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Molecular Sieves

Molybdenum–Vanadium-Based Molecular Sieves with Microchannels of Seven-Membered Rings of Corner-Sharing Metal Oxide Octahedra**

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Crystalline microporous oxides such as zeolites are indispensable materials in various applications ranging from industrial processes to everyday life, such as catalysts, ion-exchange materials, and molecular sieves.[1] Most of them contain tetrahedrally coordinated metal atoms, but octahedrally coordinated metal centers have recently attracted much attention as building blocks of crystalline microporous metal oxides.[2] Manganese oxides (pyrolusite, hollandite, todorokite, and romanechite) with micropores are the only crystalline porous materials based solely on octahedra (octahedral molecular sieves). These manganese oxides contain microtunnel pores consisting of $\{MnO_6\}$ octahedra that share edges and corners.[3]

Here we describe a novel type of octahedral molecular sieve, namely, crystalline orthorhombic Mo_3VO_x ($x = 11.2$), in which the microchannel is constructed by seven-membered rings of corner-sharing MO_6 (M = Mo or V) octahedra. It is isostructural to orthorhombic MoVNbTeO compounds,[4] which are very active and selective oxidation catalysts for light alkanes.[5] These mixed metal oxides have a layered orthorhombic structure with a slab composed of six- and seven-membered rings of corner-sharing $\{MO_6\}$ octahedra and pentagonal $\{(M)M_5O_{27}\}$ units with a $\{MO_7\}$ pentagonal bipyramid and five edge-sharing $\{MO_6\}$ octahedra, where M is Mo, V, or Nb. The layered six- and seven-membered rings form channel structures. The Te atom is believed to be located both in the six- and seven-membered rings[4] and block the channel. Recently, we succeeded in preparing an orthorhombic Mo_3VO_x compound that contains only Mo and V,[6] in which the channel is expected not to be blocked (Figure 1).[7]

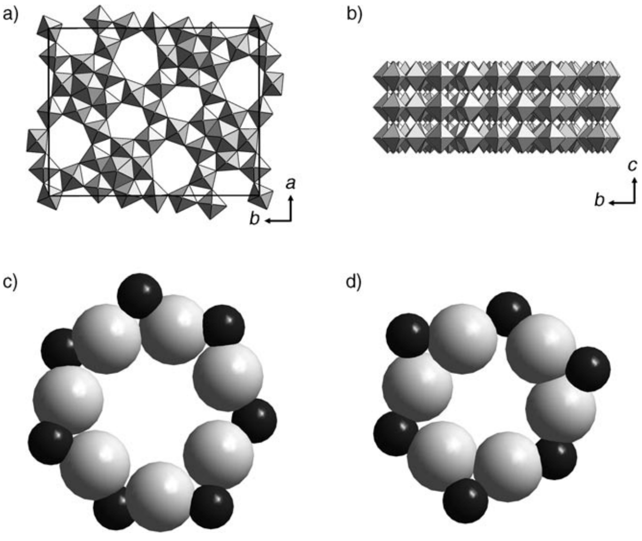

Figure 1. a,b) Polyhedral representation of the orthorhombic Mo_3VO_x ($x = 11.2$): *ab* plane (a), *bc* plane (b). c,d) Space-filling representation of a seven-membered ring (c) and a six-membered ring (d). Black and gray balls represent metal and oxygen atoms, respectively.

Aperture diameters of the seven- and six-membered rings are estimated to be about 0.33–0.37 nm and about 0.25–0.28 nm, respectively.[8]

The orthorhombic Mo_3VO_x mixed-metal oxide was synthesized from a reaction mixture of ammonium heptamolybdate $(NH_4)_6Mo_7O_{24}{\cdot}4\,H_2O$, and vanadyl sulfate $VOSO_4{\cdot}n\,H_2O$ (Mo/V 4:1) in H_2O under hydrothermal conditions.[6] The crude material contained an amorphous phase as a byproduct, which was removed by washing the products with an aqueous solution of oxalic acid. Water and NH_3 in the micropores were removed by calcination under air without collapse of the structure, as confirmed by thermogravimetry (TG), temperature-programmed desorption (TPD), and X-ray diffraction studies. The TG data and TPD revealed a weight loss in the range of 320–460 K corresponding to water evaporation and

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in the range of 470–670 K corresponding to water evaporation and NH_4 decomposition in the pores, which result in a microporous framework. The structure of the framework, determined by powder XRD after guest removal (673 K, 4 h, in air), is essentially the same as that before except for a small change in the unit-cell parameters (see the Supporting Information).

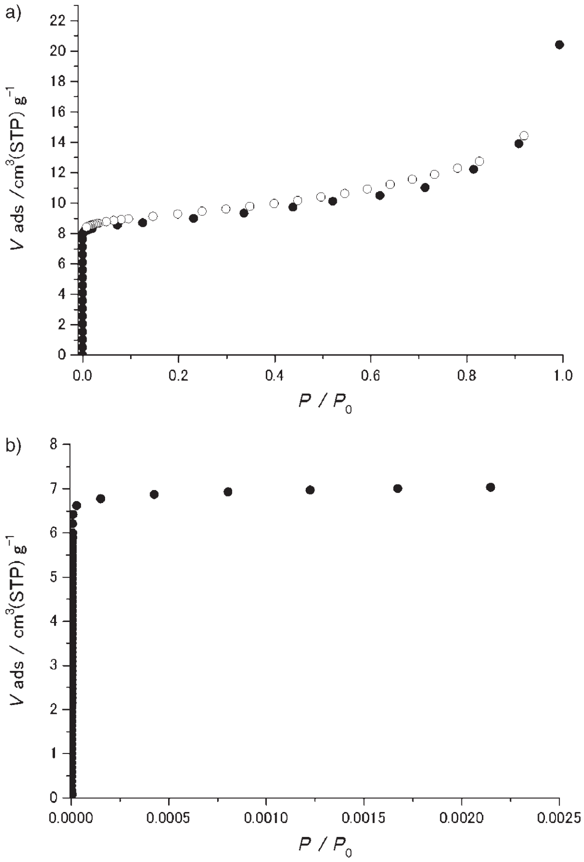

Figure 2. Adsorption and desorption isotherms for N_2 at 77 K (a) and adsorption isotherm for Ar at 87 K (b) plotted against relative pressure. Closed and open circles represent adsorption and desorption, respectively.

Microporosity was first confirmed by N_2 and Ar adsorption at 77 K and 87 K, respectively. Absorption of N_2 reproducibly revealed type I behavior typical of microporous materials[9] (Figure 2 a) after degassing treatment at 573 K for 2 h. Adsorbed amounts of both N_2 and Ar suddenly increased up to a relative pressure of 10^{-6}. Micropore volumes estimated from adsorbed amounts[9] at $P/P_0 = 0.002$ were 0.009(1) and 0.012 $cm^3 g^{-1}$ for N_2 and Ar, respectively, which is about 50–70 % of the calculated pore volume of a seven-membered ring channel.[10] The structure of the framework determined by powder XRD after gas sorption measurements is the same as before, that is, the framework structure is stable under a degassing conditions (see the Supporting Information).

Mo_3VO_x forms rodlike crystals with lengths of up to several tens of micrometers (Figure 3 a). The cross section is rhombic in shape with submicrometer thickness (Figure 3 b). The *ab* planes are oriented perpendicular to the long axis of the rodlike crystal, which coincides with the *c* direction (see Figure 3 c and the Supporting Information). The long and short diagonals of the rhombus are parallel to the *a* and *b* directions, respectively. The external surface area was estimated to be a few square meters per gram.[11] The slight increase in amount of adsorbed N_2 at high relative pressure corresponds to multilayer adsorption on the external surface.

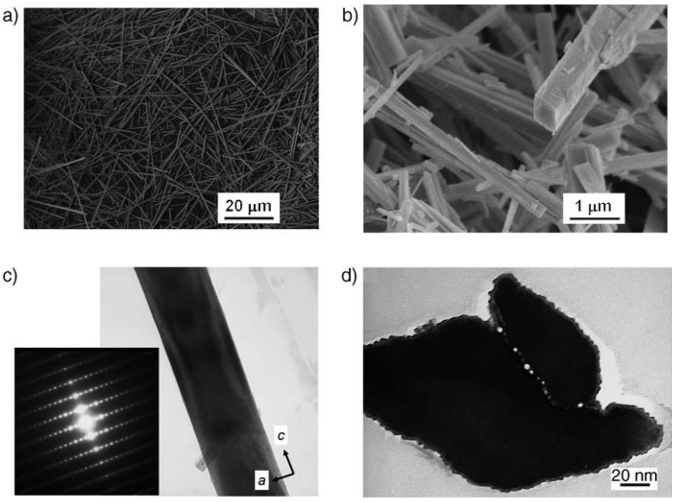

Figure 3. a,b) SEM images of orthorhombic Mo_3VO_x. c,d) TEM images viewed along the [010] direction (c) and [001] direction (d).

A few rods were formed by twin-type crystal growth, and intracrystal pores of a few nanometers in diameter were produced (Figure 3 d). However, the quality of the intracrystal micro/mesopore is poor. Therefore, the sorption of N_2 and Ar in the micropore range occurs in the structural microchannel of seven-membered rings.

The pore diameter was estimated by the molecular-probe technique (Figure 4 a). Plots of adsorbed volumes of the probes, calculated by using the Dubinin–Astakhov (DA) equation, against kinetic diameter of the probes CO_2 (0.33 nm), Kr (0.36 nm), methane (0.38 nm), ethane (0.4 nm), *n*-butane (0.43 nm), and *n*-hexane (0.49 nm)[1,12]) are shown in Figure 4 b. The pore diameter was calculated to be about 0.4 nm, which is attributed to the aperture diameter of the seven-membered ring channel, and the micropore volume calculated by the DA equation for smaller gases is about 0.025 $cm^3 g^{-1}$, which is close to the calculated pore volume of a seven-membered ring channel.[10] These results indicate that the orthorhombic Mo_3VO_x acts as a novel type of molecular sieve material in which the seven-membered ring channel composed of corner-sharing octahedra can act as a micropore.

Since Mo_3VO_x has high thermal stability (up to 673 K) and shows outstanding catalytic performance for oxidation of acrolein to acrylic acid,[6] this novel microporous material may have redox activity. Alternation of the redox states of Mo and V would affect the metal–oxygen bond lengths and negative charge density on oxygen, and this in turn will change the pore properties (size, volume, and affinity for adsorbates).

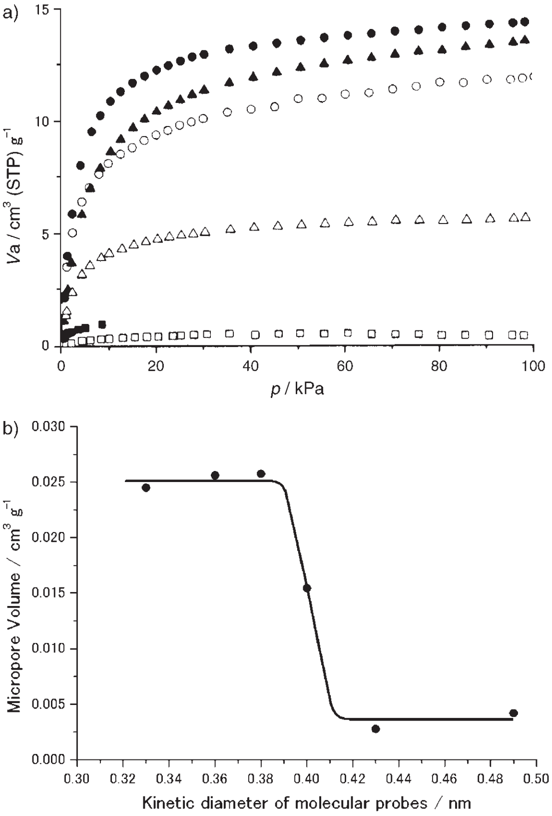

Figure 4. a) Adsorption isotherms for Kr (closed circles), methane (closed triangles), CO_2 (open circles), ethane (open triangles), *n*-butane (open squares), and *n*-hexane (closed squares) at 298 K plotted against pressure. b) Micropore volume, estimated by the DA method, plotted against kinetic diameter.

Orthorhombic Mo_3VO_x is composed of corner-sharing $\{MO_6\}$ octahedra and pentagonal $\{(M)M_5O_{27}\}$ units. Recently, pentagonal $\{(M)M_5O_{27}\}$ units have attracted much attention as unique building blocks of both molybdenum-based metal oxides[4,6a] and molecular clusters (polyoxomolybdates).[15] We have demonstrated that orthorhombic Mo_3VO_x is produced from a solution containing the pentagonal $\{(M)M_5O_{27}\}$ unit.[6a] Elucidating the formation mechanism of orthorhombic Mo_3VO_x may lead to the development of strategies to design novel octahedral molecular sieves.

In summary, we have reported the novel octahedral molecular sieve orthorhombic Mo_3VO_x, which has an ordered microchannel with a seven-membered ring of corner-sharing $\{MO_6\}$ octahedra. The aperture diameter of the channel is about 0.4 nm, and molecules with kinetic diameter of less than 0.4 nm such as methane, ethane, and CO_2 to enter. Furthermore, the pore size of this material, which is very close to that of light alkanes, enables control separation and catalytic selectivity. Our next interest is to fully understand and control the micropore properties.

Experimental Section

All chemicals were of reagent grade and used as supplied, and distilled water made in the laboratory was used throughout the study.

Preparation of orthorhombic Mo_3VO_x: $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (8.82 g, 50 mmol) dissolved in water (120 mL) was mixed at 298 K with $VOSO_4\cdot nH_2O$ (3.28 g, $n=5.4$, 12.5 mmol) dissolved in water (120 mL). The resulting solution was stirred for 10 min and then transferred to a 300-mL teflon liner of a stainless steel autoclave. The reaction mixture was purged with nitrogen for 10 min and then heated at 448 K for 48 h. A gray solid (about 2.3 g) was isolated from the reaction mixture by filtration, washed with water, and dried at 353 K overnight. The crude solid (2.0 g) was added to an aqueous solution of oxalic acid (0.4 M, 50 mL), and this mixture was stirred at 333 K for 30 min. The solid was isolated from the suspension by filtration, washed with water, and dried at 353 K overnight (1.0 g). For calcination in air, Mo_3VO_x (0.5 g) was placed in a conventional furnace and heated at 10 K min^{-1} to 673 K, and the temperature was kept at 673 K for 2 h. Elemental analysis revealed a Mo/V ratio of about 3:1.

Characterization: Scanning electron microscopy (SEM) was performed on a JSM-7400F (JEOL). Transmission electron microscopy (TEM) images were taken by a atomic-resolution high-voltage electron microscope (ARHVEM; JEOL JEM-ARM-1300) and 200-kV TEM (JEOL JEM-2000FX) at Hokkaido University. Powder specimens were dispersed in ethanol and dropped onto a carbon-coated honeycomb copper grid. Cross-sectional samples were prepared by embedding specimens in TAAB Epon 812 Resin and cutting ultrathin sections with a diamond knife. Elemental analysis was carried out by Mikroanalytisches Labor Pascher (Remagen, Germany). N_2 and Ar physisorption was performed at 77 and 87 K, respectively, in a gas adsorption analyzer (BELSORP-18; BELJAPAN, Inc. Japan). The measurements were performed at relative pressures from 10^{-8} to 1.0 in an incremental dose mode. The samples were outgassed at 573 K under vacuum for 2 h. Adsorption of the various probes was measured at 298 K. About 0.2 g of the sample was degassed at 573 K for 2 h. Molecular probes of different kinetic diameters, including CO_2 (0.33 nm), Kr (0.36 nm), methane (0.38 nm), ethane (0.4 nm), *n*-butane (0.43 nm), and *n*-hexane (0.49 nm),[1,12] were used for adsorption at 298 K to evaluate the porosity of the adsorbent in a gas adsorption analyzer (BELSORP-max; BELJAPAN, Inc. Japan).

Adsorption data were used to characterize the adsorbent by means of the Dubinin–Astakhov (DA) equation [Eq. (1)].[13]

$$W = W_0 \exp[-(A/\beta E_0)^m] \quad (1)$$

Herein, A is the Polanyi adsorption potential, calculated from the saturated vapor pressure P_0 and the adsorption pressure P by Equation (2).

$$A = RT \ln(P_0/P) \quad (2)$$

E_0 is the characteristic energy, which is a function of the microporous structure of a given adsorbent, $W_0 = a_0\nu$ the limiting micropore volume, a_0 the limiting amount adsorbed, ν the molar volume of the adsorbate, β the similarity coefficient of the characteristic curves, m a structure-related parameter, and W the adsorbed volume. W_0 can be determined from the intercept of the $\ln W$ versus $\ln^m(P_0/P)$ ($m = 3$[14]) plot under the assumption that the density of the adsorbed phase is the same as the density of the bulk liquid.

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[11] Assuming that the rodlike crystal has dimensions of 0.5 μm in the long diagonal distance and 0.3 μm in the short diagonal distance of the rhombic cross section and is 20 μm in length, the external surface area is about $2\,m^2\,g^{-1}$.

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