Microporous and Mesoporous Materials xxx (2016) 1–7

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Highly porous MnO_x prepared from $Mn(C_2O_4)\cdot 3H_2O$ as an adsorbent for the removal of SO_2 and NH_3

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ARTICLE INFO

Article history:
Received 27 August 2015
Received in revised form
6 October 2016
Accepted 15 October 2016
Available online xxx

Keywords:
Nanoporous manganese oxide
Oxalate
Calcination
Surface area
Dynamic flow test

ABSTRACT

In this work, the possibility of substituting metal impregnated activated carbon with nanoporous metal oxides for the adsorption of SO_2 and NH_3 was investigated. Nanoporous manganese oxide (MnO_x) was prepared from manganese oxalate trihydrate by thermal decomposition in air. The physical properties of the oxalate precursor and the resulting MnO_x samples were characterized with SEM, TGA-DSC, mass spectroscopy, FTIR and powder XRD. The specific surface areas and porosity of MnO_x were studied by single-point and multi-point BET measurements. The amorphous needle-like MnO_x had a specific surface area of over 500 m^2/g when the precursor was heated at 225 °C for 6 h. Dynamic SO_2 and NH_3 flow tests indicated that the adsorption capacity of MnO_x depends primarily on the surface area. Compared to Mn_3O_4-impregnated activated carbon, nanoporous MnO_x could remove about twice as much SO_2 and 15% more NH_3 per gram of adsorbent. This could lead to respirators of lower weight and smaller size which will be attractive to users.

1. Introduction

Highly porous carbon materials have been associated with broad applications such as gas capture, energy storage, catalyst supports, etc. [1–8]. In particular, activated carbons (ACs) are commonly used in respiratory protective equipment, not only for their excellent physisorption of organic gases and vapors [1–3], but also as a support to accommodate metal compounds (e.g. oxides, chlorides, carbonates, etc.) on their surface for the chemisorption of low molecular weight gases like SO_2, NH_3, HCN, H_2S, etc. [9–16]. When impregnating ACs with selected metal precursors using the incipient wetness method, the large surface area and wide pore distribution in ACs enable the even deposition of metal compounds, preferably nanosized particles or a nm-thin layer, on the surface of the ACs. After a further drying step, the well-dispersed metal compounds can largely enhance the adsorption capacities of SO_2 or NH_3 on ACs. Our previous studies on impregnated ACs treated with a variety of metal species including Cu, Zn, Co, Ni, Mn, Fe and Al compounds indicated that Mn oxides exhibit high adsorption capacity for SO_2 and Zn oxide is good for NH_3 [17–22].

Although impregnated ACs are good respirator materials, there is always a need to reduce the size and weight of respirators to improve the convenience to users. In impregnated ACs, carbon accounts for 75–90% of the total weight and is an ineffective component for adsorbing SO_2 or NH_3. Hence, it may be useful to directly use nanoporous metal oxides as the adsorbents in the absence of ACs. As a prerequisite, the oxides must inherently have high enough surface area to ensure adequate contact with the toxic gases. As an example, MnO_x obtained from precipitated $MnC_2O_4\cdot 3H_2O$ was reported to have a specific surface area over 500 m^2/g, which plays an important role in its high catalytic activity for CO oxidation [23,24].

In this work, MnO_x was prepared by thermal decomposition of $MnC_2O_4\cdot 3H_2O$. A precipitation reaction between $Mn(NO_3)_2$ and $H_2C_2O_4$ produced pure needle-like $MnC_2O_4\cdot 3H_2O$. The physical properties of the precursor and resulting MnO_x were characterized by SEM, TGA-DSC, powder XRD and FTIR. The decomposition was optimized by finding the temperature which gave the largest single point BET surface area of MnO_x. The porosity of MnO_x was investigated by gas adsorption microporosimetry measurements. The adsorption capacities of MnO_x for SO_2 or NH_3 were obtained through dynamic flow testing and compared to those obtained for activated carbons impregnated with Mn_3O_4.

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http://dx.doi.org/10.1016/j.micromeso.2016.10.019
1387-1811/

2. Experimental section

2.1. Synthesis of $MnC_2O_4{\cdot}3H_2O$ precursor

$H_2C_2O_4{\cdot}2H_2O$ powder (BDH Chemicals, 99.9%) and $Mn(NO_3)_2{\cdot}4H_2O$ powder (Sigma-Aldrich >97%) were used as received to make $Mn(NO_3)_2$ (0.05 M) and $H_2C_2O_4$ (0.06 M) aqueous solutions respectively. 400 ml $H_2C_2O_4$ was slowly added into 400 ml $Mn(NO_3)_2$ solution drop wise using a Masterflex peristaltic pump with vigorous stirring over a period of 12 h. The pH of $H_2C_2O_4$ was adjusted to between 7 and 8 (pH paper was used) using ~5% ammonia (diluted from 28% to 30% ammonia, 99.9%, BDH) before the reaction. Afterwards, the precipitate was filtered and washed with deionized water repeatedly until the pH of the filtrate reached ~7. Then the sample was dried for 24 h in an oven in air at 60 °C.

2.2. Preparation of MnO_x

The thermal decomposition of $MnC_2O_4{\cdot}3H_2O$ was optimized by varying the heating temperature and heating time. First, the precursor was calcined under air for 15 h in a muffle furnace, and the heating temperature ranged from 200 to 350 °C with steps of 25 °C. The optimum heating temperature was determined by checking the surface areas of the MnO_x product. Subsequently, $MnC_2O_4{\cdot}3H_2O$ was heated for 2, 4, 5, 6, 7, 8, 10 or 15 h, respectively, at 225 °C to determine the optimum heating time.

2.3. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM)

SEM images were obtained with a Hitatchi S-4700 field emission SEM. Typical imaging conditions include a working distance of 12.5 mm, an accelerating voltage of 5 kV and a beam extraction current of 15 μA. A small amount of sample was dispersed on a double-sided carbon tape attached to an aluminum sample stub. TEM images were obtained with a JEOL (2010F) field emission TEM/STEM, operating at 200 keV.

2.4. TGA-DSC-MS

Thermal analysis was carried out using a TA SDT Q600 equipped with a mass spectrometer on the gas exhaust stream. $MnC_2O_4{\cdot}3H_2O$ was heated at rates of 5 °C/min to 600 °C and 0.5 °C/min to 300 °C respectively in an air flow of 100 ml/min. The gas components in the effluent air flow were simultaneously inspected by MS.

2.5. Powder X-ray diffraction

Powder X-ray diffraction patterns of the oxalate precursors and manganese oxides before and after gas adsorption were collected using a Phillips PW 1720 X-ray generator operated at a voltage of 40 kV and a current of 30 mA. The system is equipped with a Cu K_α radiation source (wavelength = 1.54178 Å) and a diffracted beam monochromator. Typical conditions were a scan rate of 0.05°/step and a dwell time of 40 s/step. XRD measurements on the samples after gas adsorption were performed on an aluminum holder immediately after the flow tests were finished.

2.6. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of $MnC_2O_4{\cdot}3H_2O$ and MnO_x were collected with an Agilent Technologies Cary 630 FTIR over the range from 400 to 4000 cm^{-1}. FTIR spectra of MnO_x after NH_3 and SO_2 capture were also collected.

2.7. Single-point and multi-point BET

Single-point BET measurements were performed using a Micromeritics FlowSorb II 2300 with a nitrogen/helium flow (28.6% N_2). Samples were degassed at 150 °C for at least 1 h to remove moisture before the measurement. The measurement error of the single point BET measurements is ~2%. The N_2 adsorption isotherms and the pore size distributions of selected MnO_x were determined using a Micromeritics ASAP2010. Samples were degassed at 150 °C for 24 h before the measurement. Herein, all the specific surface areas calculated by the BET method are apparent surface areas. Pore size distributions were determined using the non-local density functional theory (NLDFT) method with a standard slit carbon model.

2.8. Dynamic SO_2 and NH_3 flow tests

Dynamic flow tests were carried out using SO_2 and NH_3 challenge gases of certified standard grade, supplied by Praxair (Dartmouth, Nova Scotia Canada). The needle-shape manganese oxides were loaded in sample tubes with an inner diameter of 6.5 mm. The tubes were tapped gently for 10 min to settle the samples in 1.7 ml. The amount of particles was about 0.3 g. The challenge gas streams were 1000 ± 50 ppm SO_2 or NH_3 in air and the overall flow rate was 200 ± 5 ml/min. The effluent gas stream was bubbled into a scrubbing NaCl solution and the pH of the solution was monitored. The breakthrough time was determined when a sharp pH change was observed. Detailed description of the method can be found in the literature [12,13]. The adsorption performance of SO_2 and NH_3 on MnO_x were also compared with our previous data on Mn_3O_4-impregnated activated carbons [22].

3. Results and discussion

3.1. Characterization of $MnC_2O_4{\cdot}3H_2O$ and MnO_x

Two types of hydrous manganese oxalate can be formed by the precipitation: pink-colored $MnC_2O_4{\cdot}3H_2O$ and white $MnC_2O_4{\cdot}2H_2O$. $MnC_2O_4{\cdot}3H_2O$ crystallizes in the orthorhombic space group *Pcaa* while $MnC_2O_4{\cdot}2H_2O$ belongs to the monoclinic *C*2/*c* space group [25,26]. It has been suggested that the purity of manganese oxalate hydrates largely depends on the pH in a co-precipitation reaction [25]. Viacheslav et al. found that a mixture of $MnC_2O_4{\cdot}3H_2O$ (90%) and $MnC_2O_4{\cdot}2H_2O$ (10%) was produced through the precipitation reaction between $MnSO_4$ and $H_2C_2O_4$ when the pH was near 5–6 [24]. Here, we reacted $Mn(NO_3)_2$ and $H_2C_2O_4$ by controlling the pH at 7–8, and obtained pure $MnC_2O_4{\cdot}3H_2O$. Fig. 1 shows the powder XRD pattern of the precipitation product (bottom panel). No apparent impurity peaks were observed when compared to the literature pattern of $MnC_2O_4{\cdot}3H_2O$ (JCPDS No.32-0648). The reaction between $Mn(NO_3)_2$ and $(NH_4)_2C_2O_4$ forms $MnC_2O_4{\cdot}2H_2O$ when the pH is above 8, which will be discussed in an upcoming paper.

The FTIR spectrum of $MnC_2O_4{\cdot}3H_2O$ is shown in Fig. 2. The IR bands below 2000 cm^{-1} are mainly related to C–O vibrations. The adsorption peak at 480 cm^{-1} corresponds to the O–C–O bending vibration and the peaks at 754 and 794 cm^{-1} are related to the C═C–O bending vibration. The peaks at 1308 and 1360 cm^{-1} derive from O–C–O symmetric stretches whereas the peak of 1590 cm^{-1} arises from its asymmetric stretch. These assignments are reasonably consistent with the previous literature reports for transition metal oxalates [27–29]. The broad band from O–H stretching vibration in the range 3500–3000 cm^{-1} splits into three peaks, because of the coordination difference of water molecules likely participating in hydrogen bonds [29].

Please cite this article in press as: X. Ma, et al., Highly porous MnO_x prepared from $Mn(C_2O_4){\cdot}3H_2O$ as an adsorbent for the removal of SO_2 and NH_3, Microporous and Mesoporous Materials (2016), http://dx.doi.org/10.1016/j.micromeso.2016.10.019