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Synthesis, characterization, and catalytic activity of cryptomelane nanomaterials produced with industrial manganese sulfate

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ABSTRACT

Industrial manganese sulfate from manganese mines has been utilized to synthesize cryptomelane in a simple and feasible route. K-birnessite precursor was prepared by air oxidation of the mixture of $MnSO_4$ and KOH solutions under alkaline conditions, and then transformed to cryptomelane under a heating process. The effects of OH^- concentration, airflow rate, liquid reaction temperature, stirring rate, liquid reaction time, washing condition, calcination time, and temperature were investigated. X-ray diffraction (XRD), scanning electron microscopy (SEM), and high-resolution transmission electron microscopy (HRTEM) revealed that cryptomelane prepared under optimal conditions had a tetragonal symmetry and the particles were mostly in short lathy form with sizes of 20–30 nm. The average pore size and BET surface area of cryptomelane examined by N_2 adsorption methods were 24.15 nm and 32.21 m^2/g, respectively. X-ray photoelectron spectroscopy (XPS) studies demonstrated that the average oxidation state of manganese in cryptomelane was about 3.9 in comparison with prephase K-birnessite of 3.4. The synthesized cryptomelane sample showed improved catalytic activity for decomposition of hydrogen peroxide as compared with natural cryptomelane, but lower than those synthesized with hydrothermal and sol–gel methods. The results of this investigation will provide fundamental information for developing a large-scale production process for transforming manganese sulfate to cryptomelane.

1. Introduction

As an important member of manganese oxides, cryptomelane has attracted great attention since a large number of octahedral molecular sieves (OMS) of manganese oxides were found in manganese nodules in the deep-sea region [1]. It is a typical 2 × 2 tunnel structure manganese oxide (OMS-2), which is composed of edge-sharing double $[MnO_6]$ octahedral chains [2,3]. By incorporation of K ions within the tunnels, cryptomelane can be accommodated by mix-valence manganese in the framework [2]. These special properties make cryptomelane a useful and promising material for catalytic oxidation of organic pollutants and as cathode material for lithium batteries [4–6]. Strategies for preparation of cryptomelane are mainly as follows: (1) High-temperature solid-state routes involve the transformation from birnessite which has been ion-exchanged with K ion under high temperature [7,8]. (2) In hydrothermal routes, manganese(II) compounds are oxidized with strong oxidants such as $KMnO_4$, H_2O_2, and $K_2S_2O_8$ by hydrothermal refluxing under acidic conditions to form cryptomelane [9,10]. (3) Sol–gel routes can be explained as reducing $KMnO_4$ with organic reducing agents and result in the formation of a sol or gel [11,12]. At present, organic reducing agents are mainly divided into two groups: multifunctional carboxylic acids such as maleic and fumaric acid and polyols including sugars [11]. Although some work has been done on the synthesis of cryptomelane by a high-temperature solid-state route previously, there are limited studies on synthetic parameters, characterizations, and practical applications [7,8,13]. Recently, great interest has been shown in the latter two methods, because hydrothermal and sol–gel routes can lead to high surface areas and small particle sizes which have been attractive goals for material scientists [14]. However, more fastidious and complicated preparation conditions such as expensive materials or long times (days or even months) for hydrothermal reaction and aging process limit its further expansion of production [15].

Manganese sulfate is a kind of raw product with low added value from manganese mines, which has been mostly used in feeds and raw material for electrolytic manganese preparation [16,17]. Especially, in silver–manganese deposits, it is prevalent to recover more valuable silver from the ores by reducing leaching manganese with sulfuric acid, pyrite, and other new reductants [18]. Manganese sulfate is generated as a by-product from this process. It is significant to develop further processing of manganese sulfate for manganese mines in China.

In this study, a simple and low-cost method was proposed to synthesize cryptomelane with industrial manganese sulfate, by re-

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acting manganese sulfate with excessive potassium hydroxide to form K-birnessite precursors and then transformed into cryptomelane at high temperatures. The preparation parameters, optimal synthetic conditions, characteristics, catalytic activity, and mechanism of cryptomelane formation were well illustrated.

2. Materials and methods

2.1. Materials

Industrial manganese sulfate used in this study was provided by Guangxi Dameng Industry Co., Ltd., with specifications containing $MnSO_4 \cdot H_2O$ 98.0% min, Fe 0.004% max, chloride 0.02% max, and water insoluble 0.05% max. Other chemicals were of analytical grade and purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. Deionized water was used as the solvent and scour.

Natural cryptomelane was collected from a manganese oxide mine in Guangxi Province, southwest of China. Natural samples NC1 and NC2 were from the central and east portions of the mining district, respectively. Within single hand specimens, sample NC1 shows a botryoidal texture in comparison with a veinlet texture in sample NC2.

2.2. Synthesis

In a typical synthesis, 500 ml 0.2 M $MnSO_4$ solutions with 1.5 M KOH solutions were mixed in a conical flask. Air was bubbled through the mixture solution at a flow rate of 30 L/min. The flask was rotary-stirred at a rate of 150 r/min in a water-bath oscillator at 10 °C for 5 h. The precipitate was centrifugally washed several times with fresh water until the filtrate had a pH within a range from neutral to weak alkaline, air-dried, and then ignited at 600 °C for 5 h to transform into cryptomelane. The above conditions were sufficient enough to obtain pure cryptomelane, so one parameter was discussed while fixing others. OH^- concentration, airflow rate, liquid reaction temperature, stirring rate, liquid reaction time, washing conditions, calcination time, and temperature were adjusted respectively to investigate the effect of each parameter. Cryptomelane synthesized under optimal experimental conditions was denoted as SC1.

For comparison, synthetic samples SC2 and SC3 were also prepared by conventional reflux and sol–gel methods, respectively. In a reflux route, a solution of 0.035 mol $KMnO_4$ in 80 ml deionized distilled water was heated to 60 °C and poured into a 60 °C solution of 0.05 mol $MnCl_2$ in 100 ml 2 M diluted acetic acid. The mixture was boiled and stirred under reflux conditions for 1 h. The solid was filtrated, washed, and dried at 50 °C for 1 day. The sol–gel route was used to prepare amorphous manganese oxide precursor and then change it into cryptomelane. Amorphous manganese oxide was obtained by mild reduction of 200 ml 0.15 M $KMnO_4$ with 200 ml 0.0013 M maleic acid. A solution of fresh amorphous manganese oxide, 200 ml 0.1 M KNO_3, and 8 ml concentrated HNO_3 was refluxed for 9 h under 100 °C. Additional details of these syntheses were reported elsewhere [13,19].

2.3. Characterization

The phase and crystal structure of all samples were characterized by XRD using a RIGAKU-RA diffractometer with Cu$K\alpha$ X-ray source ($\lambda = 1.5406$ Å). DSC–TGA curves were obtained on Q600 thermal analyzer at a heating rate of 10 °C in air. The morphology was observed using a Tecnai XL30 SFEG scanning electron microscopy. The powder sample was dispersed in alcohol with an ultrasonator, dropped on a silicon slice, and then coated with carbon. TEM observation was carried out on a Tecnai F30 transmission electron microscope. The pore size distribution and surface area were measured with a Micromeritics ASA2010 surface and porosimetry analyzer. Nitrogen was used as the adsorbent. Each powder sample was degassed in vacuum at 300 °C for 3–5 h to remove pore water. XPS analyses were performed with an AXIS-Ultra spectrometer from Kratos Analytical using Al$K\alpha$ radiation (1486.71 eV). Charging effects were corrected by adjusting the binding energy of C1s to 284.80 eV.

2.4. Catalytic activity

H_2O_2 catalytic decomposition reactions $H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2$ were performed to test the catalytic activities of cryptomelane prepared in different routes. Ten milligrams of each cryptomelane powder was utilized as catalysts to decompose 20 ml 1 M H_2O_2 solution at 0 °C. We did these experiments in triplicate for each sample and calculated the average times for various displacement volumes. The experimental error of time record was controlled in ±1 s. The relation between the concentration of H_2O_2 ($[H_2O_2]_t$) and reaction time could be calculated with

$$[H_2O_2]_t = [H_2O_2]_o - 2n/V, \qquad (1)$$

where $[H_2O_2]_o$ is the initial concentration of H_2O_2, and n represents the moles of O_2 released from H_2O_2 at time t, which can be calculated from the ideal gas law, and V is the initial volume of H_2O_2 (20 ml) [20]. pH value was measured at starting time and final, respectively.

3. Results and discussion

3.1. Experimental parameters

3.1.1. Effect of OH^- concentration

OH^- with high initial concentration, such as $C_{OH^-}:C_{Mn^{2+}} > 10$ was usually used for synthesis of birnessite by oxidation of Mn^{2+} with oxygen [15,21]. In our study, initial $C_{OH^-}:C_{Mn^{2+}}$ values were varied by changing the concentration of KOH. A high concentration of 5.5 mol/L KOH referenced from the dosage of NaOH in the literature [22] was taken into account initially, but too much water was required to wash alkali waste, otherwise no cryptomelane was formed. Four concentrations of half of 5.5, 1.5, and 1.0 M and minimum 0.4 M KOH were examined. In Fig. 1, the characteristic peaks at a 2θ value of 19° assigned to feitknechtite exist in all four patterns before calcination. When $C_{OH^-}:C_{Mn^{2+}} = 2:1$, only feitknechtite is formed as the intermediate, even under highly oxidized conditions. Feitknechtite and K-birnessite are both layerd materials composed of sheets of edge-shared $MnO_x(OH)_{6-x}$ units ($x = 3$ or 6, respectively) [23]. Here feitknechtite cannot transform into cryptomelane while decomposed into hausmannite by a heating process. Along with gradual increase of OH^- concentration, the amount of feitknechtite prephase decreases, corresponding to the appearance of K-birnessite. However, too much OH^- will prevent the formation of K-birnessite when the amount of KOH is further added, which is similar to the process of birnessite formation in concentrated NaOH solution [24]. It might be due to the potential change between manganese oxide phase and oxygen with pH, but the exact mechanism is still unknown [24,25]. When $C_{OH^-}:C_{Mn^{2+}} \geqslant 5:1$, pure cryptomelane phases are obtained after calcinations in our experiments, which are demonstrated only by the differences in crystallinity according to the intensity of diffraction peaks. As shown in Table 1, cryptomelane in sizes of about 25–35 nm are synthesized when $C_{OH^-}:C_{Mn^{2+}} = 5:1$ or 7.5:1. When initial KOH concentration reaches 2.75 M, it results in a poorer crystallization behavior and smaller crystal sizes about 10 nm of cryptomelane. Therefore, it is believed that the alkalinity of the media determines the phase states and crystallinity of the products. An initial $C_{OH^-}:C_{Mn^{2+}}$ range of (7.5–5):1 is proper for synthesis of cryptomelane under alkaline conditions.