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Hydrothermal synthesis of W–Ta–O complex metal oxides by assembling MO_6 (M = W or Ta) octahedra and creation of solid acid

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ABSTRACT

Layered-type tungsten and tantalum oxides (W–Ta–O) were synthesized by the hydrothermal method. The synthesized W–Ta–O showed characteristic peaks at $2\theta = 22.7°$ and 46.2° in an X-ray diffraction pattern (Cu Kα), indicating linear corner sharing of MO_6 (M = W, Ta) octahedra in the *c*-direction. The same layered-type materials were obtained with a wide range of W and Ta composition ratios using soluble Lindqvist-type tantalum polyoxometalate ($Na_8(Ta_6O_{19})\cdot 24.5H_2O$). Na^+ cations of as-synthesized W–Ta–O were replaced with NH_4^+ and then calcined at 500 °C to form Brønsted acid sites. The catalytic activity of W–Ta–O increased with increasing W ratio, suggesting that strong acid sites were generated. From Raman and adsorption measurements of W–Ta–O with various crystalline structures, it was revealed that the crystalline motif of W–Ta–O in the *a*–*b* plane was an interconnection of MO_6 (M = W, Ta) octahedra and $\{M_6O_{21}\}$ pentagonal units and micropore channels, but without long-range order.

1. Introduction

Complex metal oxides of transition metals are important inorganic materials as catalysts and ceramics. It is expected that the demand for solid acid catalysts will increase because they are reusable and readily separable from the liquid phase. One of the typical solid acid catalysts is niobium oxide. Hydrated niobium oxide ($Nb_2O_5\cdot nH_2O$, niobic acid) has high acid strength ($H_0 \leqslant -5.6$) and has Lewis and Brønsted acidity. Niobium oxide (or hydrated niobium oxide) has been widely used as a water-tolerant solid acid catalyst [1–5].

In parallel with studies on solid acid catalytic activity and the structure of acid sites for $Nb_2O_5\cdot nH_2O$, interest has also been shown in tantalum oxide ($Ta_2O_5\cdot nH_2O$). The formation mechanisms of acid sites are similar for $Ta_2O_5\cdot nH_2O$ and $Nb_2O_5\cdot nH_2O$ and, moreover, the strength of the acid and thermal stability of $Ta_2O_5\cdot nH_2O$ are higher than these of $Nb_2O_5\cdot nH_2O$ [6]. Ushikubo reported that a Lewis acid is formed mainly in the absence of water for $Ta_2O_5\cdot nH_2O$ and that a Brønsted acid is formed by steam treatment at 100 °C [7]. Tanaka and Shishido and co-workers [8,9] reported that a Ta_2O_5/Al_2O_3 catalyst prepared by an impregnation method showed solid acidity and high thermal stability. Brønsted acids were generated by a two-dimensional Ta–O–Ta network consisting of TaO_6 units having distorted octahedral symmetry.

To enhance the solid acidity, modification of $Ta_2O_5\cdot nH_2O$ by sulfate and synthesis of a complex oxide catalyst have been investigated. Domen et al. reported a W–(Nb, Ta)–O layered complex oxide synthesized by a solid state method [10]. Brønsted acid sites are formed on the monolayer surface by proton exchange treatment. Tungsten oxide is a class of solid acids, which form tungsten bronze based on octahedra structure [11]. The formation of complex oxides between M^V (Group 5 elements) and tungsten or the replacement of W in the WO_3 structure with M^V enhances the solid acidity and the catalytic performance [12]. The acidity of these catalysts has been shown to be attributable to bridging hydroxyl groups M–(OH)–M′ (M = Nb or Ta, M′ = Mo or W), representing a strong Brønsted acid site [9,13,14].

We have studied the relationship between the crystalline structure of complex metal oxides and their catalytic activity [15–17]. Studies on crystalline metal oxides of Mo_3VO_x have demonstrated that the oxidation activities depend on their crystalline arrangement of pentagonal $\{Mo_6O_{21}\}$ units and MO_6 octahedra in the *a*–*b* plane. These materials contain heptagonal channels in their structures. For the synthesis of these catalysts, the formation of pentagonal $\{Mo_6O_{21}\}$ units in the precursor solution was important, and the pentagonal units assembled further into a complex metal oxide under hydrothermal conditions [18]. A complex metal oxide that possess a similar layered structure in the *c*-direction by

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corner sharing of MO_6 (M = Mo, W, V, Ta, Nb) octahedra has been synthesized by a hydrothermal method [19–21]. These catalysts were found to function as solid acids, the properties of which were understood from a structural point of view.

We report here the synthesis of W–Ta–O by a hydrothermal process from ammonium metatungstate and tantalic acid or tantalum Lindqvist-type polyoxometalate ($Na_8(Ta_6O_{19})\cdot 24.5H_2O$) precursors. The Lindqvist-type polyoxometalate is a simple structure formed by TaO_6 octahedra and it can be synthesized under basic conditions [22,23]. The complex oxide W–Ta–O having a novel crystal structure can be synthesized by the assembly of MO_6 units. The obtained W–Ta–O samples were octahedra-based layered-type materials. We demonstrated the relationships between their crystalline structure and their catalytic activity and acidity.

2. Experimental

2.1. Synthesis of $Na_8(Ta_6O_{19})\cdot 24.5H_2O$

Lindqvist-type polyoxometalate ($Na_8(Ta_6O_{19})\cdot 24.5H_2O$) was prepared according to the literature [23]. First, 2.5 g (5.7 mmol) Ta_2O_5 was calcined with 4.3 g (0.11 mol) NaOH in an alumina crucible at 400 °C for 5 h. The resulting sample was treated with 30 mL of cold water and then stirred for 30 min while cooling in an ice bath. Distilled water (120 mL) was added to the liquid, and the liquid was separated by centrifugation for 10 min at 1500 rpm. The obtained solid was dried under vacuum. The collected solid was refluxed with distilled water (80 mL) at 80–85 °C until the solution became clear. After the transparent solution was filtered, the filtrate was placed in a refrigerator for 1 day. The obtained $Na_8(Ta_6O_{19})\cdot 24.5H_2O$ crystal was filtered and dried in air overnight.

2.2. Preparation of W–Ta–O samples

W–Ta–O oxides were synthesized by a hydrothermal method from ammonium metatungstate (AMT, $(NH_4)_6H_2W_{12}O_{40}\cdot nH_2O$) and several Ta precursors. Typically, the Ta precursor (2.7 mmol based on Ta) was added to 25 mL of water and dispersed by ultrasonic agitation for 10 min. AMT (Nippon Inorganic Colour & Chemical Co.) containing 2 mmol W was dissolved in 20 mL of deionized water and then the W precursor solution was added to the Ta dispersed liquid. Then the mixture was sealed in a 60 mL Teflon liner stainless steel autoclave. Hydrothermal treatment was carried out at 175 °C for 3 days. The obtained solid was filtered, washed thoroughly with deionized water, and dried at 80 °C overnight. Lindqvist-type polyoxometalate ($Na_8(Ta_6O_{19})\cdot 24.5H_2O$), $Ta_2O_5\cdot nH_2O$ (Mitsuwa Chemical), Ta_2O_5 (Wako), $TaCl_5$ (Wako), TaF_5 (Wako), Ta oxalate solution (H. C. Stark), and $K(TaO_3)$ (Alfa Aesar) were used as Ta precursors, and the obtained W–Ta–O samples were denoted as W_xTa_yO (TaL), W_xTa_yO (TaA), W_xTa_yO (TaO), W_xTa_yO (TaCl), W_xTa_yO (TaF), W_xTa_yO (TaOxa), and W_xTa_yO (KTaO), respectively. The elemental ratios (x = W/(W + Ta), y = Ta/(W + Ta)) were measured by ICP for the synthesized W–Ta–O samples. For W–Ta–O(TaCl), the elemental ratio of the precursor was represented because the obtained sample did not dissolve in the mixed solution of HF and HNO_3. The samples were calcined at 500 °C for 2 h under air before use as catalysts. The rate of temperature increase was 10 °C min^{-1} from room temperature.

As-synthesized material (W_xTa_yO (TaL), 0.3 g) was dispersed in 15 mL of NaCl solution (0.1 mol L^{-1}) for ion-exchange treatment. The dispersed sample was stirred at 80 °C for 8 h. The resulting solid was collected by filtration. Then the sample was washed with water (3 × 100 mL) and dried at 80 °C overnight. The obtained sample was denoted as Na^+–W_xTa_yO (TaL). A W_xTa_yO (TaL) sample treated with NH_4Cl solution was denoted as NH_4^+–W_xTa_yO (TaL). NH_4^+–W_xTa_yO (TaL) was prepared by ion-exchange treatment of W_xTa_yO (TaL) in 15 mL of NH_4Cl solution (0.1 mol L^{-1}) at 80 °C for 8 h.

To compare the relationships between crystalline structure and catalytic activity, various crystalline W–Ta–O samples were synthesized. Tetragonal $Ta_{16}W_{18}O_{94}$ was obtained by calcination of $W_{58}Ta_{42}O$(TaA) at 1100 °C for 6 h. Orthorhombic $Cs_{0.5}[Ta_{2.5}W_{2.5}]O_{14}$ was synthesized according to the literature for orthorhombic $Cs_x(Nb,W)_5O_{14}$ [24]. Cs_2CO_3, $Ta_2O_5\cdot nH_2O$, and AMT (Cs:Ta:W = 1:5:5) were dispersed in 40 mL of distilled water. The mixture was stirred and dried at 60 °C, and Cs–W–Ta powder was obtained. The powder was calcined at 1100 °C for 6 h to obtain orthorhombic $Cs_{0.5}[Ta_{2.5}W_{2.5}]O_{14}$. Pyrochlore W–Ta–O was synthesized by a hydrothermal method. AMT (W: 2 mmol) and $Ta_2O_5\cdot nH_2O$ (2.7 mmol) precursors were added to 45 mL of water and dispersed. The pH of the mixture liquid was adjusted to 10.3 using NH_3 solution. Then the mixture was sealed in a 60 mL Teflon liner stainless steel autoclave. Hydrothermal treatment was carried out at 175 °C for 3 days. Hexagonal WO_3 was synthesized by the same hydrothermal method from only the AMT precursor.

2.3. Alkylation reaction

A 50 mL round-bottomed three-necked flask equipped with a reflux condenser was used as a stirred bed reactor to test the catalytic activities. Typically, a mixture of benzyl alcohol (10 mmol), anisole (100 mmol), and an internal standard, decane (5 mmol), was added to the reactor and the reaction temperature was adjusted to 100 °C. Then 0.1 g of a catalyst and a Teflon-coated magnetic stir bar were loaded into the reactor. Aliquots (each 0.1 mL) were collected at intervals. The concentrations of the reactant and product were measured by gas chromatography using a flame ionization detector (GL Science GC390B) with a ZB-1 column.

2.4. Characterization

The catalysts were characterized by the following techniques. Elemental compositions were determined by an inductive coupling plasma (ICP-AES) method (ICPE-9000, Shimadzu). Samples were dissolved in a mixed acid solution of HF and HNO_3. CHN powder XRD patterns were measured with a diffractometer (RINT Ultima +, Rigaku) using CuKα radiation (tube voltage 40 kV, tube current 20 mA). Diffractions were recorded in the range of 4–60° at 5° min^{-1}. Morphology was investigated using a scanning transmission electron microscope (HD-2000, Hitachi) at 200 kV. The samples were dispersed in ethanol with ultrasonic treatment for several minutes, and drops of the suspension were placed on a copper grid for STEM observations. Raman spectra were obtained using a spectrometer (in Via Reflex, Renishaw, 2 cm^{-1} spectral resolution) under conditions of wavelength of 532 nm and collection time of 10 s. N_2 adsorption isotherms at liquid N_2 temperature were measured using an auto adsorption system (Belsorp Max, Bel Japan) for the samples. Prior to N_2 adsorption, the catalysts were evacuated under vacuum at 300 °C for 2 h. External surface area was calculated by a multipoint Brunauer–Emmett–Teller (BET) method and the t method. Temperature-programmed desorption (TPD) of ammonia, NH_3 TPD, was used to measure oxide surface acidity. The experiment was carried out using an auto chemisorption system (Bel Japan). The experimental procedure was as follows. The catalyst (ca. 50 mg) was set between two layers of quartz wool and preheated under helium (50 mL min^{-1}) at 400 °C for 1 h. Then ammonia was introduced at 100 °C for 30 min. The desorption profile from 100 to 700 °C was recorded with a mass spectrometer under helium flow (50 mL min^{-1}). Temperature-programmed decomposition mass spectrometry