

四方柱 γ -MnOOH 纳米棒的合成和表征

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摘要: 采用水热法, 以十六烷基三甲基溴化铵(CTAB)为表面活性剂, 在 160 °C 的条件下, 用乙醇还原 KMnO_4 合成了四方柱 γ -MnOOH 纳米棒。粉末 XRD 衍射表明合成的材料为单斜的 γ -MnOOH 晶体结构, 扫描电镜观察到四方柱纳米棒的直径为几十纳米, 长度几微米; 纳米棒的形貌随 CTAB 用量增加趋于均一。催化活性测试表明 γ -MnOOH 纳米棒在 120 °C 的低温下可以将甲醛完全氧化为 CO_2 和 H_2O 。

关键词: γ -MnOOH 纳米棒; 水热法; 甲醛氧化; CTAB

中图分类号: O614.7+11 文献标识码: A 文章编号: 1001-4861(2008)09-1468-06

Synthesis and Characterization of γ -MnOOH Nanorods with Tetragonal Prism Cross Section

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Abstract: The γ -MnOOH nanorods with tetragonal prism cross section were synthesized by the hydrothermal route at 160 °C through reacting KMnO_4 with ethanol in the presence of different amounts of cationic surfactant cetyltrimethylammonium bromide (CTAB). The powder X-ray diffraction results reveal that the materials are γ -MnOOH with the monoclinic crystal structure. The SEM observations show that the diameters of the nanorods are several tens of nanometers and lengths of several micrometers, and that the shapes of the tetragonal prism cross section nanorods become more uniform with increasing amounts of CTAB. The catalytic activity of the γ -MnOOH material towards formaldehyde oxidation shows that complete conversion of formaldehyde to CO_2 and H_2O can be achieved at a temperature as low as 120 °C.

Key words: γ -MnOOH nanorod; hydrothermal method; formaldehyde oxidation; CTAB

0 Introduction

The structure of monoclinic manganite (γ -MnOOH) consists of MnO_6 octahedra sharing edges to form single octahedral chains. These chains are corner-linked by oxygen atoms parallel to the b-axis to a three-dimensional framework^[1]. The octahedral framework of manganite is characterized by endless 1×1 edge-shared

MnO_6 octahedral chains, which are corner-connected to form one-dimensional channels of about 0.23 nm×0.23 nm parallel to the c-axis. The hydrogen position is located in the interstitial channels between the chains, and bonds to oxygen together with a hydrogen bond to another oxygen^[2].

Manganite, γ -MnOOH, possesses also a structurally related MnO_2 modification named pyrolusite, β -

收稿日期: 2008-04-15。收修改稿日期: 2008-06-05。

国家自然科学基金(No.20707012, 20437010); 中国博士后自然科学基金(No.20070410070) 资助项目。

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MnO₂ (rutile structure type), and thus γ -MnOOH is a precursor for the preparation of β -MnO₂. Due to the one-dimensional channels, manganite and pyrolusite are of considerable importance in several technological applications such as catalysts^[3], rechargeable batteries^[4], adsorption materials^[5]. Various synthetic routes have been employed to prepare γ -MnOOH, such as a precipitation process with a surface active agent^[6], the hydrothermal route with oxidizing agents, KMnO₄^[7] or NaClO₃^[8]. Among them, the redox hydrothermal method is the most commonly used route. Sharma et al^[9] used a hydrothermal method with KMnO₄ and tetraethyl ammonium hydroxide as reagents to obtain fiber-like MnOOH at 170 °C for 4 d. Two phases of MnOOH (manganite and feitknechtite) have been simultaneously synthesized with cetyltrimethylammonium bromide (CTAB) as a cationic surfactant at 120 °C in an autoclave for 72 h^[10].

The surfactant plays a key role in controlling the morphologies of the samples. Cetyltrimethylammonium bromide (CTAB) is a versatile cationic surfactant favoring for the formation of one-dimensional (1D) nanostructures^[11] and has been used to efficiently tune the morphology of MnOOH nanomaterials. Single crystalline MnOOH multipods were synthesized by a reductive hydrothermal method with the use of PEG200 to reduce KMnO₄. When the surfactant CTAB was added into the starting reactant, 1D single crystalline MnOOH nanowires were formed instead of multipods^[7]. MnOOH whiskers were chemically synthesized in the presence of CTAB using MnSO₄·H₂O as the manganese source and ethylamine as the alkali source^[10]. Large-scale γ -MnOOH was synthesized via the hydrothermal process assisted with CTAB at 200 °C for 20 h using MnSO₄ and NaOH^[12].

Here we report the synthesis and catalytic performance for formaldehyde oxidation of the γ -MnOOH nanorod with tetragonal prism cross section. This is motivated by the fact that formaldehyde is becoming a major indoor pollutant emitted from widely used construction and decoration materials, and a long-term exposure to indoor air containing just a very low concentration of formaldehyde may be harmful to human health^[13].

1 Experimental

1.1 Synthesis of MnOOH nanorods

1.0 g of KMnO₄, 5 mL of CH₃CH₂OH, a desired amount of cetyltrimethylammonium bromide (CTAB) and 70 mL of distilled water were put in a stainless steel autoclave (100 mL) and kept at 160 °C for 24 h before naturally cooling to room temperature. The obtained precipitates were filtered, washed with distilled water and then dried at 110 °C in air for 12 h. The yield of the MnOOH product was about 95%. The amounts of CTAB were adjusted to be 1.0, 2.0 and 3.0 g, respectively. These obtained materials were denoted as MnOOH-1, MnOOH-2, and MnOOH-3, where the number represents the amount of CTAB in grams in the process of synthesis.

1.2 Characterization of MnOOH nanorods

The products were characterized by powder X-ray diffraction (XRD) on Bruker D8-advance X-ray diffractometer at 40 kV and 40 mA for monochromatized Cu K α (λ =0.154 18 nm) radiation.

BET-surface area was measured by N₂ adsorption at liquid nitrogen temperature using a Micromeritics ASAP 2010 automated gas sorption system. Prior to measurements, the samples were degassed in vacuum at 100 °C for 2 h.

Temperature programmed reduction (TPR) of the samples was carried out using ChemiSorb 2720, Micromeritics. 0.2 g catalyst was reduced in the stream of 10.0% H₂/Ar mixture at a flow of 30 mL·min⁻¹ by 10 °C·min⁻¹ ramp rate.

Thermogravimetric analysis (TGA) and differential thermogravimetry (DTG) were carried out on a TGA 2050 thermogravimetric analyzer with a heating rate of 10 °C·min⁻¹ from 30 °C to 700 °C in the flowing air.

Morphologies of the MnOOH materials were investigated by field-emission scanning electron microscopy (SEM) images using (JEOL JSM-6700F) operated at a beam energy of 3.0 kV, and the structure of MnOOH-1 was examined with transmission electron microscopy (TEM) by a JEM 1010 electron microscope operated at an accelerating voltage of 200 kV.

1.3 Catalytic activity of MnOOH nanorods

The oxidation of formaldehyde was performed in a fixed-bed reactor under atmospheric pressure. The catalyst (200 mg, 40~60 mesh (841~420 μm)) was sandwiched by quartz wool layers in a quartz tube reactor ($\Phi=8$ mm). Gaseous HCHO was generated by passing an O_2/He gas mixture over paraformaldehyde (96%, Acros) in an incubator kept at 45 $^\circ\text{C}$, leading to a feed gas composition of 0.04% (volume percent, φ) and 10.0% oxygen balanced with nitrogen. The total flow rate was 100 $\text{mL} \cdot \text{min}^{-1}$. The effluents from the reactor were analyzed with an on-line Agilent 7890A gas chromatograph equipped with TCD and FID detectors.

2 Results and discussion

2.1 Crystal structure

Fig.1 shows the XRD patterns of the samples hydrothermally synthesized with different amounts of CTAB at 160 $^\circ\text{C}$ for 24 h. All samples have the same XRD pattern with intensive and sharp diffractions at $2\theta=26.4^\circ$, 34.1° , 37.4° , 54.0° , 55.1° and 65.3° , which can be readily indexed to a monoclinic γ -MnOOH (PDF 41-1379). With increasing amounts of CTAB in the process of synthesis, the XRD peaks of the obtained MnOOH products become increasingly intensive, indicating that the degree of the crystalline is higher. The XRD results indicate that phase-pure γ -MnOOH is synthesized through the hydrothermal reaction between KMnO_4 and ethanol in distilled water, similar to the previous reports^[14,15].

2.2 Morphology

Fig.2 shows SEM images of the γ -MnOOH nanostructure synthesized with varied amounts of CTAB surfactant, and Fig.3 gives the TEM image of the

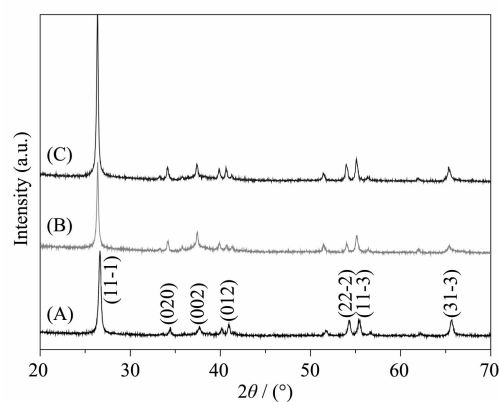


Fig.1 XRD patterns of MnOOH nanorods: (A) MnOOH-1, (B) MnOOH-2, and (C) MnOOH-3

MnOOH-1 nanostructure. For the materials prepared using 1.0 g CTAB in the starting solution, the nanofibrous shapes with diameters of several tens nanometers and lengths of several micrometers were produced. Simultaneously, significant amounts (up to about 50%) of whiskers with sizes of several nanometers were also produced. The selected area electron diffraction (SAED) pattern performed on the whiskers in Fig.3 indicates that the nanowhiskers are of single crystal and could be indexed as the monoclinic MnOOH phase, which is in agreement with the XRD results. When the amount of CTAB is increased, the tetragonal prism nanorods with square cross-sections could be clearly observed and the whiskers are rapidly decreased. Therefore, it is clear that the concentration of CTAB affects the morphologies of the MnOOH materials.

A versatile cation surfactant of CTAB is favorable for the synthesis of the nanorods. Yang et al.^[12] comparatively studied the function of CTAB in a manganese-containing solution, and found that the CTAB molecules played the critical role for the



Fig.2 SEM images of tetragonal prism MnOOH nanorods: (A) MnOOH-1, (B) MnOOH-2, and (C) MnOOH-3

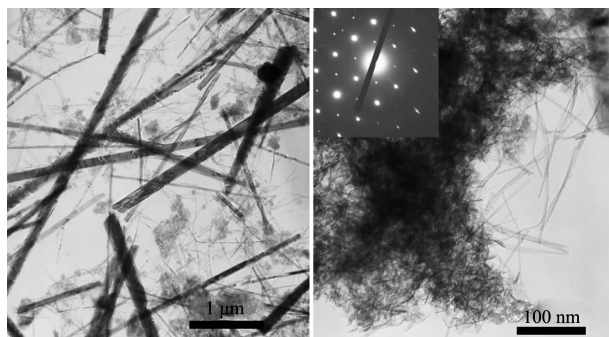


Fig.3 TEM images and SAED pattern of MnOOH-1 nanorods

formation of γ -MnOOH nanorods, whereas only MnO_2 nanoparticles were obtained without CTAB assistance by the same hydrothermal process. The experimental results reported by Li et al.^[16] indicated that the concentration of the CTAB surfactant played key roles in determining the final morphologies of nano-ZnS, and CTAB possibly acted as a molecule-directing template for the growth of nanowires. Thus, the addition of more CTAB favors for the anisotropic growth of MnOOH nanocrystals.

2.3 Thermal stability

Fig.4 shows the TG and DTG plots of the MnOOH-3 nanorods. The weight loss could be categorized into three segments. According to the literature^[10], the initial weight loss of 2.0% below 120 °C is due to the removal of physically adsorbed water, in good agreement with previous observations. The following weight loss in the temperature range of 120~300 °C should correspond to the dehydroxylation. The XRD pattern shows that γ -MnOOH completely transfers to MnO_2 calcined at 300 °C in air. The weight loss is about 11.5%, which is far more than the theoretical weight loss corresponding to the decomposition of γ -

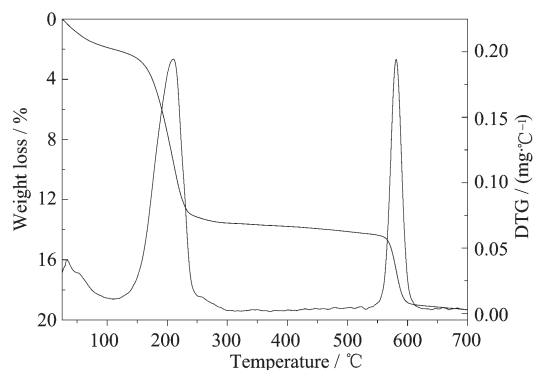


Fig.4 TG and DTG curves of the MnOOH-3 nanorods

MnOOH to MnO_2 . This presumably indicates that the CTAB existed in the layered mesostructures simultaneously decomposes and is removed in this temperature window^[17]. No weight loss is observed at the temperature from 300 up to 530 °C. The third peak at 530~630 °C is due to deoxygenation of MnO_2 to Mn_2O_3 with a weight loss of about 5.5%.

2.4 Temperature-programmed reduction

Fig.5 shows the H_2 -TPR profiles of the MnOOH-3 nanorods. The H_2 -TPR profile of MnOOH shows two strong reduction peaks. A weak reduction peak is centered at 256 °C and a strong reduction peak at 392 °C, with an area ratio of the lower to the higher temperature hydrogen consumption of 1:6. According to the thermogravimetric analysis of MnOOH in an inert atmosphere (N_2 or Ar)^[15], the following reaction will occur: $12\gamma\text{-MnOOH} \rightarrow 4\text{Mn}_3\text{O}_4 + \text{O}_2 + 6\text{H}_2\text{O}$ at temperatures lower than 300 °C. The reaction ($6\gamma\text{-MnOOH} + \text{H}_2 \rightarrow 2\text{Mn}_3\text{O}_4 + 4\text{H}_2\text{O}$) possibly takes place in the reduction atmosphere (H_2) at the same temperature window. Hence, the low temperature reduction could be assigned to the partition reduction of $\gamma\text{-MnOOH}$ to Mn_3O_4 , and the high-temperature reduction corresponds to the combined reduction of Mn_3O_4 to MnO and the residual $\gamma\text{-MnOOH}$ directly to MnO ($2\gamma\text{-MnOOH} + \text{H}_2 \rightarrow 2\text{MnO} + 2\text{H}_2\text{O}$).

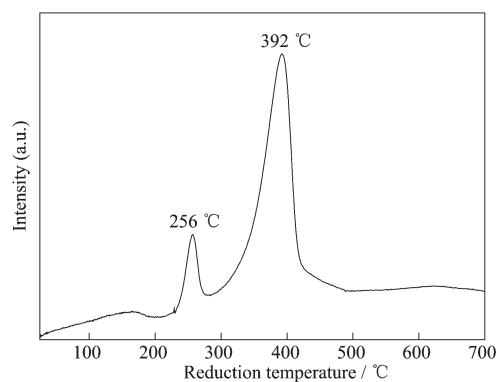


Fig.5 TPR profile of MnOOH-3 nanorods

2.5 N_2 adsorption-desorption isotherm

Fig.6 shows the N_2 adsorption-desorption isotherms of the MnOOH nanorods. The isotherm corresponds to Type II adsorption isotherm. A hysteresis loop of Type H3 for the MnOOH nanorods, according to IUPAC classifications of types of hysteresis loops^[18], occurs at

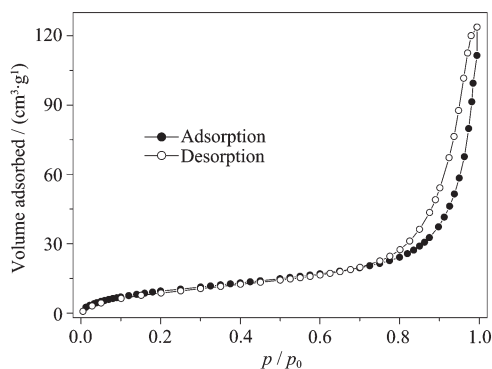


Fig. 6 N_2 adsorption-desorption isotherms for the MnOOH-3 nanorods

high p/p_0 close to saturation, suggesting the existence of slit-shaped capillaries with parallel plates (p and p_0 are the adsorption and saturation vapor pressure of N_2 at 77 K, respectively). The BET surface area of the MnOOH is $40 \text{ m}^2 \cdot \text{g}^{-1}$.

2.6 Catalytic oxidation of formaldehyde

Fig. 7 presents the conversion of formaldehyde over the MnOOH-3 nanorods as a function of reaction temperature. The MnOOH-3 nanorods show promising catalytic activity for the oxidation of formaldehyde. The products consist only of H_2O and CO_2 , and no harmful intermediates are found such as CO and formic acid. HCHO conversion of 100% could be achieved at a temperature as low as 120°C , and even at 80°C the conversion of HCHO is more than 20%, which shows as high as or even better activity than the supported precious metals at such low temperatures^[19]. Catalytic activity is much lower than the previously reported manganese dioxide nanorods^[20], where the temperature required for the total oxidation of formaldehyde is 80°C .

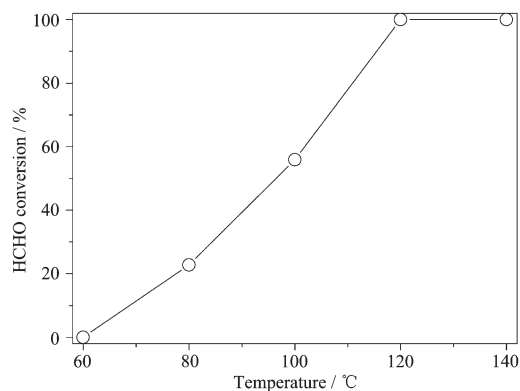


Fig. 7 Oxidation of formaldehyde over the MnOOH-3 nanorods

The results possibly indicate that the oxidation state of manganese and crystal structure has a significant effect on the catalytic activity towards formaldehyde oxidation. Further investigations are necessary to establish the activity-structure correlation of the γ -MnOOH nanorods.

3 Conclusions

Tetragonal prism cross section γ -MnOOH nanorods were synthesized by the redox hydrothermal route. The nanorods were characterized by nitrogen adsorption-desorption, XRD, TGA, SEM and TEM techniques, and investigated for complete oxidation of formaldehyde at low temperatures. The γ -MnOOH material consists of the nanorods with widths of several tens nanometers and lengths of several micrometers, and the shapes of the nanorods becomes uniform with increasing amounts of CTAB. The catalytic test results show that the γ -MnOOH nanorods has significantly high activities for low temperature oxidation of formaldehyde, and that complete conversion of formaldehyde to CO_2 and H_2O can be achieved at a temperature as low as 120°C .

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