

SO₄²⁻ ion induced synthesis of manganese oxide octahedral molecular sieves (OMS-2)

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Abstract

The investigation reports manganese oxide OMS-2 phase formation induced by sulphate ions, unlike the conventional use of the cations K⁺, Pb²⁺ or Ba²⁺. OMS-2 is synthesised by NaClO₃ oxidation of Mn(II)SO₄ and phase formation is confirmed by XRD and infrared spectral analysis. The material also showed high proton exchangeability in aprotic medium confirming the presence of active 'OH' groups in the structure.

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1. Introduction

Octahedral Manganese Molecular Sieves are currently considered as hot materials for their possible wide variety of applications such as ion exchange materials, batteries, radioactive waste immobilization materials, catalytic materials, electrode materials for electrochemical processes, as chemical sensors for reductive gases, etc. [1]. OMS-2 are MnO_x ($x = 1.85\text{--}2.0$) materials with 2 × 2 type tunnels, built up with [MnO₆] octahedra with pore diameter 4.6 Å. OMS materials are thus porous and analogous to zeolites. They can thus be used as molecular sieves and as shape selective catalysts. They are known to exhibit small particle sizes and large surface areas upto 250 m²/g, which make them outstanding materials for various oxidation reactions. The properties of these materials like acidity, pore size, shape, etc. can be varied by altering the method of preparation, doping

with suitable cations, etc. Hence their synthetic strategies are of great importance. The various OMS-2 forms viz cryptomelane, hollandite and coronadite are known to be formed in the presence of K⁺, Ba²⁺ and Pb²⁺ respectively. They can be conveniently synthesised by (i) heat treatment of birnessite at 600 °C and (ii) KMnO₄ oxidation of Mn(II)SO₄ in acidic medium [2]. Synthesis of OMS-2 has also been reported to be formed by disproportionation of Mn₂O₃ in sulphuric acid medium without the specific use of any template [3]. It is also known to be synthesised electrochemically and effect of cations like Ca²⁺, Mg²⁺, Na⁺, K⁺, Cs⁺, etc. on the phase formation has been discussed [4]. Till date there are no reports in literature in the use of anion templates. Herein we report synthesis of OMS-2 by chlorate oxidation and show the important role of sulphate ions in the formation of OMS-2 type materials.

2. Experimental

In this investigation, OMS-2 is synthesized by the chlorate method. In a typical synthesis, 0.025 mole of

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$\text{MnSO}_4 \cdot \text{H}_2\text{O}$ is dissolved in 50 ml water and then acidified with 25 ml concentrated HNO_3 . The temperature of the solution is controlled at $98 \pm 2^\circ\text{C}$ and then oxidized by adding solid KClO_3 such that Mn(II) salt and chlorate are in a 1:1.3 molar ratio. The quantities of reactants and nitric acid used here were optimized to give maximum yield of the product. In the present case, 100% yield was obtained. For comparison, OMS-2 was also synthesized by oxidation of acidified MnSO_4 with KMnO_4 by literature methods [2]. Manganese oxides were also obtained by KClO_3 oxidation of Mn(II)-nitrate. The samples were characterized by chemical analysis to determine the average oxidation state 'x' following the procedure adopted elsewhere [6].

The infrared spectra of the samples were run in the range $400\text{--}4000\text{ cm}^{-1}$ on a Shimadzu DR-8031 FTIR spectrometer. XRD analysis of the samples was carried out on Shimadzu labX-100 diffractometer to confirm the crystal phase. The H^+ ion exchange capacity was evaluated by use of KI in dimethyl formamide.

Chemical analysis of the OMS-2 samples revealed that the chemical composition was $\text{MnO}_{1.88}$ corresponding to an average oxidation state of manganese 3.76. These values were close to those reported by DeGuzman et al. [2]. Table 1 gives the details of preparation and analysis. The XRD patterns are given in Fig. 1. The d and I/I_0 values of sample S_1 [Fig. 1(a)], prepared in this work were same as that reported [2,5] (See Table 2). Both these samples were prepared by KMnO_4 oxidation of MnSO_4 . However the sample S_2 , in this work is prepared by using KClO_3 as an oxidizing agent.

It can be seen from the figure, that sample S_1 and S_2 have identical XRD profiles. This confirms that OMS-2 can also be obtained by chlorate method. The K^+ ion is known to be the template responsible for formation of (2×2) tunnels of OMS-2 [2]. In order to understand the role of SO_4^{2-} ion in phase formation, the sample S_3 was prepared in a similar manner as that of S_2 , but using Mn(II)nitrate in place of Mn(II)sulphate. As can be seen in the figure, its XRD pattern has become significantly diffuse, similar to that of nsutite or $\gamma\text{-MnO}_2$ [6–8]. Also the characteristic peak of cryptomelane or OMS-2, seen at $d \sim 1.80 \text{ \AA}$ ($2\theta \sim 50^\circ$), in S_1 or S_2 is greatly reduced in

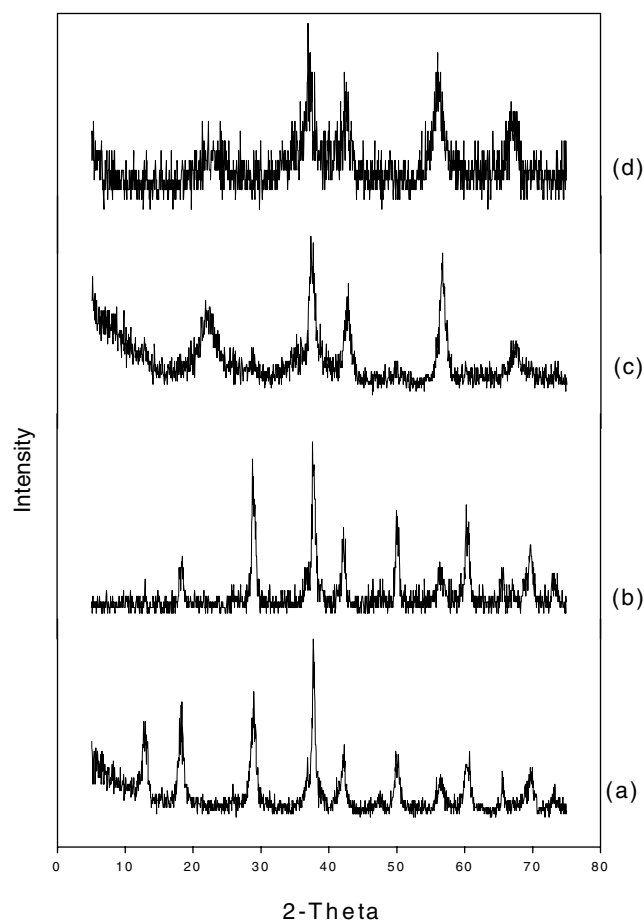


Fig. 1. XRD profiles of the samples obtained by various methods (a) KMnO_4 oxidation of $\text{MnSO}_{4(\text{aq})}$ (S_1), (b) KClO_3 oxidation of $\text{MnSO}_{4(\text{aq})}$ (S_2), (c) KClO_3 oxidation of $\text{Mn}(\text{NO}_3)_2(\text{aq})$ (S_3) and (d) same as S_3 but solid state reaction (S_4). All samples were prepared in nitric acid medium.

intensity for S_3 . Thus S_3 is an OMS-2/nsutite mixed phase. This confirms the crucial role of the SO_4^{2-} ion in formation of OMS-2 phase, even though the precipitation was carried out in the presence of K^+ ions. In fact in a similarly prepared sample S_4 , even the residual OMS-2 peak that could be seen at $2\theta \sim 50^\circ$ has vanished, and the pattern is akin to the nsutite phase. Thus, among the Mn(II) salt precursors, Mn(II) NO_3 seemed

Table 1

Synthesis of manganese oxides in relation to its crystal phase and H^+ ion exchange capacity

Sample	Reagents	Chemical analysis		Oxidation state 'x'	Crystal phase	$V_{\text{S}_2\text{O}_3}$ (ml)
		% MnO_2	%Mn			
S_1	$\text{MnSO}_4 + \text{HNO}_3 + \text{KMnO}_4$	86	61.81	3.76	OMS-2	3.4
S_2	$\text{MnSO}_4 + \text{HNO}_3 + \text{KClO}_3$	81.51	63.18	3.63	OMS-2	1.3
S_3	$\text{Mn}(\text{NO}_3)_2 + \text{HNO}_3 + \text{KClO}_3$	92.38	63.18	3.85	OMS-2/nsutite	1.8
S_4	$\text{Mn}(\text{NO}_3)_2 + \text{HNO}_3 + \text{KClO}_3^{\text{a}}$	83.42	61.81	3.69	Nsutite	3.3
S_5	$\text{MnSO}_4 + \text{HNO}_3 + \text{NaClO}_3$	91.48	60.43	3.91	OMS-2	5.8

All the precipitation reactions were aqueous and carried out at $\sim 100^\circ\text{C}$.

^a SSR—solid-state reaction—the salt solutions were mixed together, evaporated to dryness on a water bath and then calcined at 200°C .

Table 2
Typical X-ray powder diffraction pattern of the samples

S ₁		S ₂		S ₃		S ₄		S ₅	
<i>d</i>	<i>hkl</i> ₀	<i>d</i>	<i>hkl</i> ₀	<i>d</i>	<i>hkl</i> ₀	<i>d</i>	<i>hkl</i> ₀	<i>d</i>	<i>hkl</i> ₀
6.91	59	–	–	–	–	–	–	6.80	40
–	–	–	–	4.07	83	4.15	43	–	–
4.84	72	4.81	26	–	–	–	–	4.85	27
3.08	87	3.10	90	3.07	15	–	–	3.08	37
2.38	100	2.39	100	2.40	100	2.43	100	2.39	100
2.14	36	2.14	40	2.11	49	2.13	52	2.14	42
1.91	15	1.91	–	–	–	–	–	2.00	11
1.83	40	1.82	40	1.83	11	–	–	1.81	20
1.63	33	1.63	41	1.62	51	1.64	73	1.62	20
1.52	39	1.53	52	–	–	–	–	1.52	25
–	–	–	–	1.39	34	1.40	54	–	–

to favour nsutite formation while Mn(II)SO₄ favoured cryptomelane or OMS-2 formation under similar experimental conditions. In order to further confirm that SO₄²⁻ ion is essential for OMS-2 formation rather than K⁺ ion, synthesis of another sample S₅ was subsequently carried out in a similar manner as S₂, the only difference being that, an equivalent amount of NaClO₃ was used as oxidizing agent in place of KClO₃. In both cases, MnSO₄ concentration was same. Once again XRD pattern revealed that OMS-2 was formed. Thus one can conclude that OMS-2 can be formed irrespective of whether the cation is K⁺ or Na⁺ ion, but in either case, SO₄²⁻ ion is essential. Whether the manganese dioxide is OMS-2 type or nsutite can also be detected by IR spectroscopy (Fig. 2), wherein OMS-2 samples show characteristic absorption at around 700 cm⁻¹ [6]. Such an absorption is prominent in OMS-2 samples S₁, S₂ and S₅. In the nsutite sample S₄, however, this absorption

has almost disappeared, while it appears as a shoulder in the OMS-2/nsutite mixed phase sample, S₃.

In order to understand the reactivity of the samples, the H⁺ ion exchange capacity was determined in DMF medium [6]. It is seen from Table 1, that the H⁺ ion exchange capacity expressed as volumes of thiosulphate consumed, *V*_{S₂O₃²⁻}. The H⁺ ion exchange capacity is directly related to the presence of acidic 'OH' groups attached to Mn³⁺ in the host Mn(IV) oxide lattice [9]. The reaction involves liberation of iodine from KI after the exchange of H⁺ from MnOOH groups by K⁺ ions. The iodine thus liberated was estimated by titrating with 0.01 M Na₂S₂O₃ solution. The volume of the thiosulphate consumed is considered to give a fair measure of the relative activity of the manganese dioxides. It is known from literature that the stoichiometric Mn(IV) oxide has no exchangeable 'OH' groups, is catalytically and electrochemically inactive, and shows no evolution of I₂ in the ion exchange experiment [6,9]. It is seen from the volumes of thiosulphate consumed (Table 1) that all the Mn(IV) oxides prepared in this investigation, are active materials.

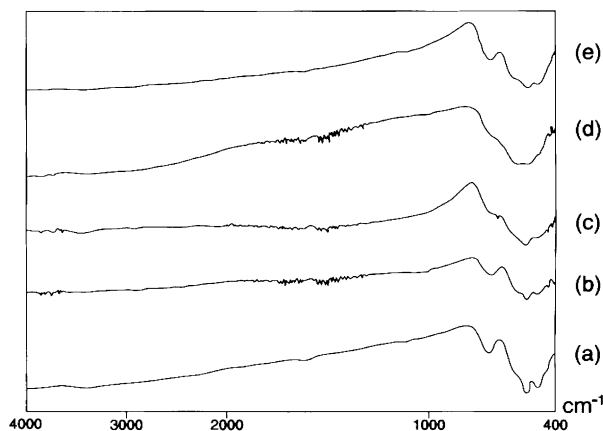


Fig. 2. Infrared spectra of the samples obtained by various methods (a) KMnO₄ oxidation of MnSO_{4(aq)} (S₁), (b) KClO₃ oxidation of MnSO_{4(aq)} (S₂), (c) KClO₃ oxidation of Mn(NO₃)_{2(aq)} (S₃), (d) same as S₃ but solid state reaction (S₄) and (e) NaClO₃ oxidation of MnSO₄ (S₅). All samples were prepared in nitric acid medium.

3. Conclusions

This is the first report which shows the formation of OMS-2 in the presence of SO₄²⁻ ion without the need for K⁺, Pb²⁺ or Ba²⁺ ions. Although pH has been considered as a factor which controls the OMS-2 phase formation [2], it cannot be a determining factor in this case since the synthesis is carried out in a strongly acidic medium. Thus, under the present conditions, the investigation confirms that (i) SO₄²⁻ ion has a crucial role in OMS-2 phase formation, (ii) OMS-2 could be synthesized without the presence of K⁺ ion, (iii) OMS-2 could be formed in a facile manner by use of chlorate as oxidizing agent in place of permanganate and (iv) OMS-2 samples could be successfully characterized both by IR and XRD techniques.

The investigation needs to be extended further to examine possible OMS-2 phase formation in presence of other anions.

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