Synthesis of β-MoO_3 by Simple Evaporation of Molybdic Acid Solution Containing Nitric Acid

Takanori Mizushima,* Kazuya Fukushima, Tran Mai Huong, Hironobu Ohkita, and Noriyoshi Kakuta
Department of Materials Science, Toyohashi University of Technology, Tempaku-cho, Toyohashi 441-8580

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β-MoO_3 was successfully synthesized through a simple evaporation of a molybdic acid solution prepared by a cation exchange of an aqueous solution of $Na_2MoO_4{\cdot}2H_2O$. The key was an addition of a small amount of nitric acid before the evaporation. Heating the dried molybdic acid at 573 K in oxygen resulted in a formation of a bright yellow powder, which was confirmed to be β-MoO_3 free from α-MoO_3 by XRD and Raman spectroscopy.

The thermodynamically stable normal phase of molybdenum trioxide is well known as α-MoO_3, which consists of orthorhombic lattices with a layer-structural arrangement of edge- and corner-linked MoO_6 octahedra. Molybdenum trioxide also crystallizes in a monoclinic ReO_3 structure in which the MoO_6 octahedra share only the corners with each other. This form of molybdenum trioxide is called β-MoO_3. It was detected as a metastable phase in 1985 by Rao et al.,[1] who observed an electron diffraction pattern characteristic of the ReO_3-type structure during a dehydration process of $MoO_3{\cdot}H_2O$ by an electron beam.

At about the same time, MaCarron has succeeded in a synthesis of β-MoO_3 through a spray drying of a molybdic acid solution prepared by passing an aqueous solution of sodium molybdate over an ion-exchange resin.[2] Subsequently, other preparation routes for the β-phase have been reported.[3–5] Juárez Ramírez and Martínez-de la Cruz[6] have recently demonstrated that β-MoO_3 can be obtained free from the α-phase by vacuum drying the molybdic acid solution. However, this method has a disadvantage of slowness in the drying process: it required 36 h to dry the solution in a 50-cm^3 vessel. A more simple and efficient way to obtain pure β-MoO_3 is desired because it has a high catalytic activity in oxidation of methanol to formaldehyde[2] and an ability to form lithium molybdenum bronzes as an active material for a lithium battery.[6,7]

In this study, we attempted to develop a new synthesis route of β-MoO_3 with a high purity. As a result, we found that an addition of a small amount of nitric acid to the molybdic acid solution before a simple evaporation into dryness led to a selective formation of the β-form of molybdenum trioxide.

The molybdic acid solution was prepared by passing an aqueous solution of $Na_2MoO_4{\cdot}2H_2O$ (1 mol/dm^3) through a column of a cation-exchange resin (Rohm and Haas, Amberlite IR120B Na) to remove Na^+ ions. This treatment was repeated until the Na concentration in the solution was below 5×10^{-5} mol/dm^3. Thirty cm^3 of the solution was then placed in a 50-cm^3 vessel and evaporated into dryness at 323 K and 300–400 Pa after an addition of 3 drops (about 0.12 cm^3) of 60% nitric acid solution. The drying was completed within 1 h. The obtained powder was heated at 573 K for 1 h in a stream of oxygen. Crystallographic data was collected with an X-ray powder diffractometer (Rigaku, RINT2000) with a copper X-ray tube operated at 30 kV and 20 mA. Raman spectroscopy (JASCO, NR-1800) was also employed at an excitation wavelength of 488 nm to identify the molybdenum oxide. The formation process of the MoO_3 crystallites from the dried precursor was investigated by TG-DTA (Mac Science, TG8110) in an oxygen stream at an elevating rate of 10 K/min.

The cation-exchanged solution was tinged with blue and the final pH was about 1.6. Evaporating the solution after the addition of HNO_3 resulted in a formation of a pale yellow powder. In contrast, the powder obtained from the HNO_3-free solution was yellowish green. The XRD measurements showed both dried products to be amorphous.

By the thermal treatment at 573 K in a flowing oxygen atmosphere, the HNO_3-added and -free powders turned bright yellow and pale green, respectively. Their XRD data are shown in Figure 1. It is evident that the addition of HNO_3 caused a remarkable change in the crystallographic structures of the molybdenum oxides. In the absence of HNO_3 (Figure 1a), the powder exhibited the spectrum identifiable as α-MoO_3 (JCPDS 5-0508). On the other hand, Figure 1b is in agreement with the data previously reported for β-MoO_3 (JCPDS 47-1081) and no peak due to other crystallographic phases is observed, indicating a formation of pure β-MoO_3. When the sample was heated

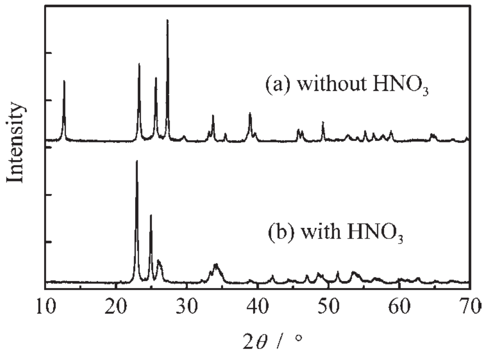

Figure 1. XRD patterns of the molybdenum oxides obtained (a) without and (b) with the addition of HNO_3.

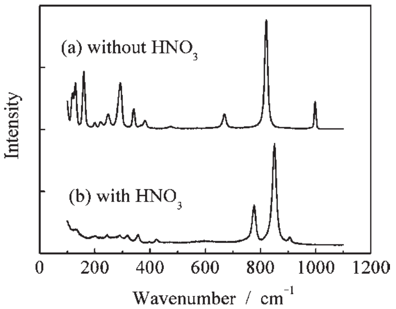

Figure 2. Raman spectra of the molybdenum oxides obtained (a) without and (b) with the addition of HNO_3.

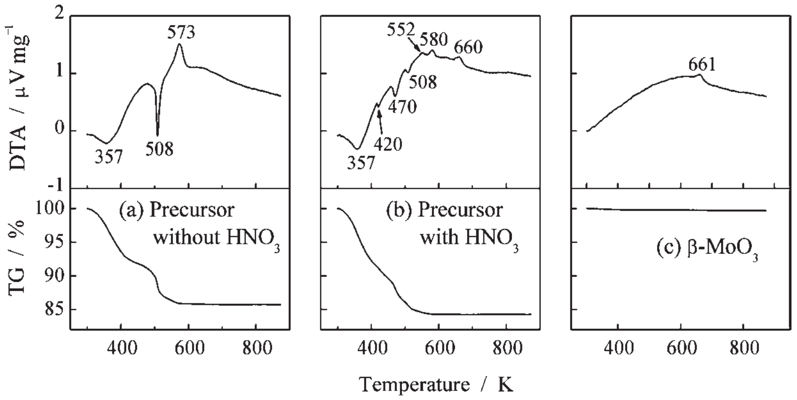

Figure 3. TG-DTA curves for the dried molybdenum precursors obtained (a) without and (b) with the addition of HNO_3 and (c) for β-MoO_3.

at 673 K, the pattern changed to that for α-MoO_3; therefore, β-MoO_3 is the metastable phase, which transforms into the thermodynamically stable α-form.

The structural differences were also examined by Raman spectroscopy. The results are illustrated in Figure 2. In the Mo–O stretching region (above 600 cm^{-1}) for the HNO_3-free product (Figure 2a), we detected three peaks at 997, 821, and 667 cm^{-1}, which were assigned to the stretching mode of the terminal Mo=O groups, and the asymmetric and symmetric stretching modes of the Mo–O–Mo bridges in α-MoO_3, respectively.[8] In contrast, the molybdenum oxide obtained with the HNO_3 addition (Figure 2b) was characterized by the absence of the Mo=O peak at 997 cm^{-1} and the presence of a small peak at 905 cm^{-1}. These features agree with the results reported for β-MoO_3 by McCarron.[2] The peaks due to the α-phase were not observed in Figure 2b, supporting the XRD result that the addition of HNO_3 led to a selective formation of β-MoO_3. When hydrochloric acid or aqueous ammonia was added to the molybdic acid solution instead of nitric acid, β-MoO_3 was not produced but α-MoO_3 was selectively generated. This means that the formation of the β-phase is attributable to the presence of nitrate ions rather than the effect of pH.

Figures 3a and 3b show TG-DTA curves for the dried precursors obtained without and with the addition of HNO_3, respectively. The result for the β-MoO_3 produced by heating the HNO_3-added precursor at 573 K for 1 h is also given in Figure 3c for comparison. In the absence of HNO_3 (Figure 3a), the weight decreased in a temperature rage of 300–570 K. A mass-spectroscopic analysis of the emitted gases elucidated that this weight loss was attributable to a dehydrating decomposition of the amorphous powder. At the end of the dehydration, the weight steeply decreased with a sharp endothermic peak at 508 K. The total weight loss was 14.3%, which corresponded to about 1.3 of n in $MoO_3 \cdot nH_2O$. After the weight was unchanged, an exothermic peak appeared at 573 K. This peak was assigned to a crystallization of the α-phase.

A similar decrease in the weight due to the dehydration was also observed for the dried precursor containing HNO_3 (Figure 3b). The total weight loss was 15.7%, which was slightly larger than that for the HNO_3-free product. It is worth noting that the DTA profile is evidently different from that in Figure 3a: two additional endothermic peaks appeared at 420 and 470 K, and the endothermic peak at 508 K was markedly weakened. A similar stepwise dehydration has been reported for the formation of β-MoO_3 from the vacuum-dried molybdic acid by Juárez Ramírez and Martínez-de la Cruz.[6]

After the dehydration processes, three exothermic peaks were observed at 552, 580, and 660 K. The highest-temperature peak was also detected for the pure β-MoO_3 (Figure 3c). By combining with the XRD results, we concluded that the β-phase was formed at 552 and/or 580 K, and transformed into the α-phase at 660 K.

In this study, we revealed an important contribution of NO_3^- ions in the selective formation of β-MoO_3 from the molybdic acid solution. A role of the NO_3^- ions may be a creation of NO_3^--containing molybdenum compounds which transform into β-MoO_3 by the calcination. This possibility, however, is unlikely because no difference was observed in EXAFS and IR spectra of the dried powders with and without HNO_3. A fact that the peculiar dry procedures such as spray drying,[2] freeze drying,[5] and vacuum drying[6] are required for a crystallization of the β-phase from the HNO_3-free molybdic acid solution suggests an importance of the evaporation process of water. The TG-DTA result that the NO_3^- ions notably affected the dehydration leads to a speculation that the NO_3^- ions control the manner and strength of coordination of water molecules to MoO_x in the dried precursor to form β-MoO_3.

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