Single-step synthesis of manganese oxide octahedral molecular sieves with large pore sizes†

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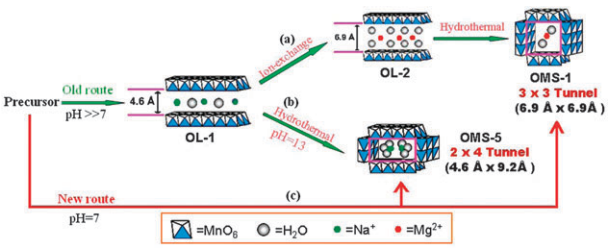
A facile single-step method was developed for synthesizing todorokite-type manganese oxide octahedral molecular seieves (OMS-1) and 2 × 4 tunnel structured manganese oxide (OMS-5) materials. Selection of starting materials and initial pH conditions in the syntheses are crucial.

Porous materials have attracted a great deal of interest in the past several decades due to their wide potential applications.[1] Recent fundamental research efforts on porous manganese oxide octahedral molecular sieves (OMS) have been directed towards controlling the tunnel size, which determines the physical and chemical properties of OMS materials.[2,3] The semiconducting OMS materials have found applications in the fields of catalysis,[4] battery material,[5,6] electrode,[7,8] sensors,[9] separation,[10] and selective absorption[11] in environmental chemistry because of their unique mixed-valence character, tunable pore size and versatile nano-structures. However, even with such versatility and promising potential of OMS materials, only the relatively small tunnel-structured OMS materials have been prepared in a single step. For example, pyrolusite type of manganese oxide with 1 × 1 tunnel structure and cryptomelane type of manganese oxide with 2 × 2 tunnel structure have been synthesized in a one-step redox reaction.[12] The syntheses of the relatively large tunnel-structured OMS materials, such as todorokite type manganese oxide with a 3 × 3 tunnel structure (OMS-1, ESI-1†) and an OMS-5 manganese oxide with a 2 × 4 tunnel structure, are usually complicated by requiring multi-steps.[3c,13] Scheme 1a and b show the traditional routes to prepare these two large tunnel OMS materials. These conventional procedures focused on preparing layered materials as a precursor under strong basic conditions and then converting the layered precursor materials to OMS-1 and OMS-5 materials. Even though different techniques were used to prepare these materials, such as microwave-assisted hydrothermal and reflux methods,[14] the preparative processes are still multi-step and time-consuming. Moreover, precursors used in the final hydrothermal treatment step require very high purities, which make the synthesis very challenging. This demanding process to some extent has significantly limited the application of big tunnel OMS materials.



Scheme 1 New and conventional routes to prepare OMS materials. (a) Conventional three-step route to synthesize OMS-1—Step 1: synthesis of layer-structured birnessite type manganese oxide, denoted as OL-1; Step 2: ion-exchanging of OL-1 to magnesium type buserite, denoted as OL-2; Step 3: hydrothermal treatment of OL-2 to obtain OMS-1.[3c] (b) Conventional route to prepare OMS-5 material.[3a] (c) Newly developed route to prepare OMS-1 and OMS-5 materials in single-step procedure.

The difficulty with all these conventional methods is to initiate the preparation with the production of a layered manganese oxide precursor which requires high pH conditions, in which the precursors can only remain in a layered structure form and cannot be further transformed into the desired OMS-1 products.[3c,d] As a result, the reaction must be stopped and restarted in another reaction with the as-prepared precursor under neutral conditions. Thus, no single-step preparation has been reported due to this fundamental difficulty of requiring two very different pH conditions in one step.

Here, we demonstrate a facile single-step hydrothermal method to synthesize these two types of OMS materials, OMS-1 and OMS-5 (ESI-2†). The key is to select a proper starting material to obtain a suitable pH condition, instead of using conventional high pH conditions. For the case of OMS-1, the chosen starting compound, $Mg(MnO_4)_2$, is able to self-adjust the pH conditions to be neutral while forming the MnOx precursor, and also have the proper template ion (Mg^{2+}) to assist in the formation of tunnel structure. With this concept, the OMS-5 material can also be prepared following this similar strategy (Scheme 1c).

Fig. 1a shows the powder X-ray diffraction (XRD) pattern of the as-synthesized OMS-1 material. Diagnostic peak positions at 9.5 Å and 4.8 Å are observed and correspond to a pure OMS-1 phase.[13b] High Resolution Transmission Electron Microscopy (HR-TEM) image in Fig. 1b shows lattice fringes from the (100) plane (d = 0.95 nm) reconfirming the crystalline character of OMS-1 materials. Fig. 1c shows XRD patterns of OMS-5. All observed peaks can be indexed

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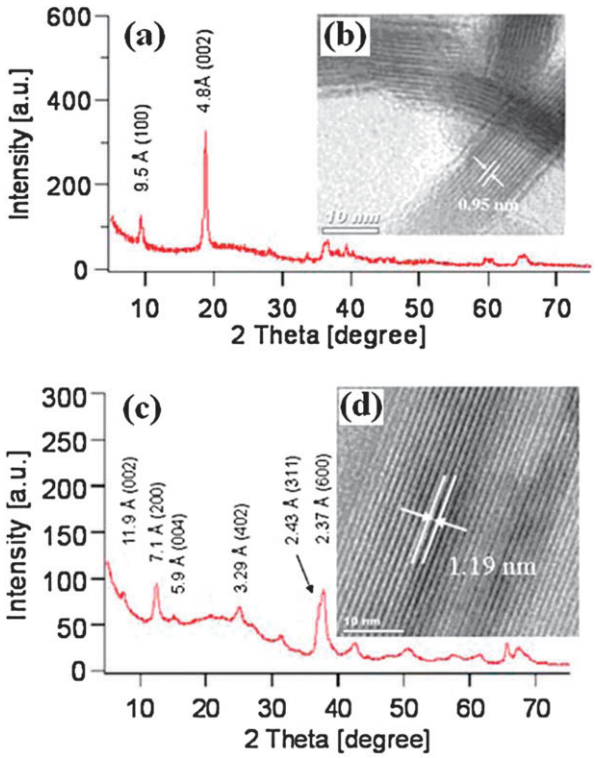

Fig. 1 (a) Powder X-ray diffraction pattern and (b) HR-TEM image of OMS-1; (c) powder X-ray diffraction pattern and (d) HR-TEM image of OMS-5.

as being due to the monoclinic 2 × 4 tunnel-structured manganese oxide phase with lattice parameters a = 14.22 Å, b = 2.853 Å, c = 24.28 Å and β = 91.32°.[3a] Fig. 1d shows the HR-TEM of OMS-5 with a 1.19 nm lattice d-spacing of the (002) plane, which is consistent with the corresponding XRD results. The structural stabilities of these two materials were also investigated by temperature resolved *in situ* X-ray diffraction (TR-XRD). These results revealed that OMS-1 is stable at 250 °C in the N_2 atmosphere and 450 °C in the air. When the heating temperature is above 600 °C, OMS-1 was transferred to $MgMn_2O_4$ in both conditions, which corresponds to reported results.[13b] OMS-5 is stable at 300 °C in N_2 and 500 °C in air. Applying higher heating temperatures in both conditions on OMS-5 results in the formation of hausmannite structure Mn_3O_4 (ESI-3†). These high-temperature stabilities for both OMS-1 and OMS-5 materials indicate that they are good candidates for high temperature catalysis.

Fig. S2 (ESI†) shows the morphologies of as-synthesized OMS-1 and OMS-5 materials by field emission Scanning Electron Microscopy. The OMS-1 material has a flake-shape morphology and possesses a BET surface area of 44.5 $m^2\ g^{-1}$, which is higher than the 13 $m^2\ g^{-1}$ surface area reported for materials prepared in a microwave-assisted traditional synthetic route.[15] The OMS-5 material is fibrous with a diameter about 40 nm and length about several micrometres and has a BET surface area of 76 $m^2\ g^{-1}$. Preliminary studies for both OMS-1 and OMS-5 materials showed that micropore volumes obtained by CO_2 adsorption at 273 K have higher adsorption capacities than N_2 adsorption at 77 K, as previously observed in zeolites with narrow micropores, due to the diffusion limitations of N_2 at its boiling temperature.[16] Our catalytic studies have shown that the catalytic activity of the OMS-5 material was comparable with the activity of Cu-containing mesoporous manganese oxide in a CO oxidation experiment under similar experimental conditions[17] (ESI-4†).

The formation of OMS-1 tunnel material requires a certain reaction temperature. Reaction intermediate study at 180 °C shows that layer structured materials were obtained without the presence of tunnel structured OMS-1 materials (ESI-5†). In addition, the pH value of the final solution remains neutral as the initial solution. Together with these results, eqn (1) is proposed for the formation of MnOx intermediate in the first stage. The OH^- ion generated from the reaction of MnO_4^- and H_2O creates a high pH condition and assists in the formation of layered MnOx intermediates. As the pH value increased, the precipitation point of $Mg(OH)_2$ was reached and the precipitation of $Mg(OH)_2$ consumes all the OH^- ion generated as shown in eqn (1). This leads to a self-adjustment of the high pH condition back to neutral as observed in our experiments. In the second stage, this neutral condition assists the as-generated layered MnOx to further transform into tunnel structure OMS-1 materials to complete this single-step preparation. Layer structured MnOx intermediate was also observed when the hydrothermal reaction time was shortened to 2 days in the case of OMS-5 single-step synthesis.

$$4MnO_4^-{}_{(aq.)} + 2H_2O_{(aq.)} = 4MnO_2\downarrow + 4OH^-{}_{(aq.)} + 3O_2\uparrow \quad (1)$$

A certain amount of Mg^{2+} dopant in the framework of the layered MnOx is crucial for producing thermally stable OMS-1 which has a reported formula of $Mg_{3.17}Mn_{5.05}O_{12}\cdot 4.52H_2O$.[3c,d] This doping procedure should be efficient since the as-generated $Mg(OH)_2$ with MgO_6 subunits has a similar layered structure as the layered MnOx with MnO_6 subunits. In addition, MgO_6 and MnO_6 units are very close in size, which increases the chance of introducing Mg^{2+} into the framework of the OMS-1 materials. However, trace amount of $Mg(OH)_2$ could possibly remain in the sample even when there were no $Mg(OH)_2$ or MgO impurities observed in the resulting XRD and TEM patterns.

The pH self-adjusting role of Mg^{2+} was verified by hydrothermal treatment of $NaMnO_4$ in a neutral condition following the same procedure as in the $Mg(MnO_4)_2$ case. As expected, the pH value of this reaction is around 13 with the production of OMS-5. The Na^+ does not have the same self-pH adjusting property as Mg^{2+} and thus gives a highly basic condition, together with the proper template ion (Na^+), leading to the selective formation of OMS-5.

In summary, a single-step hydrothermal method has been developed to synthesize OMS-1 and OMS-5 nanomaterials. This simple synthetic route opens up a new avenue for preparing large (>9.6 Å) tunnel structured OMS materials and greatly reduces working time. This synthetic method also offers great opportunity for scaled-up syntheses of these two kinds of OMS materials. Using alkaline permanganate salt such as $RbMnO_4$ and $CsMnO_4$ and other permanganate salts like $Cu(MnO_4)_2$ and $Zn(MnO_4)_2$ to prepare other large size

tunnel OMS materials, such as 2 × 5, 3 × 4 tunnel structures is ongoing in our lab. With these different dopants in the framework or tunnel sites, OMS materials may show different electrochemical performance, photosensitivity, and catalytic activity and selectivity.[18]

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