

Single-Step Synthesis of Manganese Oxide Octahedral Molecular Sieves with Large Pore Sizes

Hui Huang,^a Chun-Hu Chen,^a Linping Xu,^a Homer Genuino,^a Javier Garcia-Martinez,^c Hector F. Garces,^b Lei Jin,^a Cecil King'ondeu Kithongo^a and Steven L. Suib^{*a,b}

^a *Department of Chemistry, University of Connecticut, 55 N. Eagleville Rd., Unit 3060, Storrs, CT 06269-3060, U.S.A*

^b *Institute of Materials Science, University of Connecticut, Storrs, CT 06269, U.S.A.*

^c *University of Alicante, Molecular Nanotechnology Lab, Campus de San Vicente E-03690 Alicante, Spain.*

E-mail: steven.suib@uconn.edu

ESI-1: *Crystal structure.*

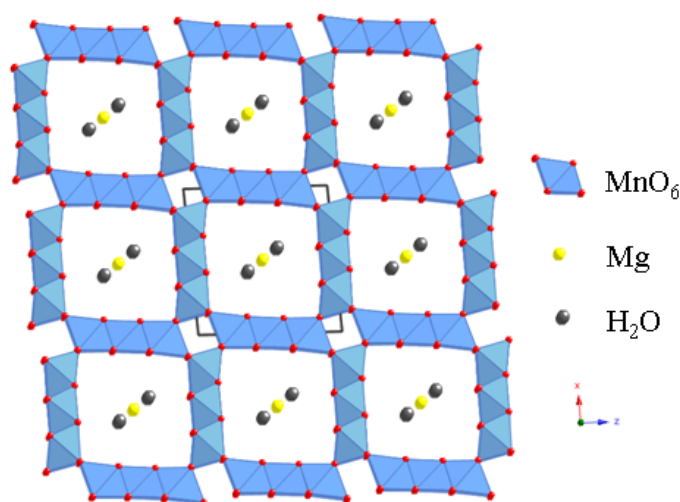


Figure S-1. A representative crystal structure of todorokite, namely OMS-1.

ESI-2: **Synthesis.** OMS-1. In a typical synthesis, 13 mL 68 mmol/L $\text{Mg}(\text{MnO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich) aqueous solution was hydrothermally treated in a Teflon-lined autoclave at 240°C for 6-96 hours under autogenous pressure in a furnace. The product was collected from the resulting slurry after the autoclave was cooled in air. Dilute acids were used to remove impurities. The product was dried at 100°C overnight for further characterization.

Electronic Supplementary Information:

OMS-5. The similar procedure was applied in preparing OMS-5 materials except $\text{NaMnO}_4 \cdot \text{H}_2\text{O}$ (Aldrich) was used as the precursor. The hydrothermal reaction time was 4 days and reaction temperature was 240°C . All reagents were analytical grade and used as received.

Characterization. The crystalline phase of as-synthesized materials were examined by using a powder X-ray diffraction instrument with a Scintag 2000 XDS with $\text{Cu K}\alpha$ X-ray source ($\lambda=1.54 \text{ \AA}$). A beam of 45 kV voltage and 40 mA current were used. As-prepared powdery sample (100 mg) was loaded on an Al holder and the data were collected in the 2θ range $5\text{-}75^\circ$ with a step scanning rate of $0.02^\circ/\text{min}$. Detailed structural information was further studied with HR-TEM using a JEOL 2010 instrument with an accelerating voltage of 200 kV. The samples were prepared by dispersing the material in ethanol. A drop of the dispersion was placed on a carbon coated copper grid and allowed to dry before analysis.

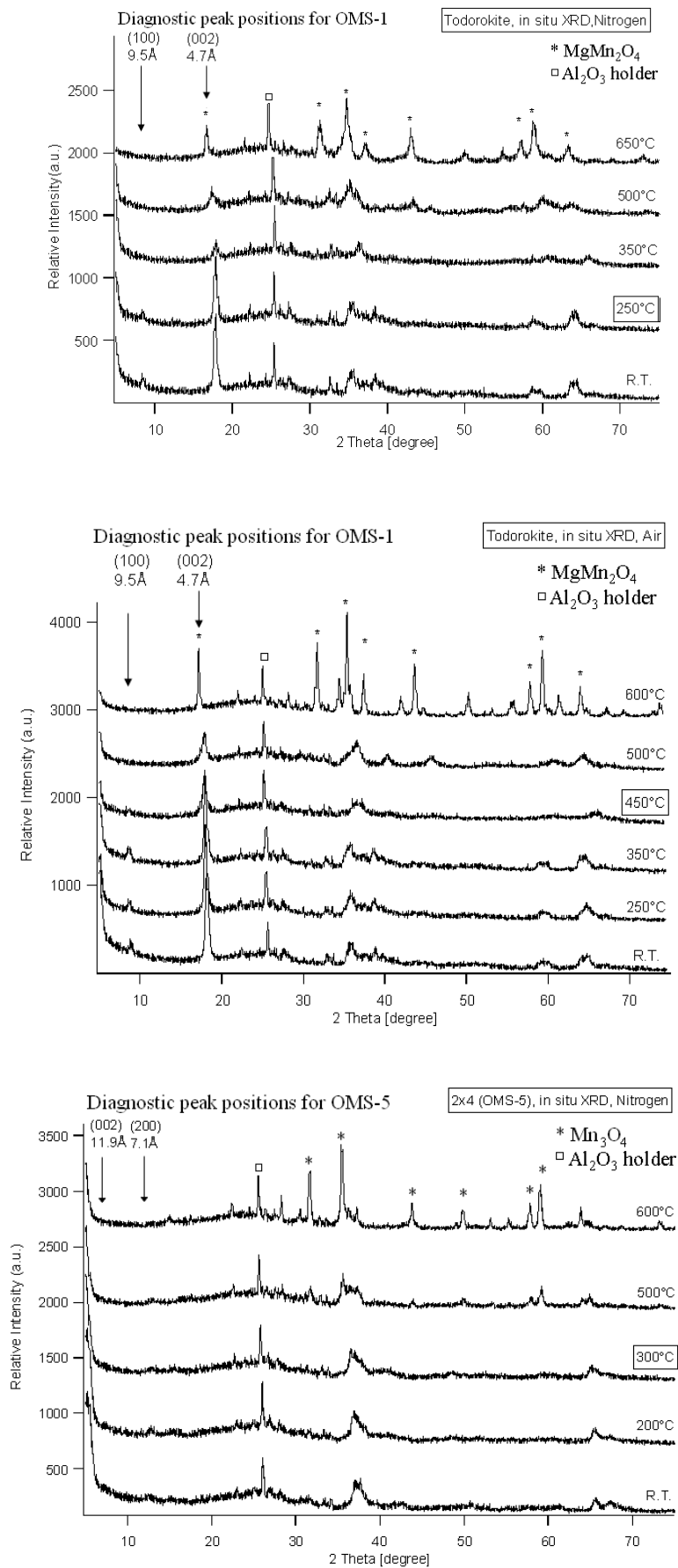
FE-SEM images were taken on a Zeiss DSM 982 Gemini emission scanning microscope with a Schottky Emitter at an accelerating voltage of 2 kV under a beam current of $1 \mu\text{A}$. The samples were ultrasonically dispersed in ethanol and the suspensions were deposited on a gold-coated silicon wafer and allowed to dry overnight in vacuum for analysis.

Surface areas were measured with a Micromeritics ASAP 2010 instrument. N_2 gas was used as the adsorbate at 77K by the multipoint method. The Brunauer-Emmet-Teller (BET) method was used to calculate the surface area. The sample (120 mg) was pre-degassed at 120°C for 12 hours before analysis.

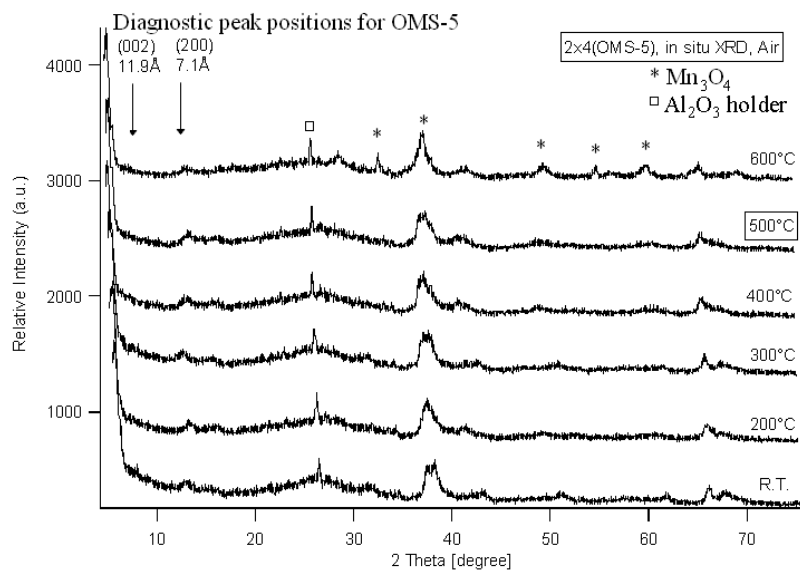
ESI-3: *Temperature-resolved in situ X-ray diffraction (TR-XRD).*

Temperature-resolved *in situ* X-ray diffraction analysis was performed in an XTRA X-ray diffractometer ($\text{Cu K}\alpha$ radiation) equipped with an Anton Parr XRK 900 heater chamber. The structural stabilities of OMS-1 and OMS-5 materials were investigated from room temperature (RT) to 600°C under both air and N_2 , respectively. The materials were ramped at $10^\circ\text{C min}^{-1}$ up to the analysis temperature. Diffraction patterns were obtained in the range of $5\text{-}75^\circ 2\theta$ degrees at a scanning rate of 2° min^{-1} . The four patterns are shown below.

Electronic Supplementary Information:



Electronic Supplementary Information:



ESI-4: *Morphology study.*

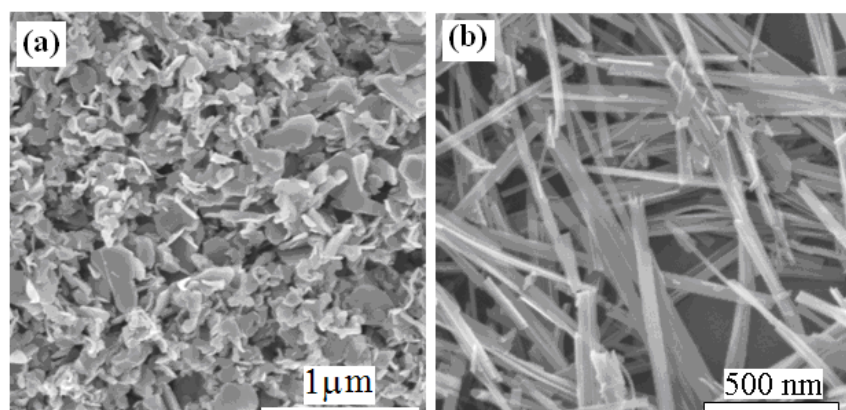


Figure S-2: FE-SEM images of (a) OMS-1 and (b) OMS-5.

ESI-5: *OMS-5 material for CO oxidation study.*

The catalytic oxidation of CO was done in a fixed-bed flow-type quartz reactor. Prior to analysis, 100 mg of the prepared catalyst loaded in the reactor was pre-treated for 2 h by passing He gas (flow rate: 50 mg L⁻¹) through the sample heated at 180 °C. The reaction was started by passing the gas mixture (composition: 1% CO, 20% O₂, 6% N₂ as internal standard, and 93% He) through the reactor at a fixed flow rate of 35000 mL h⁻¹ g_{cat}⁻¹ and at varying reaction temperatures (80, 90, 100, 110, 120 and 130 °C). Helium was used as the carrier gas and the composition of the effluent gas was analyzed using an online gas

Electronic Supplementary Information:

chromatograph (SRI model 8610C, USA) equipped with a 6' molecular sieve, a 6' silica gel column, and a TCD detector. Peak areas were used for quantitative analysis. Figure S-3 shows the catalytic activity of OMS-5 measured in terms of % conversions of CO to CO₂ at different reaction temperatures.

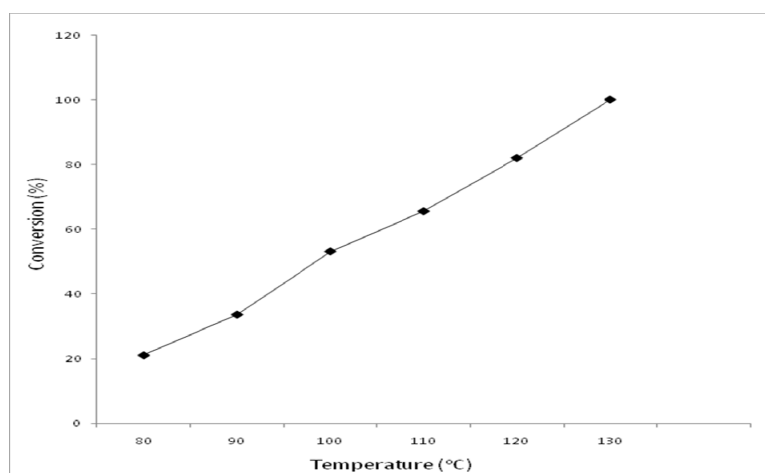


Figure S-3. Catalytic activity of OMS-5 catalyst in CO oxidation at different reaction temperatures.

ESI-6: *Intermediate study.*

When hydrothermal treatment of Mg(MnO₄)₂ was done at lower temperature (180-200 °C), layer structured materials were observed. When shorter hydrothermal treatment time (2 days) of NaMnO₄ was used, a layer structure type of manganese oxide was also observed. Figure S-4 shows the XRD patterns of obtained layered materials.

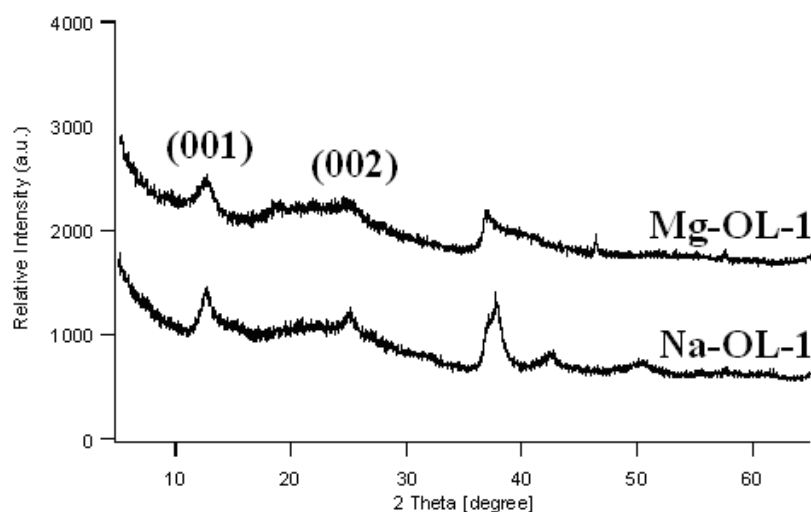


Figure S-4. XRD patterns of layered materials.