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Hydrothermal Synthesis of Birnessite-Type Potassium Manganese Oxide and its Application as Lubricant in Liquid Paraffin

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Potassium manganese oxide materials with high purity was directly synthesized in KOH-H_2O_2-$Mn(OAc)_2$-H_2O system under hydrothermal conditions. The optimum synthetic condition for K-birnessite ($KOH/H_2O_2/Mn(OAc)_2$ = 12:10:1, 150 °C, 48 h) was confirmed by investigating the synthesis processes. K-birnessite samples have been characterized by XRD, SEM, TG and FT-IR. Moreover, the lubrication of K-birnessite, as an additive, was evaluated in a four ball test. Adding K-birnessite in liquid paraffin, the P_B value can be improved from 431 N to 510 N with 1.0 wt % K-birnessite in liquid paraffin.

Keywords: Birnessite, Hydrothermal, Synthesis, Manganese oxide, Lubrication.

INTRODUCTION

Manganese oxide of octahedral layer (OL) and octahedral molecular sieve (OMS) materials have many kinds of crystal forms, which can be divided into three categories *i.e.*, 1-dimensional channels, 2-dimensional layers and 3-dimensional interconnected tunnels [1,2]. Manganese oxides with tunnel and layered structures are a unique class of materials that combine the pore structures with the oxidation-reduction capacity of manganese (+3 - +4). Connected with their interesting structure, cryptomelane (OMS-2) and todorokite (OMS-1) are large enough to accommodate small molecules as well as interstitial cations, which serve as effective absorbents of heavy metal cations and noxious gases [3-5]. These materials have been drawn special attention as a potential cathode material for rechargeable lithium batteries because of the mixed-valence to manganese [6-10]. In addition, their size-selective pores and active oxide surfaces make them excellent candidates for heterogeneous catalysis [11-13].

Birnessite-type (OL) manganese oxides have a two-dimensional layered structure, with the interlayer spacing range nearly about 7.0 Å [14,15]. It is an important precursor for the synthesis of tunnel-structured manganese oxides, such as cryptomelane and todorokite [16]. Cryptomelane (OMS-2) can be prepared by the calcinations of birnessite [17]. Todorokite (OMS-1) can be produced by the hydrothermal treatment of birnessite [18-20]. Generally, the purity of OMS-1 and OMS-2 depend on the purity of their precursor of birnessite, therefore, it seems very important to synthesize high-pure birnessite.

To the best of our knowledge, there are two synthetic methods for the preparation of birnessite. Giovanoli *et al*. [21, 22] have first reported the synthetic process for Na-birnessite, which is divided into two steps, firstly, NaOH solution was added into MnX_2 ($X^- = Cl^-, NO_3^-$, *etc.*) solution to produce the precipitate of $Mn(OH)_2$ and in the second step, the oxygen is bubbled into the suspension with vigorous stirring to oxidize $Mn(OH)_2$ to Na-birnessite. Besides, Feng *et al.* [23,24] have developed a convenient method for the preparation of Na-birnessite. In this process, a mixed solution of NaOH and H_2O_2 is added quickly into a MnX_2 solution while rapidly stirring at room temperature and the suspension was filtered, washed and moved into a reaction kettle. Na-birnessite is finally obtained by hydrothermal treatment of the precipitate in NaOH solution. Herein, it is reported that high-pure K-birnessite can be directly synthesized by one-step synthesis method in the $Mn(OAc)_2$-KOH-H_2O_2-H_2O system, SEM, TG-DSC, FT-IR spectroscopy were used to characterize typical samples. Also, a point contact test was employed to measure its solid lubrication properties as a lubricant additive in liquid paraffin for the first time. Showing that K-birnessite as lubricant additive may increase the P_B value.

EXPERIMENTAL

Manganese acetate tetrahydrate [$Mn(CH_3COO)_2{\cdot}4H_2O$, AR, 99 %], potassium hydroxide (KOH, GR, 95 %), hydrogen peroxide solution (H_2O_2, AR, 30wt % in H_2O) were purchased from Aladdin Reagent (China) Co., Ltd and used without

further purification. Distilled water was prepared in our laboratory.

General procedure: A well crystalline K-birnessite was obtained by improving the typical synthesis method [25]. A synthetic process for K-birnessite was as follows: a mixed solution of 3.4 mL (30 wt %) H_2O_2 and 9 mL (4 mol/L) KOH was quickly poured into 10 mL (0.3 mol/L) $Mn(CH_3COO)_2$ solution, while stirring vigorously. The suspension was subjected to hydrothermal treatment in a Teflon-lined autoclave at 150 °C for 48 h. After the autoclave was cooled to room temperature, the precipitate was collected by filtration, washed with distilled water until the pH value is close to 7 and finally dried at room temperature for 12 h in air.

Powder X-ray diffraction (XRD) patterns were collected on a Rigaku Miniflex II X-ray diffractometer with Cu-K_α radiation (λ = 1.5418 Å) in the 2θ range of 5-50° and with a scan rate of 2°/min. The crystal morphology and size were observed by scanning electron microscopy (SEM) (HITACHI TM-3000). Thermo gravimetric analysis (TGA) was recorded on SETARAM Labsys Evo instrument in air atmosphere with a heating rate of 5°C/min. FT-IR spectrum measurement was performed by KBr method on an infrared spectrometer (SHIMADZU IRAffinity-1).

Lubrication measurement: The load carrying capacity of the samples used as additives in the base oil were evaluated with a four-ball tester at 1450 rpm and room temperature (25 °C). The base oil employed in this work was liquid paraffin. The maximum non-seizure loads (P_B) and load-carrying capacities of K-birnessite were determined according to the China National Standard method GB/T3142-90, which is similar to those determined by ASTM D2783. For each sample, they were carefully milled prior to use until an edge length of about several micrometers was obtained. Prior to and after each test, the steel balls were each cleaned with petroleum ether and then dried in air at ambient conditions. Three identical tests were performed for an average so as to minimize data scattering.

RESULTS AND DISCUSSION

A series of syntheses has been performed to investigate the effect of the synthetic conditions on the final products-including stirring time, mole ratio of initial reactants, crystallizing time and hydrothermal temperature. The purity of K-birnessite was characterized by powder XRD methods.

Effect of the stirring time: Firstly, the effect of stirring time on the K-birnessite formation process was investigated (Fig. 1). As can be seen, the main product of K-birnessite was always accompanied by the impurity phase of Mn_3O_4 if without stirring or insufficient stirring time before hydrothermal treatment in a Teflon-lined autoclave. The diffraction intensity of Mn_3O_4 phase decreased and at the same time-the diffraction intensity of K-birnessite phase increased with extending stirring time. A pure and well crystalline K-birnessite can be obtained when the mixed solution was stirred for 6 h. However, further prolonging stirring time leads to the decrease in the intensity of the diffraction peak for K-birnessite.

Effect of mole ratio of KOH/Mn(OAc)$_2$: The relationship between the purity of products and the mixed mole ratio of

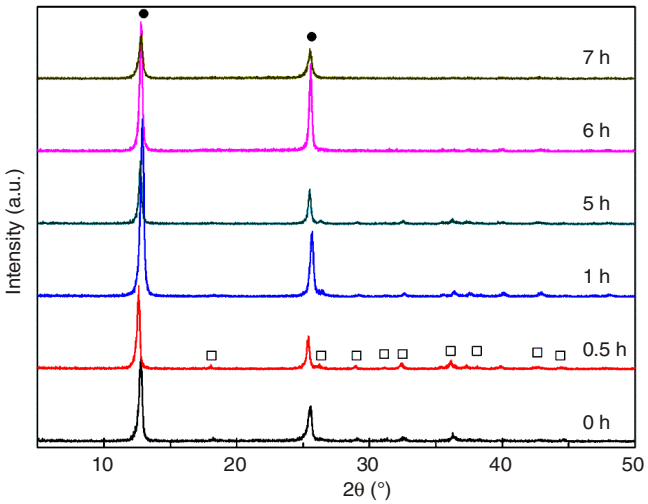

Fig. 1. X-ray diffraction patterns of samples which are prepared at different stirring time (●, K-birnessite; □, Mn_3O_4)

KOH/Mn(OAc)$_2$ are shown in Fig. 2. The mixed mole ratio of KOH/Mn(OAc)$_2$ have important influence on the purity and the diffraction intensity of products. The diffraction intensity of Mn_3O_4 phase decreased and that of the K-birnessite phase increased with the increase mole ratio of KOH/Mn(OAc)$_2$. A pure and well crystalline K-birnessite was synthesized, when the mixed mole ratio of KOH/Mn(OAc)$_2$ = 12:1. It can improve the diffraction intensity of the sample to further increase the amount of KOH, which will affect the purity and the post-processing of the sample.

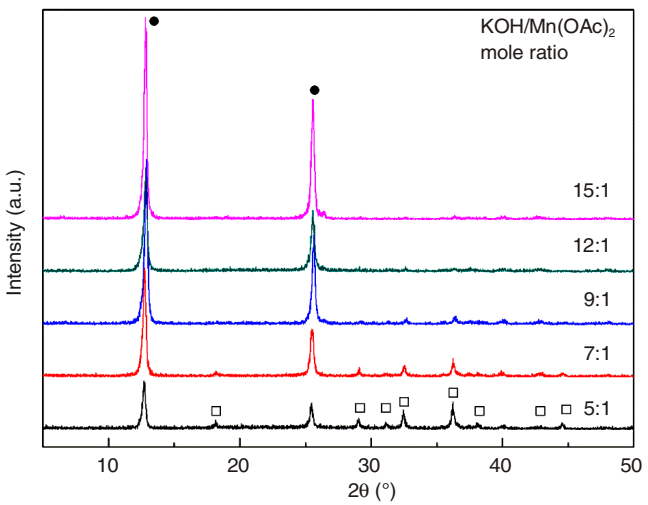

Fig. 2. X-ray diffraction patterns of samples which are prepared at different mole ratio of KOH/Mn(OAc)$_2$ (●, K-birnessite; □, Mn_3O_4)

Effect of crystallizing time: The effect of the crystallizing time on the K-birnessite formation process was studied (Fig. 3). It is observed that the main product of K-birnessite was not obvious and the impurity phase of Mn_3O_4 was predominant before hydrothermal treatment in a Teflon-lined autoclave. The diffraction intensity of Mn_3O_4 phase decreased and that of K-birnessite phase increased with extending crystallizing time. A pure and well crystalline K-birnessite can be obtained after crystallizing 48 h. However, further prolonging crystallizing time leads to the decrease in the diffraction intensity for K-birnessite.

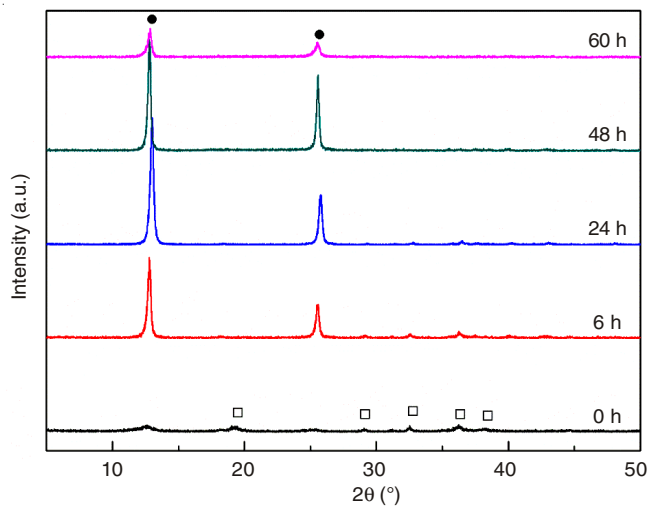

Fig. 3. X-ray diffraction patterns of samples which are prepared at different crystallizing time (●, K-birnessite; □, Mn_3O_4)

Effect of hydrothermal temperature: The effect of the hydrothermal temperature on the K-birnessite formation process was surveyed (Fig. 4). It is observed that the main product of K-birnessite was always accompanied by the impurity phase of Mn_3O_4 if hydrothermal temperature less than 100 °C in a Teflon-lined autoclave. The diffraction intensity of Mn_3O_4 phase decreased and at the same time-the diffraction intensity of K-birnessite phase increased with increasing hydrothermal temperature. A pure and well crystalline K-birnessite can be obtained when the hydrothermal temperature was 150 °C. However, further raising hydrothermal temperature leads to the decrease in the diffraction intensity for K-birnessite. And that K-birnessite will not be obtained until the hydrothermal temperature was 220 °C.

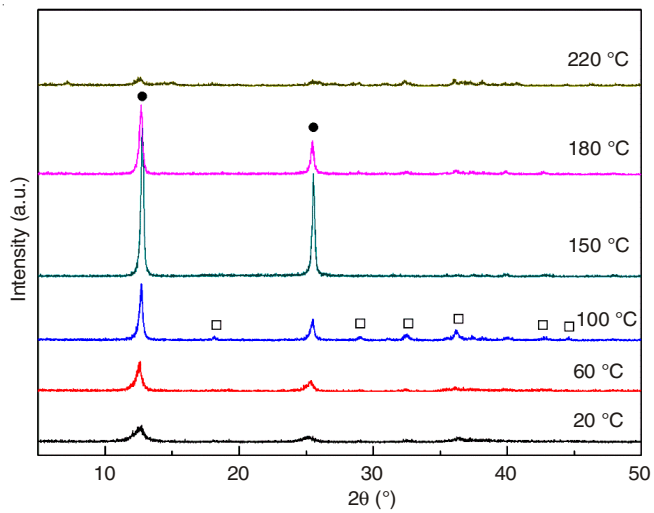

Fig. 4. X-ray diffraction patterns of samples which are prepared at different hydrothermal temperature (●, K-birnessite; □, Mn_3O_4)

In order to better describe the characterization of K-birnessite, a detailed characterization was carried out on the typical sample prepared at the mole ratio of $KOH/Mn(OAc)_2$ = 12:1 and hydrothermal temperature was 150 °C. SEM photo-graph (Fig. 5) of the K-birnessite shows that the sample was consisted of agglomerated plate-like forms.

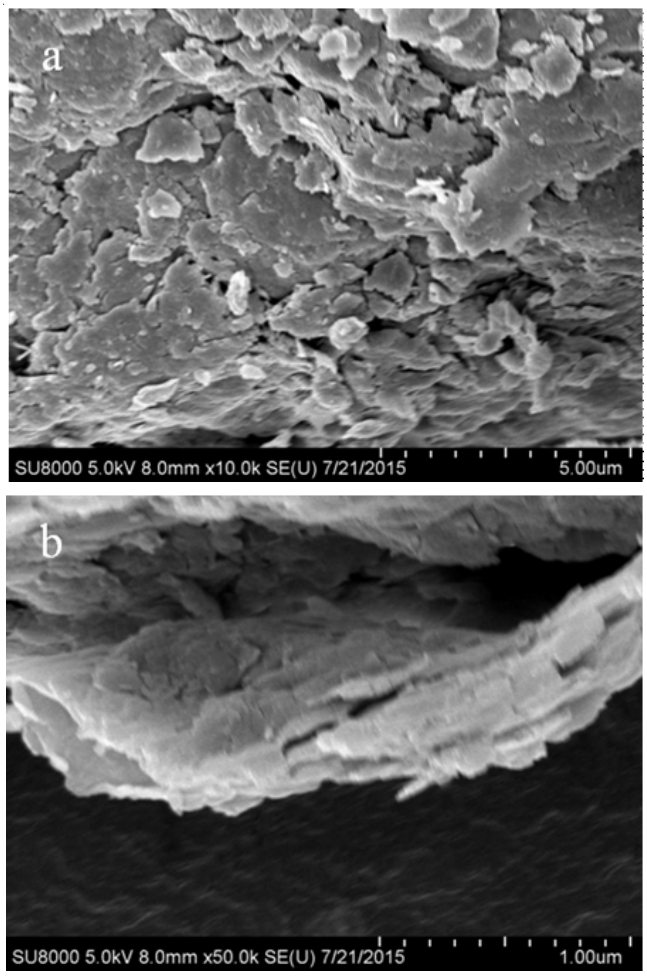

Fig. 5. SEM images of birnessite-type potassium manganese oxide

The thermal stability of K-birnessite samples was investigated by DSC and TG. Fig. 6 shows TG and DSC curves of the K-birnessite sample. In the DSC curve there are two endothermic peaks around 170 °C and 900 °C. The endothermic peak at 170 °C corresponds to the dehydration of crystal water from the interlayer in the K-birnessite. The TG curve shows two obvious weight loss at about 170 and 900 °C which corresponds to the two endothermic DSC peaks, respectively.

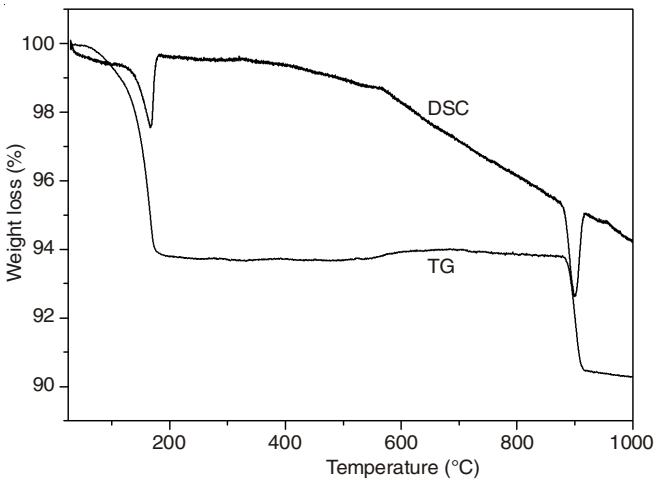

Fig. 6. TG and DSC curves of birnessite-type potassium manganese oxide

FT-IR spectrum of the K-birnessite sample is shown in Fig. 7. A broad band at around 3580 and 3305 cm^{-1} is due to the stretching of water molecules in the interlayer. The absorption bands around 1603 cm^{-1} can be assigned to -OH bending vibration. In the range of less than 800 cm^{-1}, characteristic bands for birnessite at 625, 519, 475 and 419 cm^{-1} correspond to Mn-O stretching modes of the octahedral layers in the birnessite structure [8,26,27].

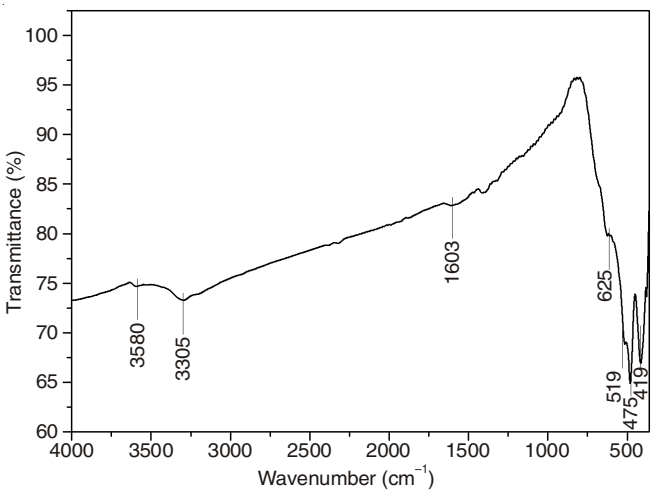

Fig. 7. IR spectrum of birnessite-type potassium manganese oxide

Lubrication properties: The wear limits and the life span of many mechanical devices with moving parts studied and thus, lubricants are often used to reduce wear and tear. When the friction and wear conditions in tribological applications become severe, solid lubricants may be the only choice for controlling friction and wear. Most solid lubricants and additives in liquid lubricants, which include graphite and MX_2 (M = Mo or W; X = S or Se), belong to a specialized class of materials known as lamellar solids [28-30]. Considering that K-birnessite have similar inorganic layered structures. So, it is interesting to investigate the tribological behaviour that as additives in liquid lubricants. The P_B value is an important index to evaluate the load carrying capacity of a lubricant. K-birnessite was first used as an additive to liquid paraffin to improve the lubricating property, the experimental results for pure oil and pure oil with different amount of K-birnessite are shown in Table-1. It was found that adding K-birnessite to liquid paraffin can improve the P_B value of liquid paraffin. The P_B value of liquid paraffin can be improved from 431 N to 510 N with 1.0 wt % K-birnessite in liquid paraffin.

TABLE-1
P_B VALUES IN LIQUID PARAFFIN (LP)

Sample	P_B (N)
LP	431
LP + 0.5 wt. % K-OL	470
LP + 1.0 wt. % K-OL	510
LP + 1.5 wt. % K-OL	470
LP + 2.0 wt. % K-OL	470

Fig. 8 presents the rubbed surface on balls lubricated with pure liquid paraffin and liquid paraffin + 1.0 wt % K-OL an additive. The worn surface lubricated with liquid paraffin presented in Fig. 8(a) is evidently rough, with many thick and deep furrows. However, the worn surface [Fig. 8(b)] lubricated with liquid paraffin + 1.0 wt % K-OL as additive is smoother than that with pure liquid paraffin and the furrows are shallower. This shows that K-OL can be used as a friction modifier of liquid paraffin and can improve the anti-wear properties of liquid paraffin.

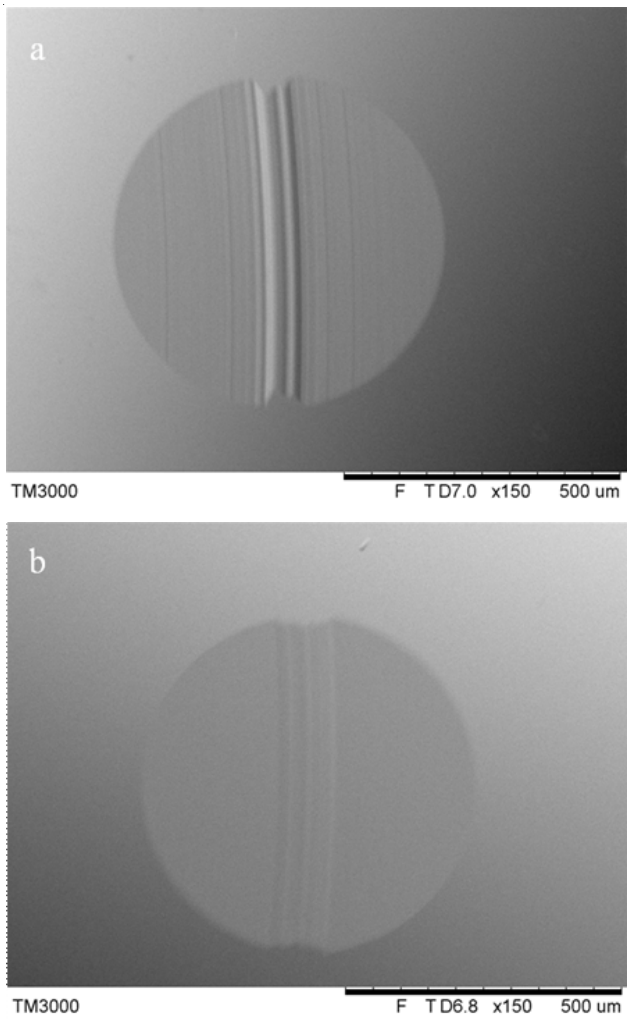

Fig. 8. SEM images of worn surfaces on balls lubricated with (a) pure oil and (b) pure oil containing K-OL (1.0 wt. %)

Conclusion

In summary, a well-crystalline K-OL with high purity was synthesized by one-step method in the $KOH-H_2O_2-Mn(OAc)_2-H_2O$ system. The optimum synthetic condition for K-birnessite was given as follows: the mole ratio of initial reactants [$KOH/H_2O_2/Mn(OAc)_2$ = 12:10:1], hydrothermal temperature (150 °C), crystallizing time (48 h). It was also found that the layered K-OL material as an additive in liquid paraffin can improve its load carrying capacity, showing the potential application as a solid lubrication additive.

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