 nm). The

diffractometer was operated at a tube voltage of 40 kV and a current of 40 mA with a scanning rate of 1°/min at a step size of 0.02°.

2.4.2. Elemental analysis and Mn AOS

The chemical composition of the samples was determined as follows: 0.1000 g of sample was dissolved in 25 mL of 0.25 mol L^{-1} NH$_2$OH·HCl and 1 mol L^{-1} H$_2$SO$_4$. The content of the metal ions was measured using AAS and flame spectrophotometry.

The Mn AOS was obtained by a titration method [20]. A mass of 0.2000 g birnessite was completely reduced to Mn^{2+} in 5 mL of 0.5000 mol L^{-1} H$_2$C$_2$O$_4$ and 10 mL of 1 mol L^{-1} H$_2$SO$_4$. Excess C$_2$O$_4$$^{2-}$ was determined by back-titration using a KMnO$_4$ standard solution at 75 °C.

2.4.3. Specific surface area

The specific surface area (SSA) was examined by nitrogen adsorption at liquid nitrogen temperature using an Autosorb-1 standard physical adsorption analyzer (Quantachrome Autosorb-1, JEDL-6390/LV). The samples were degassed at 110 °C for 3 h under vacuum prior to the adsorption measurement.

2.4.4. Field emission scanning electron microscopy

The crystallite morphologies of samples were probed by field emission scanning electron microscopy with a Jeol JSM-6700F microscope after being coated with a gold evaporated film.

2.5. X-ray photoelectron spectroscopy

X-ray photoelectron spectra were collected using a VG Multilab2000 X-ray photoelectron spectrometer with an Al Kα X-ray source (1486 eV) and a base pressure of 3×10^{-9} Torr in the analytical chamber. The scans were recorded using the large area mode. The survey scans were collected using a fixed pass energy of 100 eV and an energy step size of 1.0 eV, whereas the narrow scans has a pass energy of 25 eV and an energy step size of 0.1 eV. The charge effect was corrected by adjusting the binding energy (BE) of C (1s) to 284.62 eV. The spectra were analyzed using the Avantage software. The Shirley-type background was subtracted before deconvolution and fitting. The parameters used by Nesbitt et al. [21] for the multiplet peaks of Mn (2p$_{3/2}$) for spectra fitting were adopted. A 20:80 ratio of the Lorentzian:Gaussian mix-sum function was used for all the fittings.

3. Results and discussion

3.1. Crystal structure of the Co-doped birnessites

Fig. 1 shows the powder XRD patterns of the obtained samples. The results agree well with JCPDS 86-0666 (hexagonal, $R-3m$). Birnessite is characterized by four detectable peaks: 0.723 nm, 0.361 nm, 0.244 nm and 0.142 nm. Both peaks at 0.723 nm and 0.361 nm are symmetrical, while the other two at the higher angles are greatly widened. The d value ratio of the 0.244-nm peak to the 0.142 nm-peak is close to 1.732, indicating a hexagonal symmetry.

Co-doped birnessites have the same XRD profile as the undoped sample. There are four peaks with similar symmetry and relative intensity. As the initial molar ratios of Co/Mn increase, no extra peaks are detected, which proves that the incorporation of cobalt into the lamellar birnessite did not change the crystal structure, and no second phase was introduced. After Co^{2+} was added, it was immediately oxidized to Co^{3+} by MnO$_4$$^-$. Besides similar sizes and charges, both cobalt and manganese are generally stabilized in layered structures composed of edge-sharing octahedra of Mn^{3+} and/or Mn^{4+} to be replaced by newly formed Co^{3+}. However, there was some tiny change in the profiles, especially in the strongest reflection. As the content of cobalt increases, the intensity of the