

Synthesis and structural characterization of copper incorporated manganese oxide OMS-2 materials synthesized via potassium birnessite

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Abstract

Metal ion incorporated tunnel structured manganese oxide OMS-2 has been recently exploited as potential materials in the field of heterogeneous catalysis. Cryptomelane type copper incorporated manganese oxide OMS-2 type tunnel structured material has been synthesized by hydrothermal method using birnessite-containing potassium as a parent precursor instead of using birnessite containing sodium. Crystal structure and thermal stability of as synthesized materials are characterized by using XRD and TGA. Surface area and morphology of newly synthesized copper incorporated OMS-2 type materials have been studied by BET and SEM analyses.

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1. Introduction

Cryptomelane is one of the major manganese oxide minerals found in the deep-sea manganese nodules and in soil sediments [1]. Cryptomelane has a tunnel structure, which is shown in Fig. 1b. The tunnels consist of (2×2) matrix of edge-shared MnO_6 octahedral chains that are corner shared to form a one-dimensional tunnel structure [2]. Manganese oxide OMS type materials are widely used in many chemical processes because of their porous structure, mild surface acid–base properties and ion-exchange abilities. Especially, the divalent and trivalent transition metal ions doped cryptomelane type manganese oxide OMS-2 type materials, with specific pore size of 4.6 Å, were developed recently as promising catalysts for the oxidation of alcohols and compounds containing side chain [3]. The sorption property of manganese oxide OMS-2 material is used to remove various radionuclides from radionuclear wastes [4].

Hydrophobic property of cryptomelane type manganese oxide OMS-2 material is successfully tested for total oxidation of volatile organic compounds [5]. Conventionally, cryptomelane type K-OMS-2 material is synthesized by redox reaction between potassium permanganate and manganese(II) sulphate in acidic medium under reflux conditions [3]. Doping of various

transition metal ions in the OMS-2 material provides modified surface acid–base property and electronic property on the oxide lattice of OMS-2 material [6]. Catalytic decomposition of isopropyl alcohol on copper containing OMS-2 material has been reported [7]. Synthesis of iron(III) doped cryptomelane type OMS-2 material by calcination method has also been reported [8]. Hydrothermal synthesis of copper doped OMS-1 type (3×3) matrix tunnel structured manganese oxide from birnessite containing sodium precursor has also been investigated [9]. The main aim of the present study is to elucidate the influence of preparation method in the formation of different morphology of the manganese oxide OMS-2 materials.

In the present study, the formation of copper doped cryptomelane type OMS-2 material has been attempted from layered structured potassium birnessite (Fig. 1a). Potassium birnessite is synthesized by oxidation route in strong alkaline medium, using oxidizing agents such as potassium permanganate and potassium persulphate. Potassium containing birnessite is synthesized using potassium hydroxide as the precipitating agent for the formation of hydrous manganese oxide material. As synthesized manganese hydroxide suspension is oxidized either by potassium permanganate (designated as K-OL-1-permanganate) or potassium persulphate (designated as K-OL-1-persulphate). As synthesized layer structure potassium birnessite material is ion exchanged with copper sulphate solution in aqueous medium. Copper exchanged birnessite material is then subjected to hydrothermal treatment in the presence of copper sulphate

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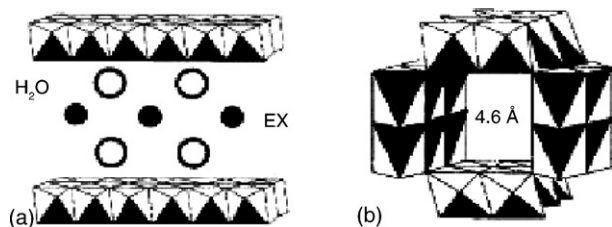


Fig. 1. (a) Potassium birnessite (Ex = K) and (b) cryptomelane type K-OMS-2 structure.

solution, resulting in the formation copper incorporated OMS-2 type tunnel structure manganese oxide material. Copper incorporated manganese oxide OMS-2 catalyst synthesized from potassium birnessite material (K-OL-1-permanganate) is designated as Cu-OMS-2-permanganate and copper incorporated manganese oxide OMS-2 catalyst synthesized from potassium birnessite (K-OL-1-persulphate) is designated as Cu-OMS-2-persulphate.

2. Experimental

2.1. Materials and methods

All chemicals were purchased from Merck (India) and the samples were characterized by powder X-ray diffraction method using Philips Diffractometer (Philips Generator, Holland, Model PW 1140) provided with an online recorder. The diffraction patterns were recorded using Fe K α ($\lambda = 1.97 \text{ \AA}$) radiation at scanning speed of 2° min^{-1} . Thermal stability and phase transitions were analyzed by using Perkin-Elmer Delta Series DSC 7 instrument, at $10^\circ \text{ min}^{-1}$ scanning rate. Scanning electron micrographs (SEM) were taken with JEM 35 model, JEOL. Co. Surface area values of as synthesized materials were obtained by Brunauer–Emmett–Teller (BET) method using Carlo–Erba sorptometer (Model 1800). All the samples were de gassed at 400 K for 12 h. Nitrogen adsorption analysis is used to characterize the textural properties of porous materials, such as the surface area, pore volume and pore size. The instrument used for nitrogen adsorption analysis is NOVA 2200 from Quantachrome Corporation. Chemical composition of the synthesized material was analyzed by using Atomic absorption spectrometry (Solaar32 AA) and Flame photometry. Oswa digital potentiometer was used for the determination of average oxidation state of manganese.

2.2. Synthesis of parent potassium birnessite

Birnessite type potassium containing octahedral layer manganese oxide materials (Fig. 1a) were synthesized by oxidation route in strong alkali medium. One hundred and twenty milliliters of 5.0 M KOH solution was added drop wise to 50 mL of 0.5 M manganese(II) acetate solution. As synthesized hydrous Mn(OH) $_2$ suspension was then oxidized by 40 mL of 0.2 M potassium permanganate solution to get potassium birnessite (which is designated as K-OL-1-permanganate). To prepare another sample, the synthesized Mn(OH) $_2$ hydrous suspension is oxidized by 55 mL of 0.2 M potassium persulphate to get potassium birnessite, which is designated as (K-OL-1-persulphate). As synthesized two types of birnessite samples (K-OL-1-permanganate and K-OL-1-persulphate) were aged for 5 days, which resulted in the formation of potassium containing birnessite type layer material.

2.3. Preparation of copper incorporated OMS-2 catalyst from K-OL-1-permanganate

The synthesized K-OL-1-permanganate layered structure birnessite (1.0 g) was ion exchanged with 50 mL of 0.2 M copper sulphate solution in aqueous medium for 2 days. Copper exchanged birnessite material was washed with distilled water and hydrothermally treated for 24 hours at 390 K, resulting in the

formation of copper incorporated manganese oxide OMS-2 catalyst, which is designated as Cu-OMS-2-permanganate.

2.4. Preparation of copper incorporated OMS-2 catalyst

As synthesized layered structure of potassium birnessite (1.0 g) {K-OL-1-permanganate} was ion exchanged with 50 mL of 0.2 M copper sulphate solution in aqueous medium for 2 days. Copper exchanged birnessite material was washed with distilled water and hydrothermally treated for 24 h at 390 K, which resulted in the formation of copper incorporated manganese oxide OMS-2 catalyst (designated as Cu-OMS-2-permanganate). In the same way Cu-OMS-2-persulphate catalyst was prepared from K-OL-1-persulphate.

3. Results and discussion

3.1. X-ray diffraction study

The X-ray diffraction patterns of potassium birnessite materials (K-OL-1-permanganate and K-OL-1-persulphate) are shown in Fig. 2a and b. The layer structure of birnessite in the synthesized samples was confirmed by X-ray diffraction pattern, having a major intense peak at 7 \AA d-spacing value and a minor peak at 3.5 \AA . These values agree with the reported data [2] and the generalized composition of birnessite is expressed as $A_xMn_{2\pm y}O_2(H_2O)_z$. Fig. 3a and b shows the XRD patterns of

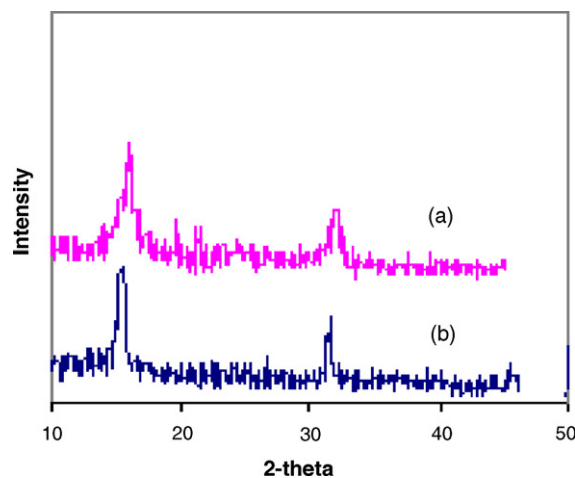


Fig. 2. XRD patterns of potassium birnessite: (a) K-OL-1-permanganate and (b) K-OL-1-persulphate.

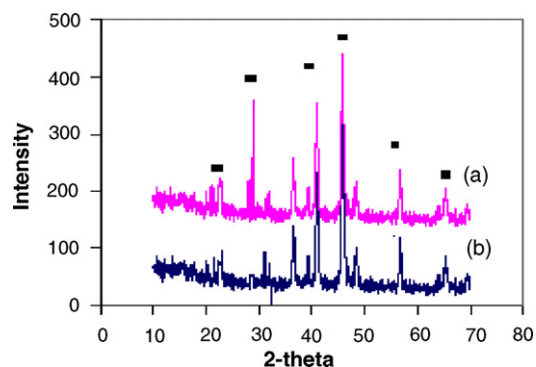


Fig. 3. XRD pattern of copper incorporated OMS-2 catalysts: (a) Cu-OMS-2-permanganate and (b) Cu-OMS-2-persulphate.

Table 1
Analysis of potassium birnessite and copper doped OMS-2 samples

Element (mol g ⁻¹)	Cu-OMS-2-permanganate	Cu-OMS-2-persulphate	K-OL-1-permanganate	K-OL-1-persulphate
K	0.0025	0.003	0.0065	0.0068
Cu	0.0016	0.0012	–	–
Mn	0.0124	0.0118	0.0082	0.0073

copper incorporated OMS-2 type manganese oxide catalysts such as Cu-OMS-2-permanganate and Cu-OMS-2-persulphate. The d-spacing values of major intense peaks of copper incorporated OMS-2 samples agree with major d-spacing lines of JCPDS data 34-168, corresponding to cryptomelane type manganese oxide OMS-2 structure, which has a generalized composition of $\text{KMn}_8\text{O}_{16}$.

3.2. TGA, elemental analysis and average oxidation state of as synthesized samples

Thermogram (TG) of potassium birnessite (K-OL-1-permanganate and K-OL-1-persulphate) materials in nitrogen atmosphere shows the initial weight loss below 353 K is due to removal of water present on the surface or physisorbed water molecules on the manganese oxide layer structure. The major weight loss (423–473 K) is due to the release of water molecules present inside the layer structure results in the formation of lower valent manganese oxide such as Mn_2O_3 or Mn_3O_4 (TG curves not shown in this article). Fig. 4a and b shows the TG curves of as synthesized copper incorporated OMS-2 type manganese oxide materials such as Cu-OMS-2-permanganate and Cu-OMS-2-persulphate in nitrogen atmosphere. In both the samples, the weight loss below 383 K is due to the removal of water molecules present on the surface of manganese oxide lattice and weight loss around 583 K, due to the release of chemisorbed water molecules present in the manganese oxide lattice [10]. As synthesized copper incorporated OMS-2 type manganese oxide phase is (Cu-OMS-2-permanganate and Cu-OMS-2-persulphate) decomposed into a stable lower valent manganese oxide like Mn_2O_3 at 753 K (Fig. 4a and b) due to the collapse of tunnel structure [6].

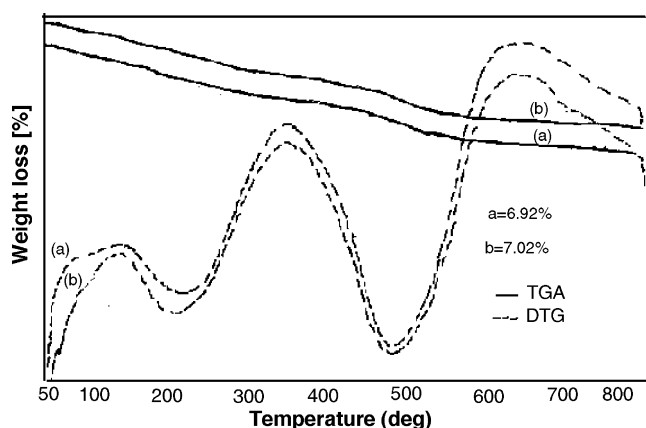


Fig. 4. TGA of copper incorporated OMS-2 catalyst: (a) Cu-OMS-2-permanganate and (b) Cu-OMS-2-persulphate.

Mixed valence state of manganese is normally determined by titration method using thiosulphate [11] or sodium bismuthate [12]. In the present study, electrochemical method such as potentiometric titration is adopted to determine the average oxidation state of manganese present in the sample [13]. Potentiometric titration contains two parts: the first part is to determine the total amount of manganese(II) present in the sample and the second part to determine the amount of manganese present in the higher valence state. An average oxidation state of manganese in copper doped cryptomelane type material (Cu-OMS-2-permanganate and Cu-OMS-2-persulphate) is found to be 3.8 and 3.76. The amounts of potassium, copper and manganese present in the as synthesized copper doped OMS-2 materials are given in Table 1. The copper content is found to be more in the as synthesized copper incorporated OMS-2 catalysts (Cu-OMS-2-permanganate and Cu-OMS-2-persulphate) when compared to that of conventionally (reflux method) synthesized copper doped OMS-2 material [10].

3.3. BET surface area and scanning electron microscopy characterization

BET surface area values of 51.5 and 46.8 m² g⁻¹ were obtained for copper incorporated OMS-2 catalysts such as Cu-OMS-2-permanganate and Cu-OMS-2-persulphate, respectively. Fig. 5a–d shows the electron microscopy picture of copper incorporated OMS-2 catalysts such as Cu-OMS-2-permanganate (Fig. 5a and b) and Cu-OMS-2-persulphate (Fig. 5c and d). Permanganate method synthesized sample (Cu-OMS-2-permanganate) at higher magnification (2 μm range) shows the fibrous needle shape morphology (Fig. 5a) with particle size of 2–5 μm and at 20 μm range aggregated particle morphology was observed (Fig. 5b). Persulphate method synthesized sample (Cu-OMS-2-persulphate) shows only the globular shape aggregated particle morphology (Fig. 5c) with crystal size of 0.5–1 μm range (Fig. 5d).

3.4. Discussion

Successful incorporation of copper ions in the cryptomelane type OMS-2 structure depends on many factors such as size and charge of the cation, preparation conditions for the formation of OMS-2 type manganese oxide materials. Copper ion exchanged potassium birnessite type layer material plays an important role for the formation of OMS-2 type tunnel structure manganese oxide in the hydrothermal process. In the hydrothermal process, the pillaring of MnO_6 octahedra between birnessite octahedral sheets results in the formation of perpendicular set of octahedral sheets of OMS-2 structure. The large K^+ ions can act

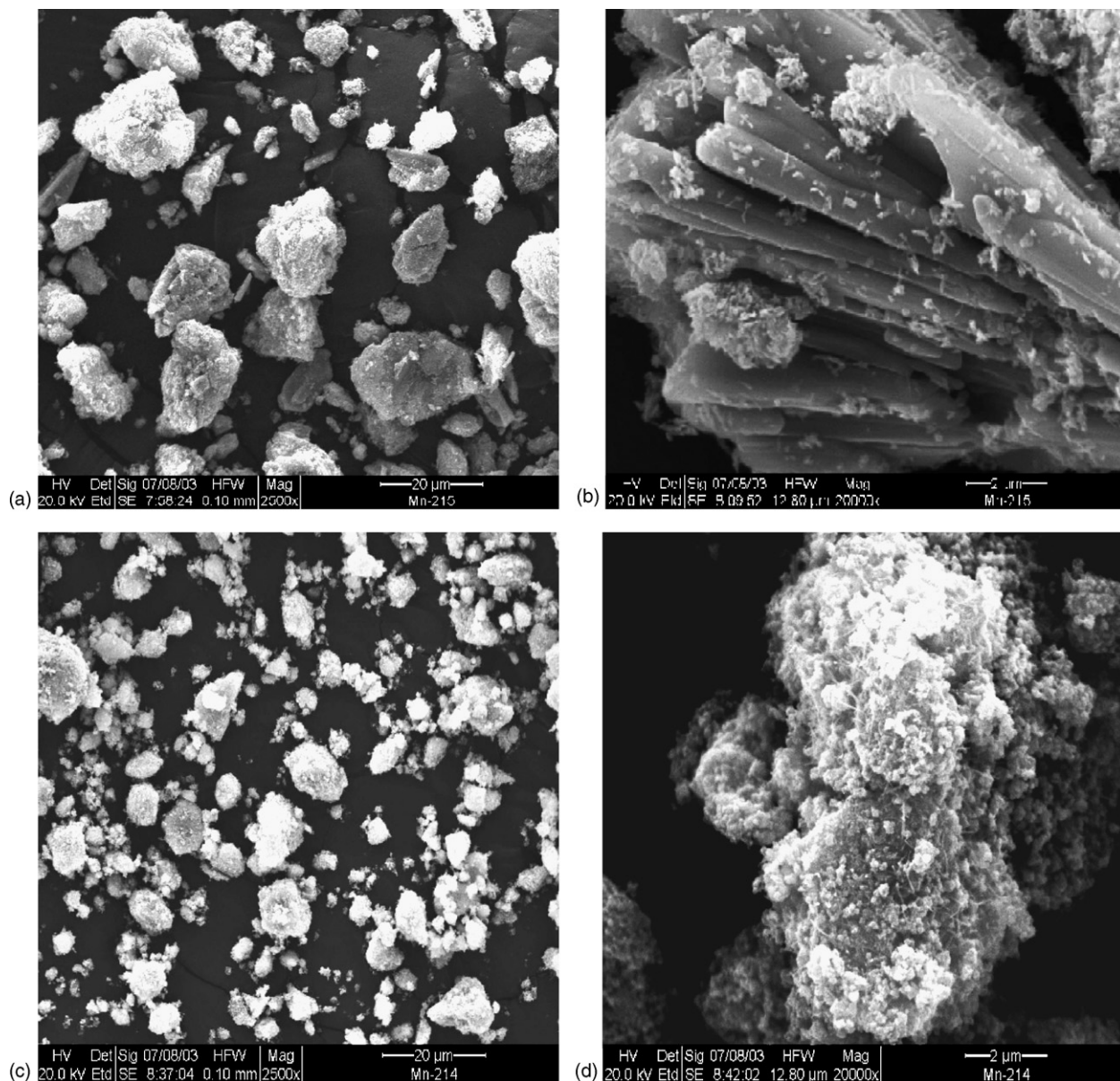


Fig. 5. SEM images of copper incorporated catalyst: (a and b) Cu-OMS-2-permanganate and (c and d) Cu-OMS-2-persulphate.

as spacers between octahedral sheets and they help to prevent the collapsing of birnessite layers in the hydrothermal process. Synthesized copper ion incorporated OMS-2 samples by potassium birnessite precursor method show higher copper content than that of conventionally synthesized copper doped OMS-2 material. XRD and TG analyses further confirm the thermal stability and stable crystalline phase of the as synthesized copper incorporated OMS-2 catalysts. Hydrothermal treatment of as synthesized copper ion exchanged potassium containing birnessite material produces the copper incorporated OMS-2 type materials, whereas copper ion exchanged sodium containing birnessite material produces OMS-1 type tunnel structure [14]. This suggests that the exchangeable alkali cation present inside the layer structure of birnessite is playing a major role in the formation of specific tunnel structure manganese oxide material.

4. Conclusions

Copper incorporated OMS-2 type manganese oxide with ordered tunnel structure has been synthesized by adopting suitable preparation conditions, instead of conventional methods such as reflux and sol-gel methods. Potassium (interlayer cation) in the birnessite type layer material plays a major role to form the OMS-2 type tunnel structure manganese oxide materials. Copper content present in the as synthesized OMS-2 (Cu-OMS-2-permanganate and Cu-OMS-2-persulphate) materials is found to be higher compared to conventionally synthesized copper doped OMS-2 samples. Cu-OMS-2-permanganate material shows fibrous and needle shape particle morphology, whereas Cu-OMS-2-persulphate shows only the globular type aggregated particle morphology. Copper incorporated manganese oxide

OMS-2 materials can function as potential redox catalyst for oxidation reactions.

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