Mesoporous Tantalum Oxide. 1. Characterization and Photocatalytic Activity for the Overall Water Decomposition

Yoshiko Takahara, Junko N. Kondo, Tsuyoshi Takata,[†] Daling Lu,[†] and Kazunari Domen*[,†]

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Magatsuta, Midori-ku, Yokohama 226-8503, Japan

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Mesoporous Ta_2O_5 was synthesized by the ligand-assisted templating method, and its stability for use as a photocatalyst was studied by X-ray diffraction, N_2 adsorption isotherm analysis, and transmission electron microscopy. The photocatalytic activity for the overall water decomposition on the mesoporous Ta_2O_5 was improved by NiO loading and pretreatment. The mesoporous structure was found to be maintained to some extent after loading of NiO (H_2 evolution site) and pretreatment for activation at a temperature as high as 673 K. Although the wall of mesoporous Ta_2O_5 was amorphous, the photocatalytic activity was higher than that of the crystallized Ta_2O_5.

Introduction

A wide variety of transition metals are successfully incorporated in mesoporous SiO_2 materials with various pore structures, and catalytic applications of these materials are also reported.[1] In addition to the transition-metal-incorporated SiO_2 mesoporous materials, the successful formation of various types of pure-transition-metal oxides has been recently reported.[1−3] Because Ta-based mixed oxides have been recently reported to be highly active for the overall water decomposition under UV irradiation,[4−9] the application of mesoporous Ta_2O_5 to the photocatalytic water decomposition seems to be of interest. There are only a few reports on the synthesis of mesoporous Ta_2O_5,[1−3,10] and its photocatalytic behavior has not been studied. The crystallized Ta_2O_5 was found to decompose water with NiO loading under the band-gap (4.0 eV) irradiation.[11] In this paper, the photocatalytic activity for the overall water decomposition and the stability of the porous structure of mesoporous Ta_2O_5 are studied at each step of the pretreatment. The activity for photodecomposition of water is further compared with a Ta_2O_5 with high crystallinity and an amorphous Ta_2O_5 prepared from the same starting materials as the mesoporous Ta_2O_5 without adding the template.

Experimental Section

Chemicals. Tantalum ethoxide [$Ta(OEt)_5$] is obtained from Aldrich or Kojundo Chemical Laboratory. Octadecylamine, tantalum oxide, alcohols, ethers, and nickel nitrate are purchased from Kanto Chemicals and used without further purification. Trifluoromethanesulfonic acid is obtained from Aldrich. Deionized water is obtained from Seiki Medicine Kogyo.

Synthesis. Mesoporous Ta_2O_5 was synthesized following the ligand-assisted templating method, the procedure reported by Antonelli and Ying.[10] Octadecylamine (1.65 g, 6.15 mmol) was mixed in $Ta(OEt)_5$ (5.0 g, 12.30 mmol) under an Ar gas atmosphere and warmed to 323 K for 10−30 min until octadecylamine was dissolved completely, and a homogeneous clear liquid was obtained. To these organic metal complexes was added deionized water slowly by means of a spray with stirring. Hydrolyzation occurred immediately, and white particles were obtained. The deionized water was added gradually up to 25 mL. The precipitation was kept in the supernatant at room temperature for 24−48 h and transferred to a Teflon beaker for aging at 353 K for 24 h, 373 K for 24 h, and 453 K for 7 days, successively. The product was collected by suction filtration and washed with deionized water, ethanol, and diethyl ether. The powder was then dried at 373 K for 12 h in air to obtain the precursor.

The precursor (1 g) was suspended in dimethoxyethane at 195 K under an Ar atmosphere, treated with trifluoromethanesulfonic acid (0.113 mL, 1.28 mmol), and kept for 1 h at the same temperature with stirring. The suspension was warmed to the ambient temperature and stirred for another 2 h. The powder was collected by suction filtration, washed with 2-propanol, and transferred to a beaker for washing in 2-propanol at room temperature for 24 h. The powder was collected by suction filtration with washing by deionized water, ethanol, and diethyl ether, successively, and then dried in evacuation at 373 K within 12 h.

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* To whom correspondence should be addressed. Fax: +81-45-924-5282. Tel: +81-45-924-5238. E-mail: kdomen@res.titech.ac.jp.

[†] Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology (JST).

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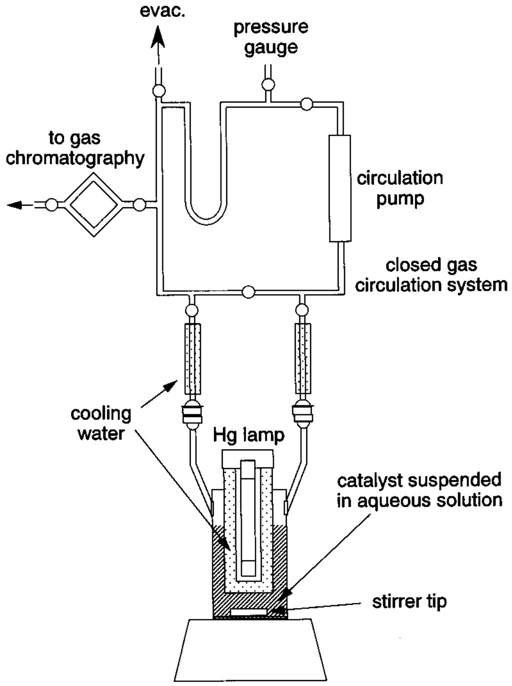

Figure 1. System used for the evaluation of the activity of photocatalytic water decomposition.

Amorphous Ta_2O_5 was prepared by the same method as that for the mesoporous Ta_2O_5 but without adding the surfactant. $Ta(OEt)_5$ (5.0 g, 12.30 mmol) was hydrolyzed by 25 mL of deionized water, leading to instantaneous precipitation. The solid was transferred to the Teflon beaker for the same aging condition followed by washing processes as that for the mesoporous Ta_2O_5. Treatment of triflic acid was not performed because of the absence of the surfactants.

Characterization. Powder X-ray diffraction (XRD) patterns of the products were obtained on a Rigaku Rint 2000 diffractometer using Cu Kα radiation (40 kV, 40 mA) at a 0.02 step size and a 1 s step time over the range $1.5° < 2\theta < 15°$. A background was subtracted in the XRD patterns in the present study. N_2 adsorption–desorption isotherms at 77 K were measured using a Micrometrics Coulter Omnisorp 100CX system. Samples were normally prepared for N_2 adsorption measurement by degassing at 373 K under vacuum until a final pressure of 1×10^{-5} Torr was reached. Brunauer–Emmett–Teller (BET) surface areas were estimated over a relative pressure (P/P_0) range from 0.05 to 0.30. Pore size distribution was obtained from the analysis of the adsorption branch of the isotherms using the Barrett–Joyner–Halenda (BJH) method. Water adsorption isotherms at 298 K were also measured by the same system after the same pretreatment. Images of transmission electron microscopy (TEM) were obtained on a JEOL 2010F electron microscope operated at 200 keV. The samples for TEM observation were prepared by dropping mesoporous Ta_2O_5 powder dispersed in 2-propanol on a copper grid covered with a carbon film.

Photocatalytic Water Decomposition. The photocatalytic activity for the overall water decomposition was studied on as-prepared, calcined, and NiO-loaded Ta_2O_5 samples. NiO was loaded from a nickel aqueous nitrate solution by impregnation, followed by calcination at 600 K for 1 h for the mesoporous and amorphous Ta_2O_5 samples. R673–O473 treatment after NiO loading was performed first by H_2 reduction at 673 K for 2 h followed by reoxidation in O_2 at 473 K for 1 h. Photocatalytic activity for the overall water splitting was studied using 0.5 g of each sample. The sample was suspended in about 400 mL of pure water and irradiated by a high-pressure Hg lamp (450 W) in a setup shown in Figure 1. Before irradiation was started, the system was evacuated several times. Amounts of evolved gases were analyzed by a gas chromatograph directly connected to the reaction system.

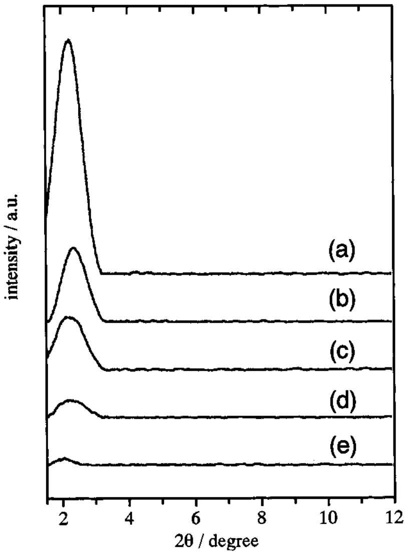

Figure 2. XRD patterns of mesoporous Ta_2O_5 (a) after surfactant removal and (b) after calcination at 473 K, (c) 573 K, (d) 673 K, and (e) 773 K for 1 h.

Results and Discussion

Thermal Stability of the Mesoporous Structure. Figure 2a shows an XRD pattern of as-synthesized mesoporous Ta_2O_5 after surfactant removal. An intense (100) diffraction at $d = 3.8$ nm is in good agreement with the reported Ta-TMS1 mesoporous material,[10] although (110) and (200) diffractions indicating the hexagonal phase were not clearly observed. Thus, the mesopores in the presently synthesized mesoporous Ta_2O_5 are not highly ordered in the hexagonal structure. Assuming the hexagonal pore structure, however, the repeat distance is estimated to be ca. 4.4 nm. The sample was then calcined in air at 473, 573, 673, and 773 K, respectively, for 1 h. The initially observed (100) diffraction gradually decreased in intensity, indicating the destruction of the mesoporous structure, and it almost disappeared after calcination at 773 K (Figure 2e). The collapse of the mesoporous structure was, therefore, found to occur not suddenly but gradually with the increase of the treatment temperature.

In agreement with the XRD results, the deviation of the N_2 adsorption isotherm from a type IV pattern indicating the mesoporous structure was noticed upon calcination, as shown in Figure 3. The surfactant-removed sample indicates the type IV isotherm (Figure 3a) with a BET surface area of 488 $m^2 \cdot g^{-1}$ and a pore size distribution at ca. 2.6 nm (after evacuation at 373 K for 2 h as a pretreatment of the measurement). These results are in accordance with Ta-TMS1 except for the absence of the (110) and (200) diffractions in the XRD pattern (Figure 2a). The BET surface area of the mesoporous Ta_2O_5 calcined at 473, 573, 673, and 773 K decreased to 462, 320, 299, and 183 $m^2 \cdot g^{-1}$, respectively, but still showed similar type IV patterns. On the other hand, the N_2 adsorption isotherm of the amorphous Ta_2O_5 which was prepared from the same starting materials without surfactant (Figure 3f) showed the type II pattern typical of nonporous solids, and the BET surface area was 145 $m^2 \cdot g^{-1}$ (also after evacuation at 373 K for 2 h as a pretreatment of the measurement). The mesoporous Ta_2O_5 showed an isotherm similar to

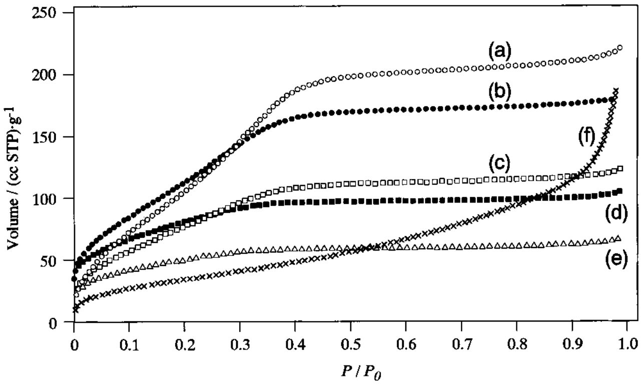

Figure 3. N_2 adsorption isotherms of the mesoporous Ta_2O_5 samples corresponding to the XRD patterns in Figure 2. Part f is the isotherm for amorphous Ta_2O_5 prepared by the same material without adding the surfactant.

that of the amorphous one after calcination at 873 K, and the surface area decreased to less than 100 $m^2 \cdot g^{-1}$. Therefore, it was found that the mesoporous Ta_2O_5 prepared in the present study maintained the porous structure to some extent after calcination up to 773 K, although gradual destruction occurred by increasing the calcination temperature. Furthermore, when the amorphous sample was calcined at 573 K, the surface area decreased to 103 $m^2 \cdot g^{-1}$. This also indicates the difference of the mesoporous Ta_2O_5 from the amorphous sample.

For the use of a series of tantalates as photocatalysts, NiO-loaded catalysts which are calcined at 670 K for 1 h are reported to be effective for water decomposition even without pretreatment,[4−8] while some other photocatalysts such as $K_4Nb_6O_{17}$ and $SrTiO_3$ require reduction at 773 K and reoxidation at 473 K (R773−O473 pretreatment) for obtaining high activity.[12−15] Here, the reduction temperature of the NiO-loaded mesoporous Ta_2O_5 was fixed to 673 K (lowest temperature for NiO reduction), where the mesoporous structure was maintained to some extent justified from Figures 2 and 3. Therefore, we have chosen R673−O473 pretreatment for the present sample.

Photocatalytic Decomposition of Water over Mesoporous Ta_2O_5. In Figure 4, photocatalytic activity for water decomposition over mesoporous Ta_2O_5 is shown. Because NiO loading was conducted by impregnation of mesoporous Ta_2O_5 with a $Ni(NO_3)_2$ solution followed by calcination at 600 K, three different mesoporous Ta_2O_5 samples were compared. One is the as-synthesized sample without any treatment (A), and others are those calcined at 600 K without NiO loading (B) and with NiO loading [calcined at 600 K (C)]. About 1.0 wt % or less of NiO is loaded as the cocatalyst on most of the previous photocatalysts because of the relatively small surface area. However, 3.0 wt % of NiO was loaded on the mesoporous Ta_2O_5 because of its larger surface area. In the case of the as-synthesized sample (A), only H_2 evolved [Figure 4A; about 50 $\mu mol \cdot h^{-1}$]. The calcination at 600 K increased the activity and enabled the mesoporous Ta_2O_5 to evolve both H_2 and O_2 in a stoichiometric ratio (H_2, 42 $\mu mol \cdot h^{-1}$; O_2, 20 $\mu mol \cdot h^{-1}$), although an induction period was observed (Figure 4B). The colors of these samples before the reaction, light brown (A) and dark brown (B), changed to white during the reaction. Therefore, the initial H_2 evolution is attributed to the reaction of the remaining surfactant, which is in agreement with our previous IR observation.[16] The stoichiometric evolution of H_2 and O_2 was considered to start after complete removal of the surfactant. When 3 wt % of NiO was loaded, the induction time became shorter and the activity increased (H_2, 117 $\mu mol \cdot h^{-1}$; O_2, 61 $\mu mol \cdot h^{-1}$). Similarly to other tantalate photocatalysts,[4−9] NiO loading was found to be beneficial for the overall water decomposition also in the case of the mesoporous Ta_2O_5.

Table 1. Optimization of the Amount of NiO Loading

amount of NiO/(wt %)	gas evolution/$\mu mol \cdot h^{-1}$	
	H_2	O_2
0.3	32	1
3.0	110	56
4.0	150	73
6.0	82	40

The optimization of the amount of NiO loading was next carried out. As shown in Table 1, NiO loading of less than 1.0 wt % did not lead to the stoichiometric gas evolution, and the activity was low. A 4.0 wt % NiO loading was found to be the optimum amount. Therefore, the effect of the pretreatment condition was studied by using 4.0 wt % of NiO-loaded mesoporous Ta_2O_5.

Effect of R673−O473 Pretreatment and Comparison with Other Ta_2O_5 Catalysts. It is known that reduction and reoxidation of the NiO loaded on photocatalysts enhance the activities of such photocatalysts as $SrTiO_3$ and $K_2La_2Ti_3O_{10}$.[12−15] The pretreatment produces Ni metal particles covered with NiO on the main photocatalysts; the first reduction by H_2 produces Ni metal particles, and the successive oxidation by O_2 under milder conditions oxidizes only the surface of the Ni metal particle. The Ni metal part makes an ohmic contact between the oxide photocatalyst and NiO. Thus, the excited electrons are smoothly transferred to the NiO surface to reduce water into H_2. This unique structure of NiO/Ni particles results in the enhancement of the photocatalytic activity.[12,15] However, the same pretreatment is not necessary for most of the tantalates because of the relatively high conduction band bottom, to which it is possible to inject the conduction electrons directly into that of NiO.[4−8]

We compared the photocatalytic activities for the overall water decomposition with and without R673−O473 treatment over three Ta_2O_5 compounds: a commercial Ta_2O_5 with high crystallinity (orthorhombic), the amorphous Ta_2O_5 prepared, and the mesoporous Ta_2O_5. The amount of NiO loading was adjusted to 1 wt % for the former two, taking their low BET surface areas into consideration. Results are listed in Table 2.

The crystallized Ta_2O_5 without pretreatment showed very low H_2 evolution but no O_2 evolution activity, while

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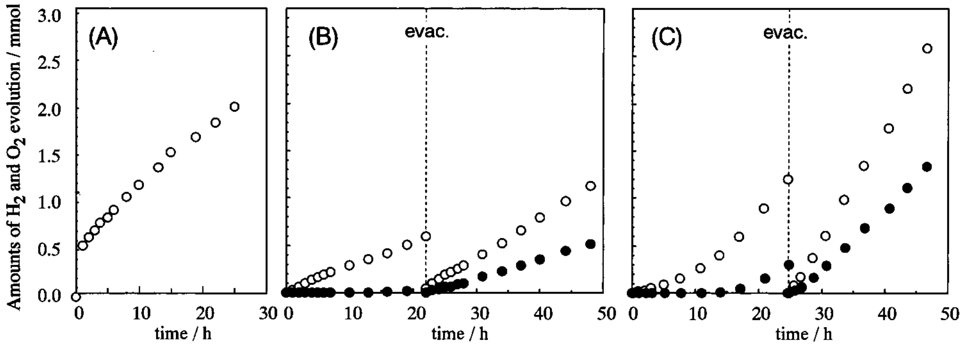

Figure 4. Time course of photocatalytic decomposition of water over mesoporous Ta_2O_5: (A) uncalcined sample; (B) calcined sample at 600 K; (C) calcined sample at 600 K after 3 wt % of NiO loading from $Ni(NO_3)_2$. Catalyst, 0.5 g; water 340 mL; light source, 500 W Hg lamp.

Table 2. Comparison of the Photocatalytic Activity of NiO-Loaded Tantalum Oxides

tantalum oxide	amount of NiO/(wt %)	condition[a]	gas evolution/μmol·h^{-1} H_2	O_2
amorphous Ta_2O_5	1.0	before pretreatment	46	24
		after pretreatment	125	43
orthrhomibic Ta_2O_5	1.0	before pretreatment	10	0
		after pretreatment	389	194
mesoporous Ta_2O_5	4.0	before pretreatment	150	73
		after pretreatment	515	272

[a] NiO-loaded catalysts were treated by H_2 at 673 K and O_2 at 473 K.

the sample with R673−O473 pretreatment after NiO loading greatly improved the photocatalytic activity. This result on the crystallized Ta_2O_5 is in good agreement with the previous results reported by Sayama and Arakawa,[11] in contrast with the case of tantalate mixed oxides where the pretreatment did not affect or even decreased the photocatalytic activity.

It is noted that the mesoporous Ta_2O_5 was active even without NiO loading (Figure 4B) and even before the R673−O473 pretreatment. It is generally known that the photocatalytic activity appears to be much higher for the crystallized material because of the efficient migration of the electrons and holes through the lattice to the surface. However, the mesoporous Ta_2O_5 is considerably photoactive, most probably because of the small wall thickness. The wall thickness is estimated from the repeated distance (4.4 nm) and the pore size distribution (2.6 nm) to ca. 1.8 nm, which corresponds to nine Ta−O bonds assuming that an octahedraly coordinated Ta−O bond length is 0.2 nm.[10,17] Therefore, it would be enough for the exited electrons to migrate the length of only several Ta−O bonds before reaching the surface. This is regarded as the most beneficial character of the mesoporous Ta_2O_5 as a photocatalyst. The considerable activity and stoichiometric H_2 and O_2 evolution on the amorphous Ta_2O_5 which was prepared in this study by the slow hydrolysis of $Ta(OEt)_5$ may also be due to the short distance from the internal region to the surface of the small particles. The stable activity of NiO (4 wt %)-loaded mesoporous Ta_2O_5 after R673−O473 pretreatment for water decomposition was observed for more than 200 h (Figure 5), although the first run exhibited a somewhat higher activity.

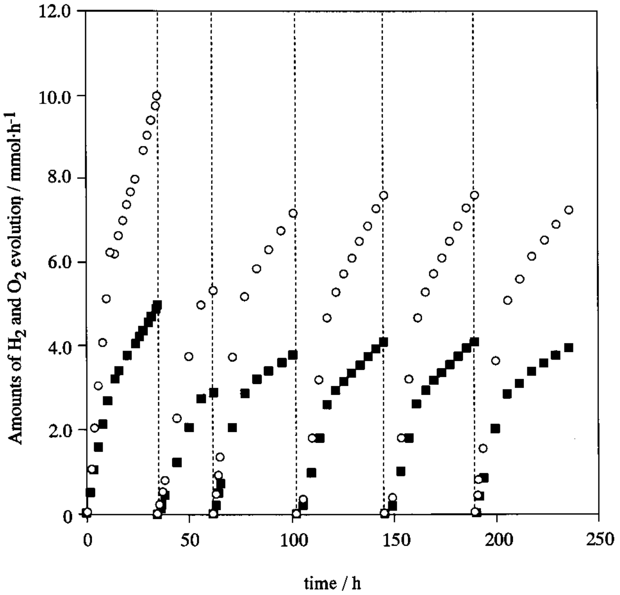

Figure 5. Time course of photocatalytic decomposition of water over NiO (4 wt %)-loaded mesoporous Ta_2O_5 after R673−O473 treatment.

Among various mesoporous materials, the photocatalytic activity was evaluated on TiO_2 by oxidative dehydrogenation of 2-propanol to acetone.[18] In the case of the mesoporous TiO_2, an amorphous wall structure resulted in poor photoactivity compared with anatase TiO_2. On the other hand, mesoporous Ta_2O_5 appeared to be considerably photoactive, although the crystal structure of Ta_2O_5 is amorphous. The difference between mesoporous Ta_2O_5 and TiO_2 in the reactivity could be attributable to the difference in the potential of the excited electrons. The band gaps of TiO_2 and Ta_2O_5 are 3.0 and 4.0 eV, respectively. Because their HOMO levels are considered to be the same (O 2p), the difference in the band gap is reflected by their LUMO levels; i.e., the

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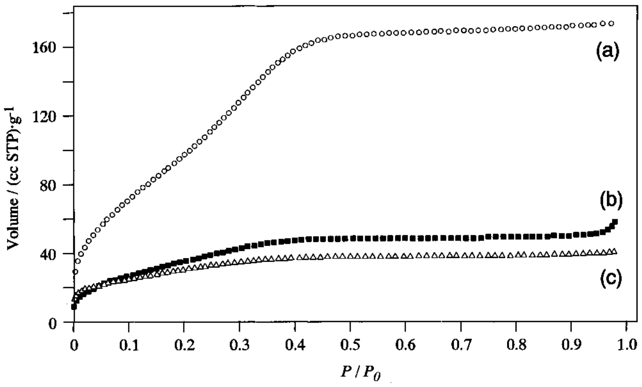

Figure 6. N_2 adsorption isotherms of the mesoporous Ta_2O_5: (a) surfactant-removed sample; (b) NiO (4 wt %)-loaded sample; (c) b after R673−O473 treatment.

excited electrons in the conduction band of Ta_2O_5 should have higher potentials than those in TiO_2. This may be responsible for the relatively high activity of amorphous Ta_2O_5.

Characterization of the NiO-Loaded Mesoporous Ta_2O_5. The NiO (4 wt %)-loaded mesoporous Ta_2O_5 photocatalyst before and after R673−O473 treatment was characterized by N_2 and H_2O adsorption isotherms and TEM. For TEM observation, the amount of NiO was increased to 5 wt %. Only a weak diffraction peak was observed at $d = 2-2.5$ ° in XRD patterns. In Figure 6, N_2 adsorption isotherms of a series of mesoporous Ta_2O_5 are shown. Although the shape of the isotherm for the mesoporous Ta_2O_5 before NiO loading (a) corresponds to type IV, similar to that observed in Figure 3a, the BET surface area was 370 $m^2 \cdot g^{-1}$ for the samples used to study the photocatalytic activity. By NiO loading and by further pretreatment, the BET surface area decreased to 141 and 112 $m^2 \cdot g^{-1}$ (Figure 6), respectively, but still showed some difference from the type II isotherm of the nonmesoporous sample (Figure 3f).

In Figure 7 TEM images of small particles of NiO (5 wt %)-loaded mesoporous Ta_2O_5 before (A) and after (B) R673−O473 treatment are shown. Wormholelike mesopores are observed in Figure 7A(a), which is the same appearance as mesoporous Ta_2O_5 before NiO loading. The elemental analysis on several spots of this image as well as other particles confirmed the homogeneous dispersion of NiO particles. The sum of the amount of Ta, Ni, and O atoms was fixed as 100%, and the Ni content appeared between 4 and 5% at all spots. An image at a high magnification is also shown in Figure 7A(b), where small dots were observed as indicated by arrows. Because these were absent in the sample before

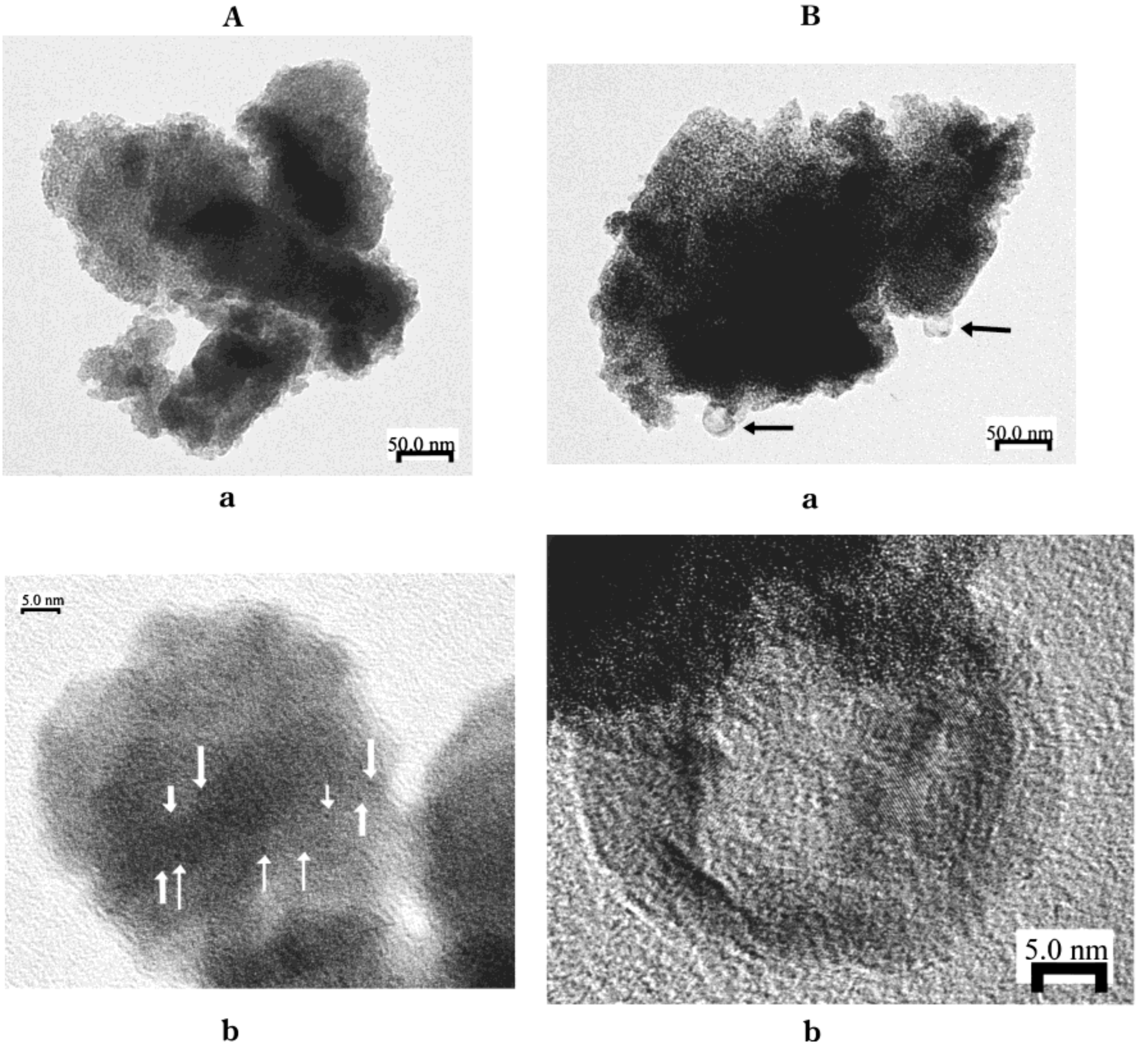

Figure 7. TEM images of NiO (5 wt %)-loaded sample before (A) and after (B) R673−O473 treatment. Parts a and b are observed at different magnifications.

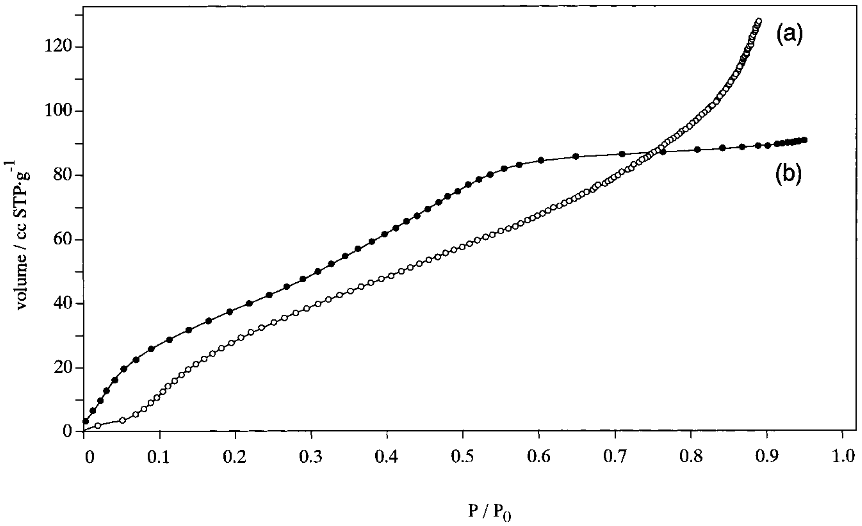

Figure 8. H_2O adsorption isotherms of (a) surfactant-removed mesoporous Ta_2O_5 and (b) a NiO (4 wt %)-loaded sample after R673−O473 treatment.

NiO loading, the black dots were considered to be NiO particles. After R673−O473 treatment, a TEM image [Figure 7B(a)] similar to that in Figure 7A(a) was observed. However, the concentration of Ni estimated by elemental analysis of this particle varied from 0 to 60%, indicating that NiO particles observed in Figure 7A(b) sintered. The small spherical subparticle indicated by an arrow was highlighted and shown in Figure 7B(b) at a higher magnification. In addition to the result from elemental analysis, the appearance of lattice images identified this particle as NiO (note that Ta_2O_5 is amorphous). A similar particle was also observed on the left side of the NiO particle in Figure 7B(b). Therefore, it was found that highly dispersed NiO particles were sintered by R673−O473 treatment. Because the photocatalytic activity of mesoporous Ta_2O_5 was improved by NiO loading even before R673−O473 treatment (Figure 4 and Tables 1 and 2), the highly dispersed NiO particles are regarded to be effective as cocatalyst. However, R673−O473 treatment further enhanced the activity even though NiO particles were sintered. This is due to the chemical activation of NiO itself, as mentioned in previous section. Accordingly, if activated NiO particles were highly dispersed, the highest activity would be obtained. While NiO was selected as a cocatalyst in this study following the result on the enhancement of photocatalytic activity on other tanlalates,[4−9] the use of Pt which is activated by UV light irradiation[12−15] would be another possible cocatalyst.

Our previous IR study of the mesoporous Ta_2O_5 found that the concentration of surface hydroxy groups is extremely small and that adsorption of H_2O was considerably weak compared with other oxides.[16] Because photocatalytic decomposition of water is the target in the present research, hydrophilicity was estimated by H_2O adsorption isotherm. As-prepared mesoporous Ta_2O_5 was found to be hydrophobic, as indicated by the isotherm at the low relative pressure range in Figure 8a. The long period to obtain all of the data points in Figure 8a (more than 1 week) also supports its hydrophobicity. Interestingly, after NiO loading and R673−O473 treatment, the material turned hydrophilic (Figure 8b). Therefore, NiO loading and preteatment of the mesoporous Ta_2O_5 improved the hydrophilicity, which is considered to be preferable for water decomposition.

In conclusion, mesoporous Ta_2O_5 was found to be an active catalyst for photocatalytic water decomposition although the wall structure was amorphous. The activity was improved by NiO loading and R673−O473 pretreatment, although the mesoporous structure collapsed to some extent. Therefore, much higher activity is expected if the stable mesoporous structure even after pretreatment would be constructed.

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