Synthesis and Structural Characterization of a Novel Three-dimensional Molybdenum–Oxygen Framework Constructed from Mo_3O_9 Units

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A novel three-dimensional molybdenum oxide $Mo_3O_9{\cdot}H_2O$ (**1**) constructed from Mo_3O_9 units has been successfully synthesized under hydrothermal conditions and structurally characterized by IR spectrum, inductively coupled plasma (ICP) analysis, powder X-ray diffraction (PXRD), X-ray photoelectron spectroscopy (XPS), and single-crystal X-ray diffraction.

Transition metal oxides can form an intriguing family of functional materials with catalytic, ion-exchange, electronic, and magnetic properties, high-temperature superconductivity, optical properties, and piezoelectrics, which makes them have wide commercial applications from structural engineering materials to more technologically advanced products in the microelectronics industry.[1–3] Importantly, inspired by the structures and properties of zeolites and zeotype materials, microporous and mesoporous open-framework materials of transition-metal oxides have attracted increasing interest. Among transition-metal oxide materials, the study and exploitation of molybdenum oxides have attracted increasing attention because of their benign catalytic, electrochromism, light-emitting diodes and gas-sensing devices and semiconductivity.[4–8] For example, orthorhombic molybdenum trioxide α-MoO_3, being the most thermodynamically stable phase of molybdenum trioxides, exhibits high catalytic selectivity to formaldehyde, but the activity is much lower compared to the industrially used ferric molybdate catalysts with excess molybdenum.[5,9,10] In 1985–1986, Farneth and co-workers studied the catalytic activity of α-MoO_3 to methanol and the mechanism of methanol oxidation involving dissociative chemisorption, rate-limiting C–H bond cleavage of the adsorbed intermediate, and reoxidation by molecular oxygen.[9,10] Subsequently, Machiels et al. asserted that β-MoO_3 was a more active catalyst than the α-MoO_3 with regard to the selective oxidation of methanol to formaldehyde.[11] Furthermore, the electrochromic response of molybdenum trioxide shows a stronger and more uniform absorption of light in its colored state and also shows a better open-circuit memory. Monk et al. reported that molybdenum trioxide showed greater apparent coloration efficiency since molybdenum bronze is more akin to the sensitivity of the human eye.[12,13] In the field of light-emitting diodes, Lee's research results indicated that applying molybdenum trioxide as an interlayer between hole injection layer (HIL) and hole transport layer (HTL) can lower driving voltage of organic light-emitting diodes (OLEDs).[14] From a structural chemistry viewpoint, to date most investigations of molybdenum oxides have been focused on polycrystalline nanostructured materials, moreover, various molybdenum oxide nanostructures, such as nanorods, nanowires, nanobelts, and nanoplatelets, have already been prepared by a variety of methods such as vapor transportation and hydro/solvothermal treatment.[15–18] However, the synthesis and exploration of novel three-dimensional molybdenum–oxygen framework determined by means of single-crystal X-ray diffraction are very rare. In the present paper, we report the synthesis and structural characterization of a novel three-dimensional molybdenum–oxygen framework $Mo_3O_9{\cdot}H_2O$ (**1**) constructed from Mo_3O_9 units.[19]

Single-crystal X-ray diffraction analysis[20] reveals that the molecular structural unit of **1** consists of a Mo_3O_9 subunit and one lattice water molecule. The Mo1 atom adopts a distorted octahedral geometry with O1A, O2, O2C, and O2D atoms building the equatorial plane [Mo–O: 1.718(5)–2.208(5) Å], and the bridging O1 atom and the terminal O3 atom standing on two opposite axial positions [Mo–O1: 2.369(5) Å and Mo–O3: 1.686(6) Å] (Figure 1a). In the Mo_3O_9 subunit, three MoO_6 octahedra are corner-shared to connect to each other forming a three-membered ring (MR) through three bridging oxygen (O1, O1A, and O1B) atoms. Interestingly, along the crystallographic *c* axis, adjacent Mo_3O_9 subunits are interlinked together by sharing triple O2 bridges, resulting in a 1-D 3-MR channel with ef-

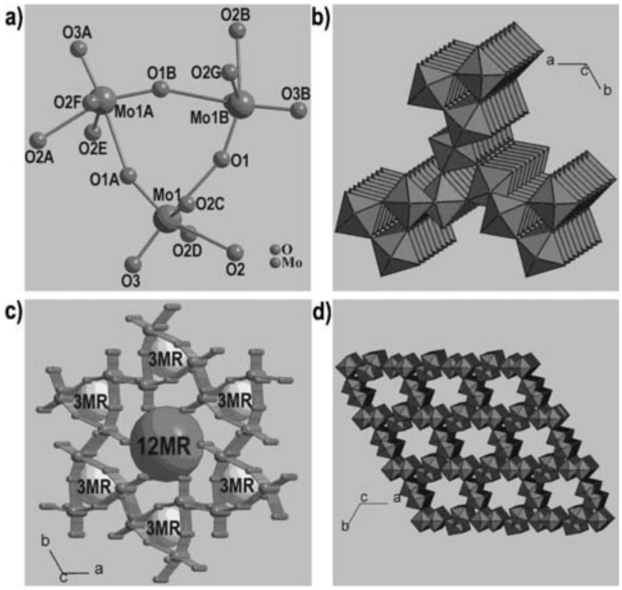

Figure 1. (a) The molecular structural unit of **1** with the labeling scheme. The atoms with the suffix A, B, C, D, E, and F are generated by the symmetry operation: A: $2-x+y, 2-x, z$; B: $2-y, x-y, z$; C: $2-x, 1-y, 0.5+z$; D: $2-x, 1-y, -0.5+z$; E: $1+x-y, x, -0.5+z$; F: $1+x-y, x, 0.5+z$; G: $1+y, 1-x+y, 0.5+z$. The lattice water molecule is omitted for clarity. (b) The combination between a 1-D 3-MR channel and three identical 1-D 3-MR channels. (c) The 1-D 12-MR channel surrounded by six 1-D 3-MR channels viewed down the crystallographic *c* axis. (d) The 3-D open framework of **1**.

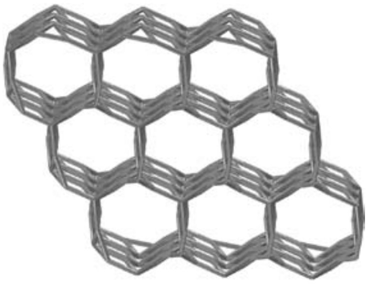

Figure 2. The 3-D topology of **1** with the Schläfli symbol of $(4^3)(4^{12}{\cdot}6^{15}{\cdot}12^9)$.

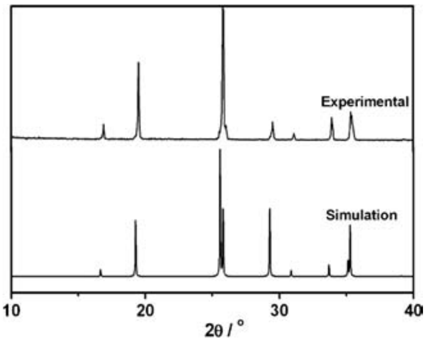

Figure 3. The PXRD pattern of **1** and its calculated pattern based on the single-crystal solution.

ficient inner diameters of 1.6 Å. Each 1-D 3-MR channel is further combined with three identical 1-D 3-MR channels (Figure 1b), and six identical 1-D 3-MR channels are orderly aligned in a hexagonal motif constructing a larger 1-D 12-MR channel with the efficient inner diameter of 6.1 Å (Figure 1c). It should be noted that the 1-D 3-MR channels communicate with the 12-MR channels through the 4-MR wall pores on the 3-MR channels (Figure S1).[21] More intriguingly, each Mo_3O_9 subunit connects eight such Mo_3O_9 subunits via nine μ_3-O atoms establishing a novel 3-D open framework (Figures 1d and S2).[21] From the topological point of view, the simplification of 3-D networks to node-and-spacer representations that illustrate their connectivity facilitates the analysis and understanding of complicated topologies by crystal engineering.[22] The circuit symbols and Schläfli (vertex) notations can be used to describe topologies. The 3-D framework of **1** is a (3,9)-connected 3-D network, where each O2 atom acts as a three-connected node and each Mo_3O_9 subunit functions as nine-connected node (Figure 2). Its Schläfli symbol is $(4^3)(4^{12}{\cdot}6^{15}{\cdot}12^9)$.

The phase purity of **1** was characterized by PXRD pattern of the bulk product (Figure 3). Their peak positions are in good agreement with each other, indicating the phase purity of the product. The difference in intensity may be due to the preferred orientation of the powder sample.

In addition, the bond valence sum (BVS) calculations show that the oxidation states of all the octahedral Mo centers are +6,[23] which has been confirmed by the result of X-ray photoelectron spectroscopy (Figure S3).[21] In **1**, the $Mo3d_{5/2}$ and $Mo3d_{3/2}$ binding energy values of 231.30 and 234.56 eV indicate the presence of the Mo^{VI} centers, which are in good agreement with the values found in the literature.[24]

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19 Preparation of **1**: A mixture of $Na_2MoO_4{\cdot}2H_2O$ (5.99 mmol, 1.45 g), $NH_2OH{\cdot}HCl$ (1.58 mmol, 0.11 g), and water (556 mmol, 10 mL) was stirred for 2 h in air, and its pH was adjusted to 1–2 with hydrochloric acid ($2\,mol{\cdot}L^{-1}$). The resulting mixture was sealed in a 20-mL Telfon-lined reactor, heated to 180 °C, and kept for 5 days. After cooling to room temperature, light blue block crystals were collected in 70% yield (based on $Na_2MoO_4{\cdot}2H_2O$), by filtration, washed with water, and dried at ambient temperature. Anal. Calcd for $H_2Mo_3O_{10}$ (%): Mo, 63.98. Found: Mo, 63.72. IR spectrum: 3506, 1625, 1417, 974, 907, 611, $520\,cm^{-1}$. Experimental results proved that when $NH_2OH{\cdot}HCl$ was removed from the reaction system, **1** could not be isolated. The role of $NH_2OH{\cdot}HCl$ is not well understood.

20 Crystal data for **1**: $H_2Mo_3O_{10}$, $M_r = 449.84$, hexagonal, space group $P6_3/m$, $a = 10.6303(4)$, $b = 10.6303(4)$, $c = 3.7215(3)$ Å, $V = 364.20(4)$ Å^3, $T = 296(2)$ K, $Z = 2$, $\mu = 5.122\,mm^{-1}$, 3603 reflections measured, 266 independent ($R_{int} = 0.0147$). $R_1 = 0.0280$, $wR_2 = 0.0846$. CSD: 420492.

21 Supporting Information is available eletronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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