Preparation of Porous MTiO_x (M=Cr, Mo, or W) Composite Oxides from a Mesostructured Material of Titanium Oxysulfate and Surfactant Micelles Based on a Wall Ion Exchange-Calcination Method

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Abstract

Wall ion exchange (WIE) and subsequent calcination were applied to prepare porous TiO₂-based composite oxides using a composite of TiOSO₄•xH₂SO₄•xH₂O and cetyltrimethylammonium bromide (TS). Chromium oxyanion HCrO₄⁻ in an aqueous solution was ion-exchanged stoichiometrically with HSO₄⁻ in TS at pH values in the range of 2.2 to 5.5. Calcination of the HCrO₄⁻-introduced TS (Cr-TS) at 673 K for 2 h in air produced Cr-Ti oxide with surface areas of 296-430 m² g⁻¹, pore diameters of 1.7-2.5 nm, and a wormhole-like pore structure. These high surface areas could be achieved at ratios of Cr and Ti in the Cr-Ti oxide of 0.30-0.39 or above. XAFS, FT-IR, and UV-vis diffuse reflectance spectra indicated the occurrence of dimerization of HCrO₄⁻ to Cr₂O₇²⁻ during drying of the Cr-TS. The Cr₂O₇²⁻ species was then reduced to Cr(III) species upon calcination at 473-573 K. The Cr(III) species located on the

surfaces of the pore walls were reoxidized to Cr(VI) upon calcination at 673 K, whereas those inside the pore walls remained unchanged. The present WIE-calcination method was applied to oxyanions of Mo, W, and V but did not produce the stoichiometric exchange that occurred in the Cr-TS system. Porous Mo- and W-Ti oxides with surface areas of 197-258 and 218-273 m² g⁻¹, respectively, were obtained upon treatment at approximately pH 10 and subsequent calcination at 673 K, although the reaction mechanisms were unknown. No porous V-Ti oxides with a high surface area could be obtained.

Keywords: Titanium, Porous composite oxides, Chromium, Wormhole pore structure, Wall ion exchange.

1. Introduction

Porous TiO₂-based composite oxides have gathered much attention for their use as catalysts and supports in photo-catalysis [1-4] and in the selective catalytic reduction of nitrogen oxide with ammonia [5,6]. These oxides can be prepared by various methods [4,7-9]. For example, a sol-gel method using inorganic precursors and templates [10] produced Cr-Ti mixed oxide with a surface area of 317 m² g⁻¹ and a pore diameter of 2.5 nm [7]. A sol-gel hydrolysis method using *n*-alkylamine as a template produced a microporous Ti-Cr mixed oxide with a surface area of 494-564 m² g⁻¹ [8]. The pore size could be controlled in the range 0.9-1.5 nm by changing the alkyl chain length of the surfactants. An evaporation-induced self-assembly method afforded highly ordered cubic W-Ti oxide (2-8 mol% of WO₃) films of 120-130 m² g⁻¹ [4]. A template free-method was also used for preparation of a mesoporous MoO₃/TiO₂ composite,

which exhibited a surface area of $173 \text{ m}^2 \text{ g}^{-1}$ and a MoO_3 content of ca. 14 wt% [9]. These synthesis methods of TiO_2 -based composite oxides are well established but were specialized for their respective materials, and no versatile method has been suggested to prepare various composites through a unified procedure.

Our group has developed the wall ion exchange (WIE) approach [11-14] using a composite material of $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ and cetyltrimethylammonium bromide (CTAB) [15]. The HSO_4^- ions in the wall of the composite were found to be readily exchanged for oxyanions of P [11,14], As [12], and Se [13] in aqueous solutions, which were effective for collecting the harmful ions in water. In addition, calcination of phosphorus oxyanions-introduced composite produced porous P-Zr oxides with high surface areas of $456\text{-}547 \text{ m}^2 \text{ g}^{-1}$ and pore diameters of 1.30-1.66 nm [14]. Recently, this WIE-calcination technique was expanded to other transition metal oxyanions, which resulted in the preparation of porous ZrO_2 -based composite oxides containing W, Cr, Mo, or V [16]. The novel and successful preparation of the porous ZrO_2 -based composite oxides through the WIE-calcination method motivated us to apply it to other materials.

As introduced in the first paragraph, various TiO_2 -based porous materials have attracted much attentions, and therefore, the present study was devoted to examine the possibility that the WIE-calcination method can be applied for preparation of porous TiO_2 -based composite oxides. Among various reported composites with hexagonally ordered arrays of surfactant micelles, the mesostructured material of titanium oxysulfate ($\text{TiOSO}_4 \cdot x\text{H}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$) and surfactant micelles [15] (abbreviated as TS) was used as the starting material. We thought that the HSO_4^- ions contained in the TS wall might be ion-exchanged with the other oxyanions in aqueous solutions. The ion-exchange

behavior between HSO_4^- in the TS wall and transition metal oxyanions in the solution was first investigated, and then, the resulting metal oxyanions-introduced TSs were calcined to prepare the porous TiO_2 -based composite oxides. The ion-exchange behaviors of TS and the physicochemical properties of the obtained materials were rather different from those of Zr-based composite. The metal oxyanions-introduced TSs just after the ion exchange process and after the calcination process were designated as M-TSs and MTiOs, respectively.

2. Experimental

2.1. Synthesis of TS

The parent TS was prepared using titanium oxysulfate $\text{TiOSO}_4 \cdot x\text{H}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$ (Sigma-Aldrich, St. Louis, MO, USA) and cetyltrimethylammonium bromide (CTAB) (Tokyo Kasei Kogyo, Co., Ltd., Tokyo, Japan) on the basis of the reported protocols [15]. An aqueous solution of $\text{TiOSO}_4 \cdot x\text{H}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$ (0.356 mol L^{-1}) was added to an aqueous solution of CTAB (0.137 mol L^{-1}) with stirring at room temperature. The molar ratios of $\text{TiOSO}_4 \cdot x\text{H}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$, CTAB, and H_2O in the mixture were 1.00, 0.54, and 434, respectively. The resulting solution was continuously stirred at the same temperature for 1 h. The obtained white precipitate was filtered, washed five times with deionized water, and dried at 353 K for 12 h. The composition of the prepared TS was $\text{TiO}(\text{HSO}_4)_x(\text{C}_{19}\text{H}_{42}\text{N})_y(\text{OH})_z \cdot n\text{H}_2\text{O}$ with $x=0.68-0.75$, $y=0.58-0.62$, $z=1.63-1.87$, and $n=0-0.52$.

2.2. Preparation of MTiOs through the WIE treatment and calcination

The WIE treatment for the parent TS was performed using an aqueous solution of K_2CrO_4 (Kanto Chemical Co. Inc., Tokyo, Japan), $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (Nippon Inorganic Colour & Chemical Co., Ltd., Tokyo, Japan), $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41}\cdot 5\text{H}_2\text{O}$ (Wako Pure Chemical Industries, Ltd., Osaka, Japan), or NH_4VO_3 (Wako Pure Chemical Industries, Ltd.). After adjustment of the pH of the solution using an aqueous solution of NH_3 or HCl , 1 g of TS was dispersed in a desired amount of a 20 mmol L^{-1} exchange solution, and then, the mixture was stirred at room temperature for 2 h, filtered, and dried at 353 K for 12 h. The resultant powder was heated at a rate of 1 K min^{-1} to the desired temperature in air and kept at this temperature for 2 h to remove/oxidize organic surfactants.

2.3. Characterization of the materials

The amount of each element was determined by ion chromatography on a Shimadzu HIC-10A and an inductively coupled plasma mass spectrometer, Perkin-Elmer ELAN DRC-e. The X-ray diffraction (XRD) patterns were obtained on a Rigaku RINT2000 with a monochromator using a Cu-K_α radiation ($\lambda = 0.15406$ nm) source operated at 40 kV and 40 mA. The nitrogen adsorption-desorption isotherm was measured at 77 K using a Bel-Japan BELSORP mini II. The samples were evacuated at 423 K for 2 h before measurement. The surface area was calculated by the Brunauer-Emmett-Teller (BET) method. The pore size was estimated from the adsorption branch of the isotherm using the Barrett-Joyner-Halenda (BJH) method. High-resolution transmission electron micrographs (TEM) were obtained on a JEOL JEM-1200EX II transmission electron microscope operated at 200 kV. Field emission scanning electron microscopy (FE-SEM) images were collected on a Hitachi HR-S5500 operated

at 30 kV. The measurement of the FT-IR spectrum was performed using a Jasco FT/IR 6300 apparatus. The samples were diluted by KBr and then pressed into a film before the measurement. The UV-vis diffuse reflectance (UV-vis DR) spectra were collected using a Perkin-Elmer Lambda 19 UV-vis-NIR spectrometer. Barium sulfate was used as a reference material. The X-ray absorption fine structure (XAFS) spectra of the Cr K-edge were obtained on the beam line BL-7C equipped with a Si(111) double-crystal monochromator of the Photon Factory at the High Energy Accelerator Research Organization in Tsukuba, Japan. The samples were diluted by boron nitride and then pressed into a disk before the measurement.

3. Results and discussion

3.1. Introduction of chromium oxyanions into TS through the WIE treatment

First, the ion-exchange behavior between sulfate anions in TS and chromium oxyanions in an aqueous solution is summarized because CrTiOs provided the highest surface areas among the materials prepared in the present study. The effects of the pH value of the exchange solution (pH_{sol}) on the introduction of chromium into TS and the release of sulfate from TS were investigated (Supplementary Data, Table S1). The pH_{sol} values before and after the WIE treatment were named $\text{pH}_{\text{sol(i)}}$ and $\text{pH}_{\text{sol(e)}}$, respectively. Because the pH_{sol} values changed during the WIE treatment, we discussed the effects of $\text{pH}_{\text{sol(e)}}$ on the ion-exchange behavior. Fig. 1 shows the amount of chromium introduced into TS upon the WIE treatment (Cr_{in}) and S released from TS (S_{re}) as a function of $\text{pH}_{\text{sol(e)}}$. The Cr_{in} increased with increasing pH, maximized at approximately $\text{pH}_{\text{sol(e)}} 5.5$, and drastically decreased above $\text{pH}_{\text{sol(e)}} 6$. The S_{re} increased with increasing pH and became constant above $\text{pH}_{\text{sol(e)}} 6$. The Cr_{in}

and S_{re} values at $pH_{sol(e)}$ 2.2-5.5 were 1.43-1.83 and 1.19-1.64 mmol g⁻¹, respectively, except for an exceptionally low value. The S_{re}/Cr_{in} ratios were varied in the region from 0.7 to 1.1. The values of the ratios were approximately one, indicating a stoichiometric ion-exchange between chromium oxyanions and HSO_4^- ions during the WIE treatment. At $pH_{sol(e)}$ 6.9 and above, the S_{re} values were almost constant at 1.83-1.88 mmol g⁻¹, which were the same as the amount of sulfate contained in the parent TS, 1.90 mmol g⁻¹.

The phase diagram of hexavalent chromium oxyanions in an aqueous solution was previously reported as a function of the Cr(VI) concentration and the pH value, as shown in Fig. 2 [17]; the present experimental results are superimposed on the figure. Figs. 1 and 2 revealed that the stoichiometric ion-exchange between chromium and sulfate proceeded only when the $pH_{sol(e)}$ value was in the $HCrO_4^-$ region, whereas the behaviors in the CrO_4^{2-} region were unknown yet. Because the radius of a monomeric chromium oxyanion (0.24 nm for CrO_4^{2-} [18]) is very close to that of HSO_4^- (0.21 nm [19]), $HCrO_4^-$ can be introduced in TS via stoichiometric ion-exchange with HSO_4^- . Similar ion-exchange behaviors have been reported in the other ion exchange systems [12,13]. Thus, the process in Equation 1 could be concluded.

Note that the pH_{sol} values decreased after the WIE treatment. The released HSO_4^- decreased the pH via dissociation to H^+ and SO_4^{2-} in the solution (Equation 2). In contrast, the excess release of sulfate compared with the introduction of chromium at $pH_{sol(e)}$ 6 and above occurred from the ion exchange between OH^- and HSO_4^- according to Equation 3, although there was no experimental evidence for this process.

On the XRD pattern of the parent TS, three peaks were observed at 2θ 2.2, 3.7, and 4.3° (Supplementary Data, Fig. S1), which were attributed to the (100), (110), and (200) diffractions, respectively, of a hexagonal structure [15]. All of the Cr-TSs obtained after the WIE treatment exhibited only (100) peaks independent of the $\text{pH}_{\text{sol(e)}}$ applied, suggesting the TS approximately maintained the mesostructure morphology. The hexagonal symmetry of Cr-TS prepared at $\text{pH}_{\text{sol(e)}}$ 4.6 was confirmed by the TEM observations (Supplementary Data, Fig. S2). The diffraction angles of Cr-TSs, however, were somewhat varied in the range 2.0 - 2.4° , and unidentified diffractions were occasionally observed.

The ion-exchange behavior between HSO_4^{-} and HCrO_4^{-} was then investigated as a function of initial amount of chromium in the exchange solution (Cr_{sol}); the results are shown in Fig. 3 and in Supplementary Data Table S2. Here, the $\text{pH}_{\text{sol(i)}}$ values were adjusted to 8.6-8.9 based on the good result of Run 9 in Table S1. In the range of Cr_{sol} of 0.38-1.90 mmol, both the Cr_{in} and the S_{re} values increased monotonically and in parallel with increasing Cr_{sol} . At Cr_{sol} 2.09-3.80 mmol, the Cr_{in} and the S_{re} values became approximately constant at 1.6-1.7 mmol g^{-1} . The excellent correlation between Cr_{in} and S_{re} , as presented in Table S2, strongly supported the stoichiometric ion-exchange of HCrO_4^{-} with HSO_4^{-} .

Fig. 4 shows the FT-IR spectra of the parent TS and Cr-TSs containing various amounts of chromium. The parent TS gave three bands at 1212, 1136, and 1046 cm^{-1} attributable to the HSO_4^{-} ion [20]. Their intensities decreased with the increase in Cr_{in} , indicating the release of HSO_4^{-} during the WIE. The band intensities at 939, 880, and 776 cm^{-1} , which are attributed to $\text{Cr}_2\text{O}_7^{2-}$ [21], increased with the increasing Cr_{in} . In

contrast, no clear bands due to HCrO_4^- , which should be observed at 916 and 786 cm^{-1} [22], were observed in the present samples. These findings and the ion-exchange behavior described above suggested that the HCrO_4^- ions introduced into the TS wall would dimerize to form $\text{Cr}_2\text{O}_7^{2-}$ during the drying process of Cr-TS at 353 K according to Equation 4.

3.2. Preparation of porous CrTiOs upon calcination

Porous CrTiOs were produced via the calcination of Cr-TSs prepared through WIE treatment, and the physicochemical properties of the resulting composite oxides were investigated as a function of the $\text{pH}_{\text{sol(e)}}$ and the Cr_{in} values. Here, calcination was performed at 673 K, which was the best temperature to obtain the clear porous structure, as described later. The N_2 adsorption-desorption isotherms of CrTiOs prepared at various $\text{pH}_{\text{sol(e)}}$ are shown in Supplementary Data, Fig. S3. Each isotherm exhibited a steep increase in the volume adsorbed at low pressure and a gradual increase at P/P_0 0.1-0.5. These results indicated the existence of micro- or meso-pores in the CrTiOs. Fig. 5a shows the relationships between the surface area or the pore diameter and the $\text{pH}_{\text{sol(e)}}$ value. At $\text{pH}_{\text{sol(e)}}$ 2.2-5.5, the surface areas of CrTiOs were 296-430 $\text{m}^2 \text{g}^{-1}$ and the pore sizes were approximately constant at 1.9 nm. At $\text{pH}_{\text{sol(e)}}$ 6.9 or above, the surface areas decreased and the pore sizes became larger. Both values in the former region were comparable to those previously reported by several researchers [7,8], indicating the effective preparation of mesoporous Cr-Ti composite oxides with high surface areas through the WIE-calcination method.

The correlation of the porosity of CrTiOs with the Cr_{in} is shown in Fig. 5b, where

the $\text{pH}_{\text{sol(i)}}$ in the preparation was adjusted to 8.6-8.9 and the Cr/Ti atomic ratio was used to express the amount of Cr because the Cr/Ti atomic ratio was a very significant factor to determine whether the pore structure is formed or not, as shown here and in a subsequent section. The surface areas of CrTiOs at Cr/Ti 0.21 or below were as low as $10 \text{ m}^2 \text{ g}^{-1}$; the surface area drastically increased above this ratio and exhibited approximately constant areas of $400 \text{ m}^2 \text{ g}^{-1}$ at Cr/Ti 0.48 or above. The pore sizes of CrTiOs were roughly constant at ca. 1.7 nm in the range Cr/Ti 0.30-0.69, although the value was somewhat smaller than the values observed at $\text{pH}_{\text{sol(e)}}$ 2.2-5.5 in Fig. 5a. The findings indicated that the porous structure was generated all at once at Cr/Ti 0.30, as shown in the figure with a blue dotted line, which will be discussed in the following sections.

Next, the effect of calcination temperature on the formation of porous structure was investigated at 473-873 K. The Cr-TSs with Cr/Ti of 0.20 and 0.56 were used as typical samples for the non-porous and porous CrTiOs. The physicochemical properties of Cr-TSs and calcined CrTiOs are summarized in Supplementary Data Table S3. In the case of Cr-TS with Cr/Ti 0.20, the surface areas of CrTiO calcined at 473-673 K were lower than $30 \text{ m}^2 \text{ g}^{-1}$, and no porosity could be detected. After calcination at 773 and 873 K, the surface areas somewhat increased to be 141 and $66 \text{ m}^2 \text{ g}^{-1}$, respectively; at 773 and 873 K, the pore sizes became 5.52 and 16.1 nm, respectively. For the CrTiO sample with Cr/Ti 0.56, the surface areas of CrTiO calcined at 473, 573, and 673 K were 198, 393, and $376 \text{ m}^2 \text{ g}^{-1}$, respectively, and the pore sizes were 1.12-1.79 nm at 473-673 K. The calcination at higher temperatures resulted in a decrease in the surface area to $66 \text{ m}^2 \text{ g}^{-1}$ and an increase in the pore size to 12.2 nm. The wide pore sizes of the CrTiOs calcined at 773 K or above, 16.1 and 12.2

nm, are due to the formation of interparticles voids [23-25] of TiO₂ and/or Cr₂O₃ particles, as described in the next paragraph.

Fig. 6 shows the XRD patterns of Cr-TSs and CrTiOs with Cr/Ti of 0.20 and 0.56. When Cr/Ti was 0.20, a diffraction peak at $2\theta = 2.2\text{-}2.3^\circ$ was observed on the Cr-TS and CrTiO calcined at 473 K, whereas the peak disappeared at 573 K or above (Fig. 6a). The diffraction peaks attributable to the anatase TiO₂ (JCPDF file 4-0477) [26] appeared at 2θ 22-62° on Cr-TS and CrTiOs (Fig. 6b) and became remarkable with the increasing temperature. This phenomenon was well reproduced on Cr-TS with Cr/Ti 0.21 (not shown). Cr-TS with Cr/Ti 0.56 resulted in diffraction peaks at 2θ 2.5 and 2.8° after calcination at 473 or 573 K and then a broad peak at approximately 1.8° upon 673 K calcination (Fig. 6c). The findings indicated the degradation of the ordered hexagonal symmetry at 673 K, which was confirmed on other CrTiO samples, as shown in Supplementary Data, Fig. S4. Fig. 6d indicated no formation of any crystalline phase upon calcination in the range of 473 to 673 K, suggesting the formation of amorphous phase consisting of the Ti oxide and Cr oxide. The calcination at 773 K or above resulted in the formation of TiO₂ anatase and Cr₂O₃ (JCPDS file 6-0504) [26]. The great difference between these samples could be well understood by the following previous reports. In the preparation of TiO₂ using TiOSO₄ [27], it was reported that the hydrolysis at pH 4-6 produced a pure anatase phase after the calcinations, whereas that at pH 7-8 primarily produced the amorphous phase. Others reported that the introduction of chromium ions into TiO₂ prevented formation of the anatase structure [7,28]. The pH_{sol(e)} values at the present preparation of Cr-TSs with Cr/Ti of 0.20 and 0.56 were 4.2 and 7.1, respectively, which corresponded well with the reported pH regions. The pH values in the preparation, 7.1, and the introduction of chromium ions

induced the suppression of crystallization of TiO_2 wall, which is a very important factor to retain the pore structure of TS.

The best calcination temperature for preparing the porous oxide was finally determined based on the surface area and the residue of the obtained sample. The surface area of the 573-K-calcined CrTiO with Cr/Ti of 0.56 was almost the same as that of 673-K-calcined sample, as shown in Supplementary Data Table S3. The amount of carbon remaining in the former sample was 9.23 mmol g^{-1} , while no carbon was detected in the latter sample. It follows that the calcination at 673 K was found to be the best conditions to obtain the CrTiO with high surface area and no carbon residue. The TEM image of the CrTiO sample prepared at $\text{pH}_{\text{sol(e)}}$ 4.6 and calcined at 673 K exhibited the wormhole-like pore structure shown in Fig. 7a, which agreed with the result of the XRD measurement. The surface of the CrTiO sample was also surveyed by a FE-SEM observation and the image is shown in Fig. 7b. Random appearance of many pores on the surface again indicated the formation of the wormhole-like pore structure. The pore diameters observed in Fig. 7b were 1.8-2.7 nm, which were in good agreement with those shown in Figs. 5a and 5b.

3.3. Characterization of Cr on porous CrTiOs

Reduction of Cr(VI) to Cr(III) upon calcination at 473-573 K. XANES and FT-EXAFS spectra of Cr-TSs and reference compounds are shown in Fig. 8. A sharp pre-edge peak was observed at 5992 eV on the XANES spectra of Cr-TSs and the Cr(VI)-containing compounds, K_2CrO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, and CrO_3 . The peak was attributed to the 1s-3d electronic transition of Cr(VI) in a tetrahedral environment [29]. The presence of the dimerized Cr(VI) species $\text{Cr}_2\text{O}_7^{2-}$ was already indicated by the FT-IR

spectra in Fig. 4, which might be supported by the similarity of the XANES spectra of Cr-TSs and $\text{K}_2\text{Cr}_2\text{O}_7$. The band at 1.20-1.23 Å (no phase-shift correction) in the FT-EXAFS spectra of Cr-TSs was assigned to back-scattering from the nearest neighboring oxygen atoms around Cr(VI) [30], which is also in good agreement with the spectra of the Cr(VI)-containing compounds.

The XANES and FT-EXAFS spectra were greatly changed with the calcination temperature, as shown in Fig. 8. The pre-edge peak decreased upon the calcination at higher temperatures and almost completely disappeared upon calcination at 573 K. Thermal decomposition of dimerized chromium species at 473-493 K has already been reported to form a highly distorted Cr_2O_3 -like structure [31], suggesting the occurrence of the similar phenomenon on the Cr-TSs calcined at 473-573 K. For the CrTiOs calcined at 473-573 K, the FT-EXAFS bands of Cr(VI)-O at 1.2 Å were hardly detected, whereas two new bands were observed at 1.5 Å and 2.4 Å. These two bands were assigned to Cr(III)-O and Cr(III)-O-Cr(III) bonds in octahedral geometry [30]. All of the results indicated that the $\text{Cr}_2\text{O}_7^{2-}$ species decomposed/reduced upon the calcination at 473-573 K to form the Cr(III) species. The typical reaction is shown in Equation 5. The intensities of Cr(III)-O-Cr(III) bands were smaller than that of Cr_2O_3 , suggesting dispersion of the Cr(III) species.

Reoxidation of Cr(III) to Cr(VI) upon calcination at 673 K. The XAFS spectra of CrTiO samples after calcination at 673 K were greatly dependent on the Cr/Ti ratios. With a Cr/Ti ratio of 0.20, the XANES and FT-EXAFS spectra were similar to those after the calcination at 473 or 573 K (Figs. 8a and d). In contrast, with a Cr/Ti ratio of 0.56, the pre-edge peak assignable to Cr(VI) was recovered and its intensity was

approximately 40 % of that of the uncalcined Cr-TS sample (Fig. 8b). On this sample, the Cr(III)-O and Cr(III)-O-Cr(III) bands were still observed, as shown in Fig. 8e. The results indicated reoxidation of a part of Cr(III) to Cr(VI) upon calcination at 673 K. The present reoxidation behavior of Cr was supported by the EXAFS parameters (Supplementary Data, Table S4), the FT-IR spectra (Fig. S5), and the UV-vis DR spectra (Fig. S6). The reoxidation of Cr(III) to Cr(VI) has also been reported to proceed on Cr-containing materials, such as Cr-MCM-41 (at 823 K in air) [32], Cr-supported MCM-41 (at 923 K in air) [33], $\text{CrO}_x/\text{ZrO}_2$ (at 823 K in O_2) [34], and Cr/ZSM-5 (at 673-773 K in CO_2) [35].

To investigate the effect of the amount of introduced Cr on the reoxidation of Cr, the XAFS spectra and the surface areas were measured on CrTiOs calcined at 673 K. The results are summarized in Table S5 and Figs. S7 and 9. Clearly, the pore structure was developed above Cr/Ti of 0.30, similar to the results already shown in Fig. 5b, although the Cr/Ti ratios were somewhat different from each other because the compositions of TSs were varied as described in the Experimental section. The Cr(III)/Ti ratio became unchanged at 0.30 or above, while the partial oxidation of Cr(III) to Cr(VI) upon calcination at 673 K began at Cr/Ti of 0.30 and linearly increased with the increasing Cr/Ti. Although the oxidation of Cr(III) to Cr(VI) upon heating the sample at high temperature in O_2 or CO_2 was widely recognized [32-35], as described in the previous paragraph, the phenomenon was limited only on the surface chromium ions. Bulk chromium ions of Cr_2O_3 were reported not to be oxidized upon heating at 673 K in O_2 [36]. The increase in the Cr(VI) amount and the plateauing of the Cr(III) amount, as well as the change in the surface area, indicated the formation of pores in CrTiOs above Cr/Ti of 0.30, which proceeded mainly at around Cr/Ti of 0.39,

as shown in Fig. 9 with a blue dotted line. The meaning of Cr/Ti of 0.39 will be discussed later in more detail.

The extraction of Cr(VI) from CrTiO with Cr_{in} of 1.57 mmol g^{-1} into water was then performed to directly confirm the presence of Cr(VI). The solubility of CrO_3 is 164.9 g per 100 mL of water at 273 K [37], while Cr_2O_3 is insoluble [37]. CrTiO (150 mg) calcined at 573 or 673 K was input into 50 mL of deionized water and then stirred at room temperature for 2 h. With CrTiO calcined at 573 K, no release of Cr was observed, indicating the presence of only insoluble Cr(III) species. With CrTiO calcined at 673 K, Cr of 0.20 mmol g^{-1} was released into water. The result indicated the presence of Cr(VI) on the CrTiO, but the observed amount was 27% of the amount of Cr(VI) determined based on the XANES spectra (Supplementary Data, Table S6), which will be discussed in the next paragraph.

Formation mechanism of porous CrTiOs. The change in the components, their valences, and their positions in the wall of porous CrTiOs with the WIE-calcination treatment is conceptually depicted in Fig. 10. In the figure, the CrTiO sample with Cr/Ti 0.50 was used as a typical example for discussion, and Ti, O, and OH ions were omitted to clearly show the ion-exchange behavior and the change in the state of chromium ions. Because the S/Ti ratio of the parent TS was approximately 0.7, as described in the Experimental section, 10 HSO_4^- ions among the 14 HSO_4^- ions shown in the figure were exchanged for the HCrO_4^- ions upon the WIE treatment. The drying process at 353 K for 12 h resulted in migration of the HCrO_4^- ions to the center of the wall and the formation of the $\text{Cr}_2\text{O}_7^{2-}$ species. The migration would result from difference between affinities of HSO_4^- and HCrO_4^- ions for the surfactant ions. The $\text{Cr}_2\text{O}_7^{2-}$ species decomposed to Cr(III) upon the calcination at 473-573 K. With a

Cr/Ti ratio of 0.50, the pore structure of the CrTiO sample was retained by an amorphous composite of Cr-Ti-oxide, which was produced at a core of the wall, because it was not converted to crystalline anatase TiO₂, which might decompose the wall structure. When the Cr/Ti ratio was smaller than 0.30-0.39, that is, approximately half of the exchangeable amount (0.68-0.75), the amount of Cr would be insufficient for supporting the wall. The surface Cr(III) ions on the Cr/Ti=0.5 sample were oxidized to Cr(VI) by the calcination at 673 K, as shown in Fig. 9. The suggested mechanism could explain all of the results shown in Figs. 4-9.

3.4. Expansion of the WIE-calcination method to the preparation of porous WTiO, MoTiO, and VTiO

The present WIE-calcination method was applied to the oxyanions of Mo, W, and V. The relationships between the pH_{sol(e)} value and the surface areas of MoTiO, WTiO, and VTiO are shown in Supplementary Data, Fig. S8. Although the dependencies were varied with the oxyanions used and appeared to not exhibit regularity, high surface areas were observed at pH_{sol(e)} 8.7-10.3; the results showing the high surface areas are summarized in Table 1 and Supplementary Data Figs. S9 and S10. The surface areas of MoTiO and WTiO were 197-258 and 218-273 m² g⁻¹, which were much greater than those of the corresponding porous materials reported so far [4,9]. Their pore sizes were 2.06 and 1.58 nm (Table 1). The hexagonal symmetries were hardly observed in the XRD patterns (Fig. S10). In contrast, VTiO prepared at pH_{sol(e)} 10.3 exhibited the surface area of 70 m² g⁻¹, which was lower than that of previous report [38]. These results revealed that the unified WIE-calcination method using TS as a starting material can achieve the synthesis of some types of porous TiO₂-based composite oxides, though

the formation mechanism was unknown yet.

Finally, the surface areas of porous TiO₂-based composite oxides obtained in this work were compared in consideration of the respective wall densities. Mesoporous silica MCM-41, prepared by using CTAB [39], with a surface area of 941 m² g⁻¹ was used as a standard material. The wall densities of MTiOs, ρ_{MTiO} (M = Cr, Mo, W, and V), were calculated by Equation 6 on the assumption that the wall density was equal to that of the mixture of TiO₂ and MO_x, where MO_x was assumed to be Cr₂O₃, MoO₃, WO₃, and V₂O₅.

$$\rho_{\text{MTiO}} = (\rho_{\text{TiO}_2} + R\rho_{\text{MO}_x}) / (1+R) \quad (6)$$

R is the M/Ti atomic ratio of MTiO, and ρ_{TiO_2} and ρ_{MO_x} are the densities of TiO₂ (4.26 g cm⁻³) and MO_x, respectively [37]. The BET surface areas of MTiOs were then divided by the ratio $\rho_{\text{SiO}_2}/\rho_{\text{MTiO}}$, where ρ_{SiO_2} is the density of cristobalite (2.20 g cm⁻³), to obtain the corrected BET surface areas (S_c). The results are summarized in Table 1. The sufficiently large S_c value of CrTiO, 850 m² g_{SiO₂}⁻¹, revealed that the apparent small BET surface area of CrTiO was due to the large wall density. The corrected BET surface areas of MoTiO and WTiO were not as large as that of the reference material.

4. Conclusions

Porous TiO₂-based composite oxides were prepared through the WIE-calcination method. In the WIE treatment of chromium, the stoichiometric ion-exchange of chromium oxyanions with HSO₄⁻ in TS was observed at pH_{sol(e)} 2.2-5.5. HCrO₄⁻ was found to be the predominant species in the exchange solution. The CrTiOs prepared at pH_{sol(e)} 2.2-5.5 and calcined at 673 K exhibited surface areas of 296-430 m² g⁻¹ and wormhole-like pores with the pore diameters of 1.7-2.5 nm, which are comparable to

those previously prepared by other researchers. The introduction of Cr/Ti above 0.30-0.39 was required to form porous CrTiOs. The best calcination temperature was 673 K, at which point carbon residue originating from the surfactant was all removed. The state of Cr was varied complicatedly with the treatments. The HCrO_4^- ions introduced in TS in the WIE treatment dimerized to form $\text{Cr}_2\text{O}_7^{2-}$ ions during the drying process. $\text{Cr}_2\text{O}_7^{2-}$ was decomposed and reduced to dispersed Cr(III) species upon the calcination at 473-573 K. After calcination at 673 K, the Cr(III) species in the pore surface were oxidized to Cr(VI) species, whereas those inside the pore wall remained unchanged. The present porous CrTiO is expected to be applied as a solid catalyst due to the surface Cr(VI) species [40-43] as well as high surface areas.

The WIE treatment with oxyanions of Mo and W at $\text{pH}_{\text{sol(e)}}$ 8.7-10.3 and the subsequent calcination also resulted in porous MoTiOs and WTiOs with surface areas of 197-258 and 218-273 $\text{m}^2 \text{g}^{-1}$, respectively, although the relationship between the ion-exchange behavior and the formation of porous structure remain unknown. In contrast, VTiOs with pore structure and high surface area could not be obtained by the present method.

The WIE-calcination treatment was successfully applied for preparation of ZrO_2 -[11-14, 16] and TiO_2 -based porous oxides by us and the followings were revealed as common phenomena or regularity. The HSO_4^- ions consisting of the parent mesostructured materials could readily be ion-exchanged with oxyanions in an aqueous solution regardless of the presence of surfactants blocking the pores. The ion-exchange proceeded via mono-anions, and the pH value of solution was an important factor to determine a pattern of the exchange, although the detailed exchange mechanism remained unclear. When metal oxyanions introduced into the wall could

form an amorphous phase with the parent metal oxide and amounts of the composite oxide became enough for supporting the wall, we could obtain porous materials upon suitable calcination. All of the porous materials produced with the current method showed very large surface areas, which were comparable or superior to those of materials prepared with respective specialized preparation methods. This technique would be applicable to prepare various combination of porous mixed oxides.

Acknowledgements

The authors thank Dr. Daling Lu of Tokyo Institute of Technology for the TEM measurements. The measurements of the XAFS spectra were performed under proposal numbers of 2009G661 of the Photon Factory Program Advisory Committee. This work was supported by Grants-in-Aid from the Japan Society for Promotion of Science (JSPS, MEXT) and the Advanced Low Carbon Technology Research and Development Program (JST, MEXT).

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Tables

Table 1. Physicochemical properties of MTiOs and MCM-41.

sample	WIE treatment ^a		After WIE	After calcination ^b				
	pH _{sol(i)} ^c	pH _{sol(e)} ^d	M/Ti /atomic ratio	S _{BET} /m ² g ⁻¹	Pore size /nm	ρ _{MOx} ^e /g cm ⁻³	ρ _{MTiO} ^f /g cm ⁻³	S _c ^g /m ² g _{SiO₂} ⁻¹
CrTiO	8.7	5.1	0.64	404	2.08	5.21	4.63	850
MoTiO	10.4	10.3	0.19	234	2.06	4.50	4.30	457
WTiO	10.4	10.2	0.37	218	1.58	7.16	5.04	499
VTiO	10.4	10.3	0.44	70	- ^h	3.36	3.99	127
MCM-41 ⁱ	-	-	-	941	3.81	2.20	-	941

^aIn the WIE treatment, 1.0 g of parent TS was stirred in 100 mL of an exchange solution containing 20 mmol L⁻¹ oxyanions of Cr, Mo, W, or V at room temperature for 2 h.

^bM-TSs were calcined at 673 K for 2 h in air, and MCM-41 at 873 K for 6 h in air.

^cpH value of the exchange solution before WIE. ^dpH value of the exchange solution

after WIE. ^eDensities of Cr₂O₃, MoO₃, WO₃, V₂O₅, and SiO₂ [37]. ^fWall density of

MTiO calculated by Equation 6. ^gS_{BET}/(ρ_{SiO₂}/ρ_{MTiO}). ^hNo porosity was detected.

ⁱCited from Reference [39].

Figures

Fig. 1. Effect of the pH value of the exchange solution after WIE ($\text{pH}_{\text{sol(e)}}$) on the amounts of Cr introduced in TS (Cr_{in}) and S released from TS (S_{re}). The dotted horizontal line represents the amount of S contained in the parent TS, 1.90 mmol g^{-1} . The samples are the same as those summarized in Supplementary Data, Table S1.

Fig. 2. Diagram of chromium oxyanion species as a function of the chromium concentration and pH at 298 K. The results of the present study are shown by the arrows from the values of the respective solutions before the WIE treatment (initial) to those after the WIE treatment (equilibrium). The numbers above the plots exhibit the respective run numbers described in Supplementary Data, Table S1. The underlying graph was reprinted with permission from Reference [17], copyright 1976 John Wiley & Sons, Inc.

Fig. 3. Amounts of Cr introduced in TS (Cr_{in}) and S released from TS (S_{re}) after the WIE treatment as a function of the amount of Cr in the exchange solution (Cr_{sol}). The dotted horizontal line represents the amount of S contained in the parent TS, 1.90 mmol g^{-1} . The detailed data are summarized in Supplementary Data Table S2.

Fig. 4. FT-IR spectra of (i) the parent TS and (ii-v) Cr-TSs. The $\text{pH}_{\text{sol(i)}}$ in the preparation of Cr-TSs were adjusted to 8.4-8.6, and the amounts of Cr in the samples were (ii) 0.42, (iii) 0.90, (iv) 1.46, and (v) 1.71 mmol g⁻¹.

Fig. 5. Change in the BET surface areas (closed circle) and the BJH pore diameters (open diamond) of CrTiOs with (a) the pH value of the exchange solution after WIE ($\text{pH}_{\text{sol(e)}}$) and (b) Cr/Ti atomic ratio. The detailed data are listed in Supplementary Data Tables S1 and S2.

Fig 6. (a, c) Small-angle and (b, d) wide-angle XRD patterns of Cr-TS and CrTiOs with Cr/Ti atomic ratio of (a, b) 0.20 and (c, d) 0.56. The temperatures in the figures represent the calcination temperatures of CrTiOs. All of the samples correspond to those summarized in Supplementary Data Table S3.

Fig. 7. TEM (a) and SEM (b) images of CrTiO (Cr/Ti=0.56) calcined at 673 K. The sample corresponds to Run 8 in Supplementary Data Table S1.

Fig. 8. (a-c) Cr K-edge XANES and (d-f) FT-EXAFS spectra of Cr-TSs and CrTiOs with Cr/Ti of (a, d) 0.20 and (b, e) 0.56 and (c, f) reference compounds. The temperatures in figures represent the calcination temperatures of CrTiOs. All of the samples correspond to those listed in Supplementary Data Table S3

Fig. 9. Change in Cr(VI)/Ti (closed circle), Cr(III)/Ti (open diamond), and BET surface areas (closed circle) with Cr/Ti of CrTiOs. The detailed data are summarized in Supplementary Data Table S5.

Fig. 10. Proposed formation mechanism of porous CrTiOs and redox behavior of Cr ions upon WIE-calcination. Ti, O, and OH ions in TS wall were omitted to clearly show the change in the states of S and Cr. Detailed explanations are provided in the text.

Graphical Abstract

S: HSO_4^- , Cr: Cr(VI), Cr: Cr(III)

Pore wall
including
Ti, O, and
OH ions

Cr/Ti>0.30

$$S_{\text{BET}} = 296\text{-}430 \text{ m}^2 \text{ g}^{-1}$$

$$\bar{D}_{\text{BJH}} = 1.7\text{-}2.5 \text{ nm}$$