

Supporting Information

Redox Tunable Reversible Molecular Sieves: Orthorhombic Molybdenum

Vanadium Oxide.

Masahiro Sadakane,^{a*} Shunpei Ohmura,^b Katsunori Kodato,^b Kazuo Kato,^c Kenichi Shimidzu,^b Toru Murayama,^b and Wataru Ueda^{b*}

a) Chemistry and Chemical Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima, 739-8527, Japan

b) Catalysis Research Center, Hokkaido University, N-21, W-10, Sapporo, 001-0021, Japan

c) Research & Utilization Division, Japan Synchrotron Radiation Research Institute (JASRI), SPring-8, 1-1-1 Kouto, Sayo, Hyogo, 679-5198, Japan

Experimental

Materials: All chemicals were reagent grade and used as supplied and distilled water made in the laboratory was used throughout the study. Orthorhombic Mo–V oxide was produced and purified using our previous method.^[4]

Air calcination: Mo_3VO_x (0.5 g) was placed in a conventional furnace and heated at a rate of $10 \text{ K} \cdot \text{min}^{-1}$ to 673 K; this temperature was then maintained for 2 h.

Reduction: The air-calcined sample (0.1 g) was placed in glass sample tube. The temperature was increased to the reduction temperature at a rate of 10 K min^{-1} and this temperature was then maintained for 1 h under H_2/Ar (5/95) flow (70 ml min^{-1}) with a CHEMBET 3000 (Quantachrome Instruments).

Characterization: H_2 -TPD was measured using a CHEMBET 3000 (Quantachrome Instruments). A sample (0.1 g) was placed in a glass tube and calcined at 673 K under N_2 flow. After the temperature was reduced under N_2 flow, the gas was changed to H_2/Ar (5/95) flow (70 ml min^{-1}) and temperature was raised at a rate of 10 K min^{-1} . DR UV–vis spectra were obtained using a JASCO V-570 spectrophotometer equipped with an ISN-470 reflectance spectroscopy accessory.

Molecular probes with various kinetic diameters, including carbon dioxide (CO_2 ; 0.33 nm), krypton (Kr; 0.36 nm), methane (CH_4 ; 0.38 nm), ethane (C_2H_6 ; 0.4 nm), n-butane ($\text{n-C}_4\text{H}_{10}$; 0.43 nm), and n-hexane ($\text{n-C}_6\text{H}_{14}$; 0.49 nm)(ref 1a; J. S. Gregg and M. M.

Tayyab, *J. Chem. Soc. Faraday Trans. 1*, 1978, **74**, 348.), were used for adsorption at 298 K to evaluate the porosity of the adsorbent using a gas adsorption analyzer (BELSORP-max; BELJAPAN, Inc. Japan). About 0.2 g of the samples was degassed at 573 K under vacuum for 2 h. Adsorptions of the various probes were measured at 298 K.

Adsorption data were used to characterize the adsorbent using the Dubinin–Astakhov (DA) equation (M. M. Dubinin, *Prog. Surf. Membr. Sci.* 1975, **9**, 1.):

$$W = W_0 \exp[-(A/\beta E_0)^m],$$

where A is the Polanyi's adsorption potential, which is calculated from the saturated vapor pressure P_0 and the adsorption pressure P using

$$A = RT \ln(P_0/P),$$

where E_0 is a characteristic energy that depends on the microporous structure of a given adsorbent, $W_0 = a_0 \nu$ is the limiting micropore volume, a_0 is the limiting amount adsorbed, ν is the molar volume of the adsorbate, β is the similarity coefficient of the characteristic curves, m is a structure-related parameter and W is the adsorbed volume.

W_0 can be determined from the intercept of the $\ln W$ vs. $\ln^m(P_0/P)$ ($m = 3$, K. Kawazoe, T. Kawai, Y. Eguchi and K. Itoga, *J. Chem. Eng. Jpn.* 1974, **7**, 158; K. Kawazoe, V. A. Astakhov and T. Kawai, *Seisan Kenkyu* 1970, **22**, 491.)) plot assuming that the adsorbed phase has the same density as the bulk liquid.

Room-temperature vanadium (5464 eV) and molybdenum (20,000 eV) K-edge X-ray absorption fine structure (XAFS) spectra were measured with the BL01B1 beamline at SPring-8 in transmission mode. Samples were mixed with boron nitride, and the mixture was pressed into a self-supporting pellet. Energy calibration was performed with metallic copper foil for vanadium K-edge absorption and with a molybdenum foil for molybdenum K-edge absorption. The synchrotron X-ray beam was monochromatized with Si(111) or Si(311) for vanadium or molybdenum K-edge absorption, respectively. The V K-edge or Mo K-edge X-ray absorption near edge fine structure (XANES) spectra were recorded for 300 s with energy steps of ca. 0.42 eV in the range of ca. 5,136–6,983 eV and ca. 0.36 eV in the range of ca. 19,700–21,526 eV, respectively. XANES spectra were normalized and background-corrected using the Athena program (B. Ravel and M. Newville, *J. Synchrotron Rad.* 2005, **12**, 537–541).

The first small peak in Figure 2 does not indicate a reduction, but rather nitrogen released from the micropores detected by the TCD (see Supporting Information, Figure S1 and S2) for the following reasons; 1) the temperature programmed desorption (TPD) profile of orthorhombic Mo–V oxide (which was calcined in air at 673 K and cooled in air) indicates that N₂ and O₂ gasses were detected together with H₂O around 390 K (Figure S1) and 2) the TCD signal around 400 K was observed without H₂ gas (Figure S2). Nitrogen was trapped in the micropores during pre-heating step under nitrogen, and water molecules included in this nitrogen gas capped the micropores. Therefore, we concluded that the second peak is a reduction peak.

Removal of this capping water opens the micropores so that pre-heating at 573 K was necessary before adsorption could be measured.

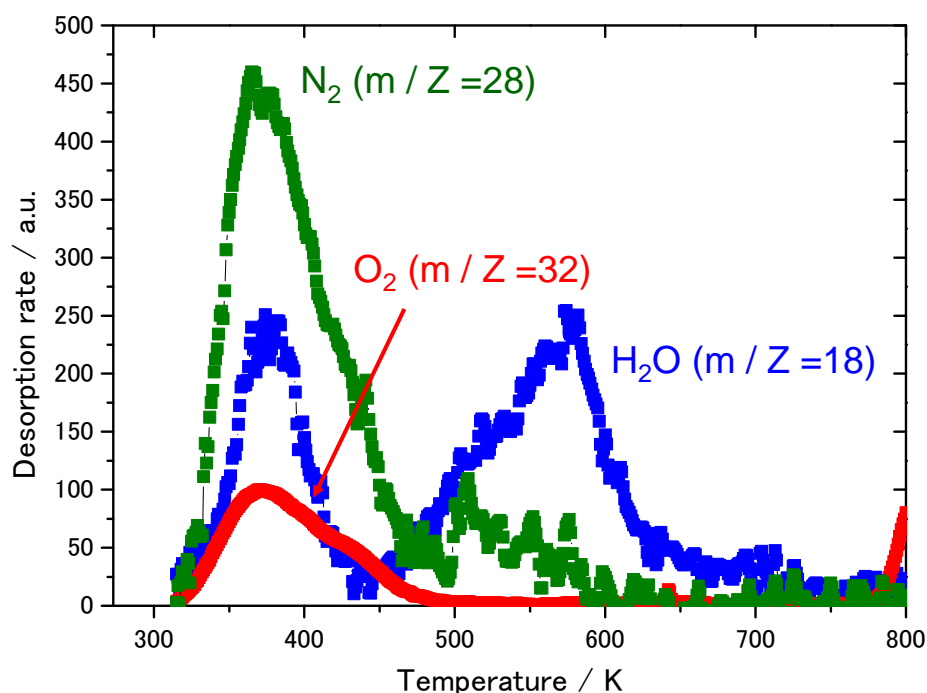


Figure S1. TPD curves of the air-calcined orthorhombic Mo-V oxide obtained using a heating rate of 10 K min⁻¹ under He flow (50 ml min⁻¹). A TPD apparatus

(BELJAPN, Inc.) equipped with a quadrupole mass spectrometer (M-100QA; Anelva) was used to detect H₂O ($m/Z = 18$; blue), O₂ ($m/Z = 32$; red), and N₂ ($m/Z = 38$; green).

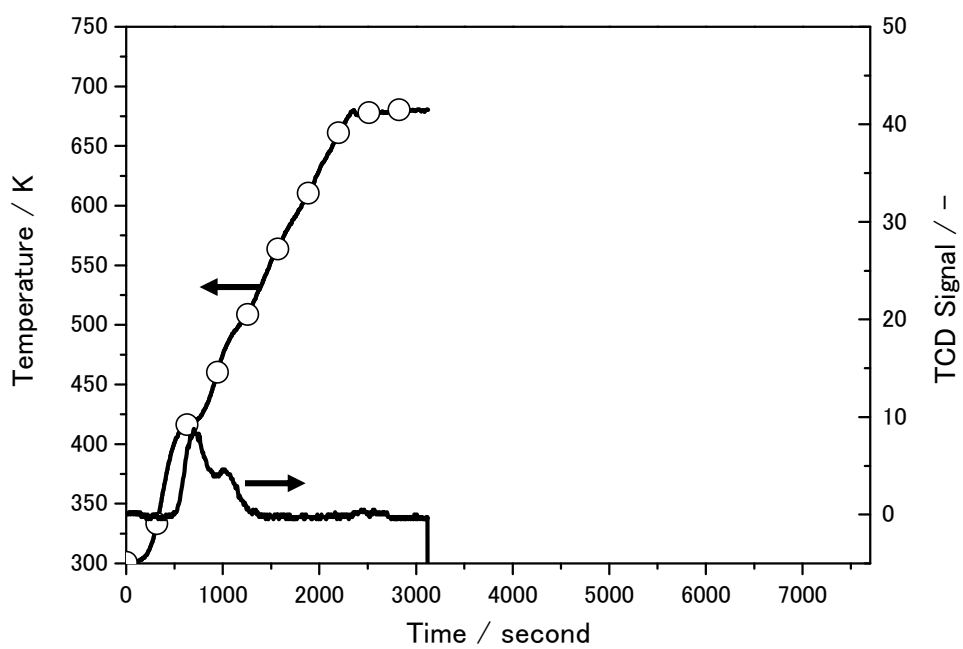


Figure S2. TPD profile of air-calcined orthorhombic Mo–V oxide under He flow (70 ml min⁻¹). TCD signal (solid line) and temperature (solid line with open circles).

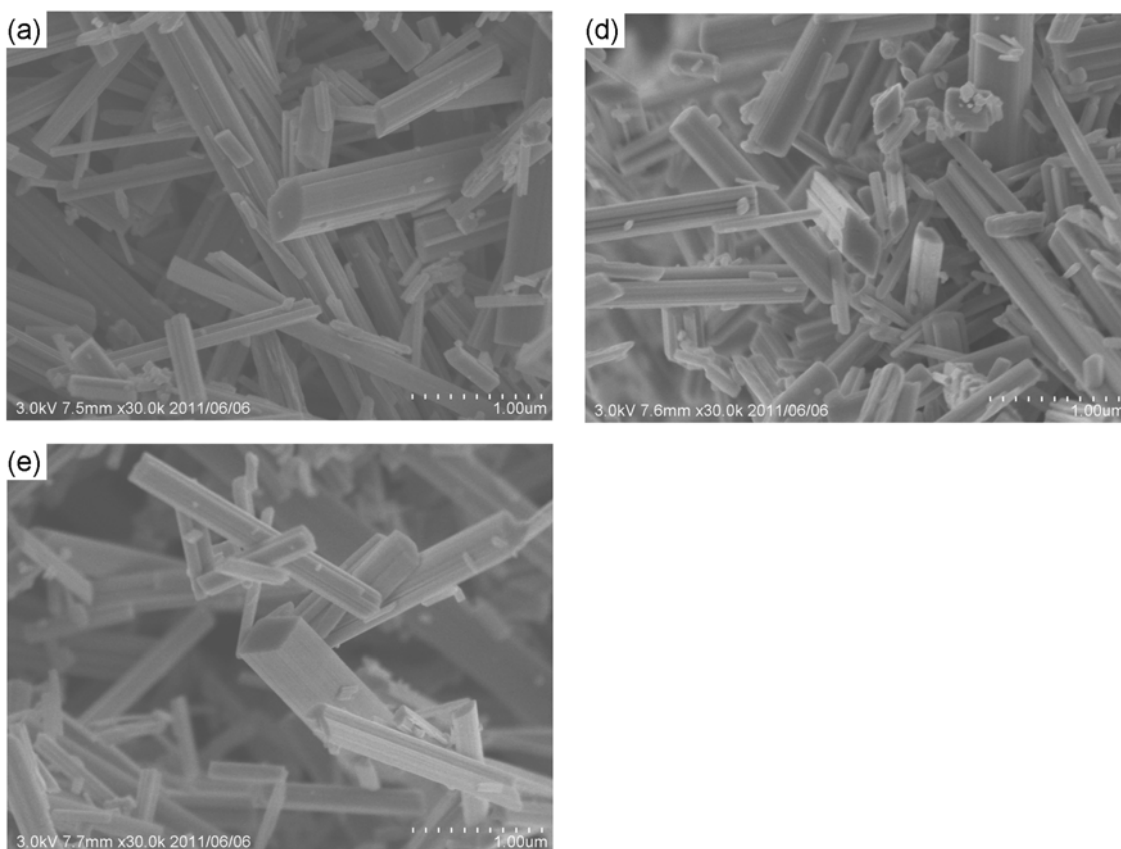
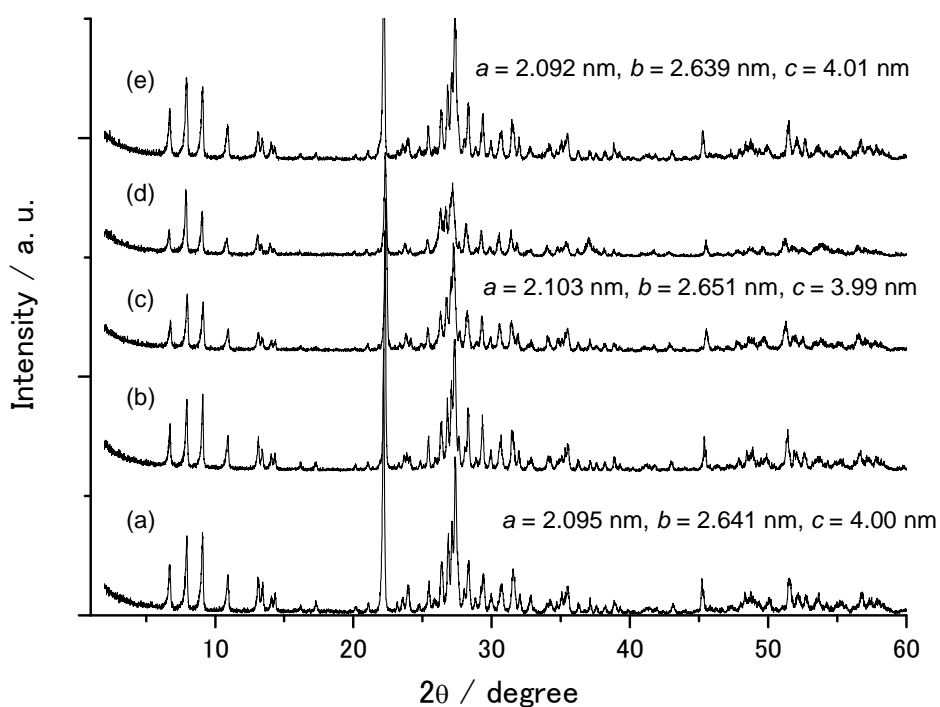


Figure S3. XRD profiles and SEM images for orthorhombic Mo-V oxide (a) calcined at 673 K in air, (b) calcined at 623 K under H_2/Ar (5 %) flow, (c) calcined at 673 K under H_2/Ar (5 %) flow, (d) calcined at 723 K under H_2/Ar (5 %) flow, and (e) calcined at 673 K in air after calcination at 723 K under H_2/Ar (5 %) flow. Powder XRD pattern was recorded with a diffractometer (RINT

Ultima+, Rigaku) with Cu K α radiation. Cell parameters were calculated using the least-squares method from 21 XRD lines. Scanning electron microscopy (SEM) was performed on a S-4800 (Hitachi).

It was shown that the positions of both the main absorption edge and the pre-edge of the V K-edge X-ray absorption spectrum shift linearly to higher energies with increasing vanadium valence. (G. W. Coulston et al., *Science*, 1997, **275**, 191; J. Wong, et al. *Phys. Rev. B*, 1984, **30**, 5596). In our sample, the peak positions of both the pre-edges and the main absorption edges shift to lower energies on reduction and to higher energies on oxidation, indicating that the valence of V is altered by redox treatment.

It was shown that the Mo-K edge position shifts linearly to higher energies with increasing molybdenum valence (T. Ressler, et al. *J. Catal.* 2000, **191**, 75; *J. Catal.* 2002, **210**, 67). In our sample, both Mo-K edge positions shift to lower energies on reduction and to higher energies on oxidation, indicating that the valence of Mo was altered by redox treatment.

Several studies have investigated XANES of orthorhombic Mo–V based oxides. O. V. Safonova et al. reported that the valences of V and Sb in orthorhombic Mo–V–Nb–Sb oxide change on redox treatment, whereas the valence of Mo remains the same (*J. Phys. Chem. B*. 2006, **110**, 23962). N. R. Shiju et al. reported that only V oxidation states in orthorhombic Mo–V oxide, Mo–V–Nb–Te oxide, and Mo–V–Te oxide change on redox treatment under their redox conditions (*Chem. Mater.* 2008, **20**, 6611). In orthorhombic Mo–V based oxides, the oxidation state of V seems to change more readily than that of Mo.

Under our conditions, the oxidation states of both V and Mo seem to be changed by our redox treatment. We are currently further investigating the oxidation state change in orthorhombic Mo–V oxide.

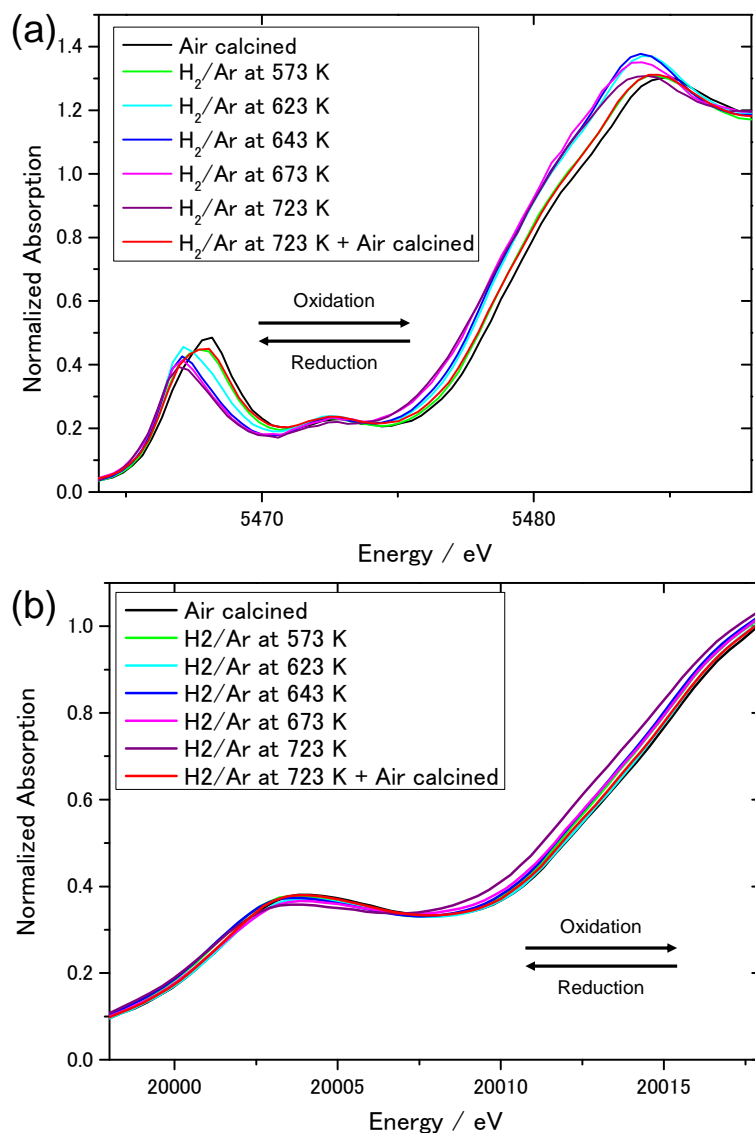


Table S1. Energy shift on redox treatment

Redox treatment	Energy at Normalized Absorption of 0.5	
	V K-edge / eV	Mo K-edge / eV
Calcined in air at 673 K	5475.18	20011.96
H ₂ reduction at 573 K	5477.99	20011.76
H ₂ reduction at 623 K	5477.67	20011.93
H ₂ reduction at 643 K	5477.59	20011.68
H ₂ reduction at 673 K	5477.44	20011.64
H ₂ reduction at 723 K	5477.36	20011.26
H ₂ reduction at 723 K, then calcined in air at 673 K	5477.95	20011.86

Figure S4. Normalized XANES spectra at (a) V K-edge and (b) Mo K-edge.

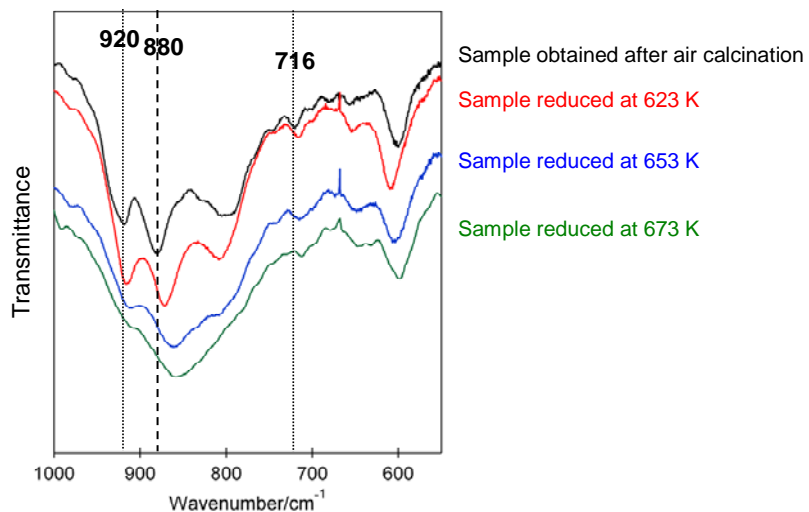


Figure S5. FT-IR spectra of orthorhombic Mo-V oxide after air calcination (black), after reduction at 623 K (red), 653 K (red), and 673 K (blue).

FT-IR spectra were recorded on a Perkin-Elmer Paragon 1000 FT-IR infrared spectrometer with a resolution of 2 cm⁻¹.

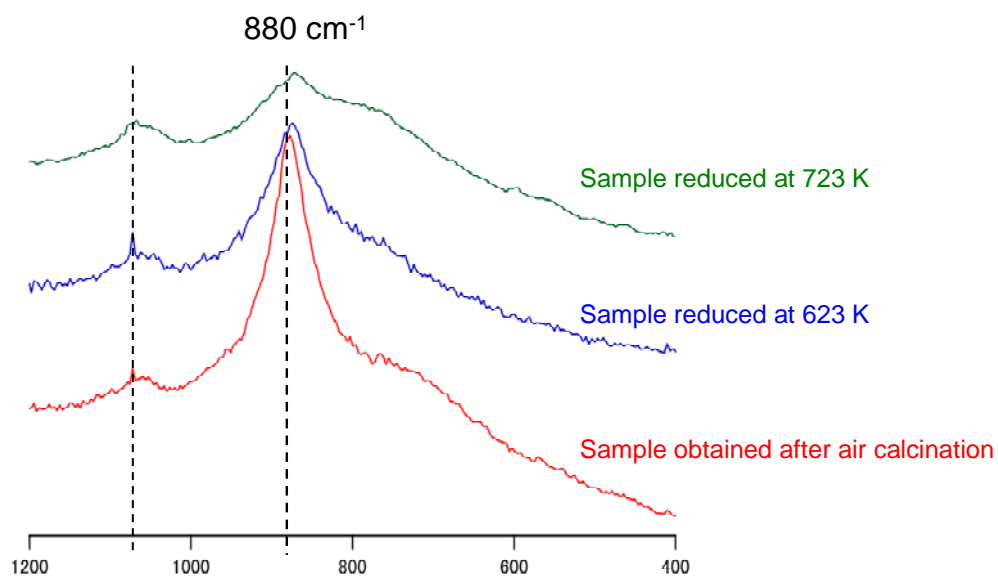


Figure S6. Raman spectra of orthorhombic Mo–V oxide after air calcination (red) and reduction at 623 K (blue) and 723 K (green).

Raman spectra of the solid-state sample were measured with an NRS-1000 (JASCO).

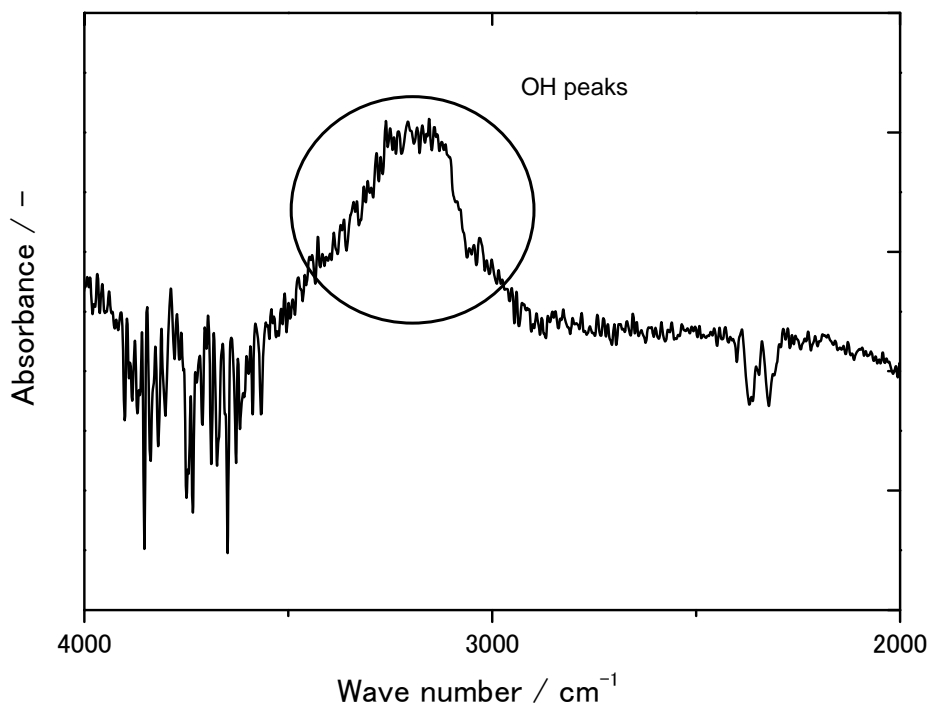


Figure S7. IR spectra of reduced orthorhombic Mo–V oxide. The spectrum was obtained by subtracting the spectrum of air-calcined Mo–V oxide (measured at 573 K after Ar flow for 70 min at 573 K to remove H₂O) from that of reduced orthorhombic Mo–V oxide (measured at 623 K after H₂/Ar flow for 120 min at 623 K). The peak around 3000 cm⁻¹ indicates the presence of OH groups.

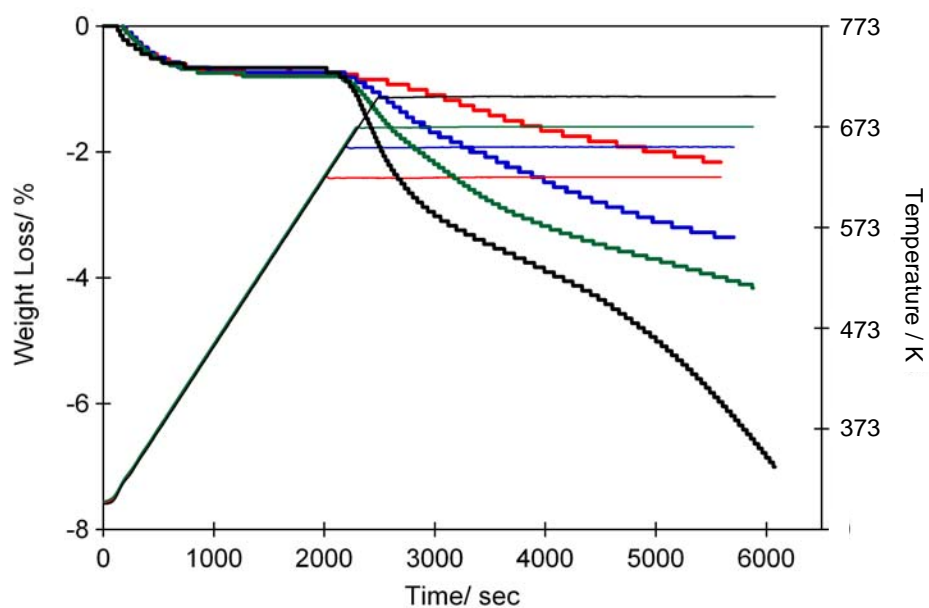


Figure S8. TG curve of orthorhombic Mo–V oxide under H_2/Ar (5/95) flow (70 ml min^{-1}).

The sample (ca. 0.01 g) was placed on a sample pan and calcined at 673 K under N_2 flow (70 ml min^{-1}) for 1 h. After the temperature was reduced under N_2 flow, the gas was changed to H_2/Ar (5/95) flow (70 ml min^{-1}) and the temperature was raised at a rate of 10 K min^{-1} and maintained at that temperature for 1 h.