

Synthesis, Mesostructure, and Photocatalysis of a Highly Ordered and Thermally Stable Mesoporous Mg and Ta Mixed Oxide

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Received November 12, 2003. Revised Manuscript Received June 9, 2004

An ordered (2D-hexagonal) mesoporous Mg and Ta mixed oxide (Mg–Ta oxide) is successfully prepared. The mesoporous Mg–Ta oxide is stable after calcination at 773 K for 30 h, and has a BET surface area of $123 \text{ m}^2 \text{ g}^{-1}$, pore size of 5.0 nm, and wall thickness of 2.8 nm. Removal of the template by washing in water results in a wormhole-like microporous material with a BET surface area of $424 \text{ m}^2 \text{ g}^{-1}$. The ordered mesoporous structure is not achieved after aging alone (313 K), but becomes complete through structural rearrangement in the initial stage of calcination (<423 K) for template removal. The presence of the template during calcination is found to be indispensable, and the ordered mesoporous material is not obtained when the template is removed by washing with water prior to calcination. Although the inorganic phase is amorphous, the photocatalytic activity for overall water decomposition over the 2D hexagonal mesoporous Mg–Ta oxide is much higher than over crystallized MgTa_2O_6 . The highest activity (ca. $100 \mu\text{mol h}^{-1}$ for H_2 and $50 \mu\text{mol h}^{-1}$ for O_2) is attained by loading with 0.1 wt % NiO followed by reduction and reoxidation pretreatment.

Introduction

Reports on the preparation of mesoporous metal oxides are becoming more numerous due to the wide range of properties and potential applications of these new materials.¹ As one application of mesoporous metal oxides, the present authors have been studying photocatalytic overall water decomposition over pure and mixed Ta oxides with mesoporous structures.^{2,3} Crystallized Ta oxide and tantalates are known active photocatalysts under ultraviolet (UV) irradiation.^{4–9} In the initial study, wormhole-like mesoporous Ta oxide was prepared by following a previously reported method,¹⁰ and its photocatalytic performance for overall water decomposition was evaluated.² One of the important findings is that this material exhibits high activity

despite the amorphous structure of the oxide phase. However, the material had characteristically poor thermal stability due to the very thin amorphous walls, which resulted in the destruction of the porous structure and decrease in the BET surface area after pretreatment for improving the photocatalytic activity. In addition, the wormhole porous structure prevented detailed characterization of the NiO-loaded and pretreated catalyst.

When Ta is mixed with the second component in the oxide phase, an ordered mesoporous structure is formed in the case of Mg–Ta mixed oxide.³ The mesoporous Mg–Ta mixed oxide thus prepared is stable after calcination at 773 K for 30 h and also exhibits stable photocatalytic activity for overall water decomposition. In this paper, the modified (NiO-loaded and pretreated) mesoporous Mg–Ta mixed oxide exhibiting high photocatalytic activity is characterized, and the NiO-loaded (0.1 wt %) mesoporous Mg–Ta oxide is analyzed in detail by energy-dispersive X-ray analysis using transmission electron microscopy (TEM) apparatus.

In addition to the photocatalytic characteristics, the formation process of the mesoporous structure in metal oxides is worth clarifying. In the synthesis of mesoporous transition metal oxides and mixed metal oxides undertaken by our group, it was suspected that the mesoporous structure observed after calcination for template removal might be absent in samples after aging and that the porous structure changed during calcination, even after aging. In the case of the mesoporous Nb oxide, for example, when the template was removed after aging by washing in water, super-

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microporous (1.5 nm pore size) material was obtained,¹¹ whereas template removal by calcination gave a mesoporous material (5 nm pore size). Therefore, the pore structure is considered to change during the calcination process. This is supported by recent experimental results of light scattering from films of mesoporous transition-metal oxides, where transformation of the pore structure was observed in the dry film after evaporation of the solvent.¹² In the case of the mesoporous Mg-Ta mixed oxide, the pore arrangement was found to be greatly affected by the conditions of calcination for template removal. Therefore, the details of the formation of mesopores in Mg-Ta mixed oxide is studied here to improve our understanding of the role of the template in the calcination process.

Experimental Section

Preparation of Mesoporous Mg-Ta Oxide. Tantalum chloride ($TaCl_5$, 0.007 mol) and magnesium chloride ($MgCl_2$, 0.003 mol) were dissolved in ethanol (10 g) containing 1 g of poly(alkylene oxide) block copolymer $HO(CH_2CH_2O)_{20}(CH_2CH_2O)_{70}(CH_2CH_2O)_{20}H$ (Pluronic P-123). After vigorous stirring for 30 min, the resulting sol solution was aged at 313 K for 7–10 days. Mesoporous Mg-Ta oxides obtained using different methods for template removal were compared using the same template-containing precursor. One-half of the sample in each case was calcined at 773 K for 10 h (calcined sample), and the other half was washed with 300 mL of water three times at room temperature, followed by drying at room temperature (washed sample). One-half of the washed sample was then calcined at 773 K for 30 h in order to compare with the other calcined sample.

Crystallized $MgTa_2O_6$ was prepared by a solid-state reaction of tantalum oxide (Ta_2O_5 , 0.9 mol), magnesium carbonate ($MgCO_3$, 1.0 mol), and boric acid (H_3BO_3 , 0.2 mol) at 1173 K for 6 h, followed by further calcination at 1773 K for 24 h after grinding. The formation of the crystallized $MgTa_2O_6$ was confirmed by powder X-ray diffraction (XRD) analysis.

Characterization. Small-angle powder XRD patterns of the products were obtained on a Philips X'Pert-MPD PW3050 diffractometer using $Cu K\alpha$ radiation (40 kV, 40 mA) at a resolution of 0.02°. 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 outgassing at 373 K under vacuum to a final pressure of 1×10^{-5} Torr. The BET surface areas were estimated over a relative pressure (P/P_0) range of 0.05–0.30. The pore-size distribution was obtained from analysis of the adsorption branch of the isotherms by the BJH (Barrett–Joyner–Halenda) method. An Ar adsorption–desorption isotherm was also measured for a microporous sample using the same system after the same pretreatment. TEM images were captured using a JEOL 2010F electron microscope operated at 200 keV. The samples for TEM observation were prepared by dropping mesoporous Mg-Ta oxide powder dispersed in 2-propanol on a copper grid covered with carbon film. Elemental analysis of carbon, hydrogen, and nitrogen was performed using a Leco CHN-932, and chloride was analyzed using a Yanaco SX-Elements Micro Analyzer YS-10.

Photocatalytic Water Decomposition. The photocatalytic activity for overall water decomposition was studied using as-prepared and NiO -loaded mesoporous Mg-Ta oxide samples as well as crystallized $MgTa_2O_6$ bulk material. NiO was loaded by impregnation using an aqueous nickel nitrate solution, followed by calcination at 600 K for 1 h for the mesoporous and amorphous Ta_2O_5 samples. The NiO -loaded samples were

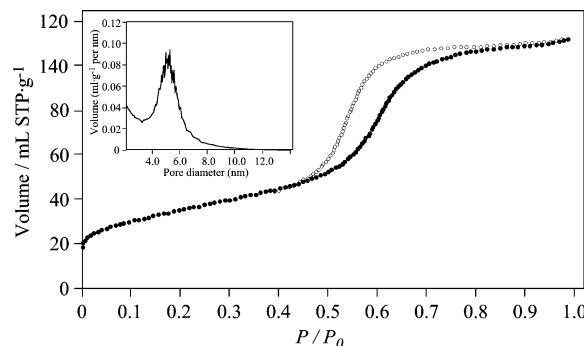


Figure 1. N_2 adsorption–desorption isotherm of mesoporous Mg-Ta oxide and pore size distribution (inset). Open and closed circles correspond to adsorption and desorption branches, respectively.

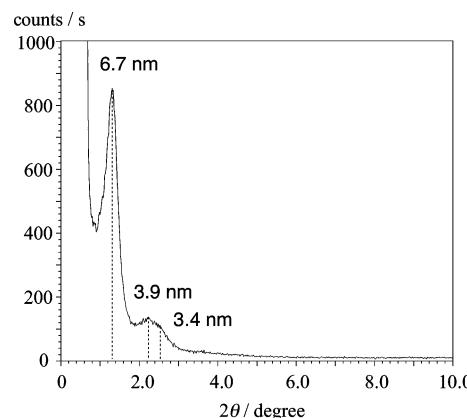


Figure 2. Small-angle XRD pattern of mesoporous Mg-Ta oxide.

pretreated first by H_2 reduction at 773 K for 2 h followed by reoxidation in O_2 at 473 K for 1 h. The photocatalytic activity for overall water splitting was investigated using 0.3 g of each sample, suspended in about 420 mL of pure water and irradiated using a high-pressure Hg lamp (450 W).² Before irradiation, the system was evacuated several times. The amounts of evolved gases were analyzed by gas chromatography using an instrument connected directly to the reaction system.

Results and Discussion

1. Preparation of Highly Ordered Mesoporous Mg-Ta Oxide. The preparation of mesoporous Mg-Ta oxide is reported in a previous paper and will be mentioned only briefly here. The N_2 adsorption–desorption isotherm of the prepared mesoporous Mg-Ta oxide is a typical type-IV pattern characteristic of many mesoporous materials, as shown in Figure 1. The estimated BET surface area was $123 \text{ m}^2 \text{ g}^{-1}$, and the pore size distribution was centered around ca. 5.5 nm. A conventional X-ray diffractometer was used in the previous study, and as such the $d(100)$ value may not be reliable at small angles of X-ray incidence. Therefore, the small-angle XRD pattern was measured again in the present study in order to verify the repeat distance and wall thickness. As shown in Figure 2, an intense peak corresponding to a $d(100)$ value of 6.7 nm was observed, together with additional peaks at 2–3°, implying a 2D-hexagonal mesoporous structure. From the observed repeat distance (6.7 nm), the wall thickness is estimated to be 2.8 nm, assuming a 2D-hexagonal

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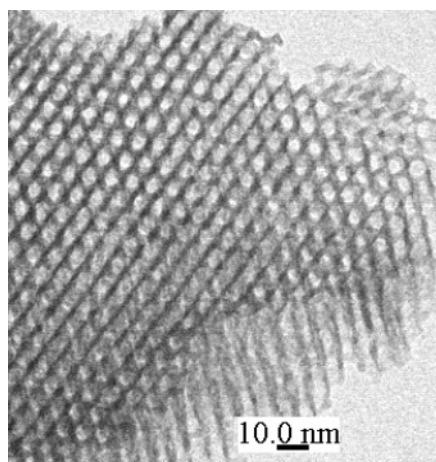


Figure 3. TEM image of mesoporous Mg-Ta oxide.

mesoporous structure. Therefore, the previously reported wall thickness (3.6 nm) is somewhat overestimated. The mesoporous structure of the prepared Mg-Ta oxide was observed directly by TEM measurements in this study, and a typical TEM image is shown in Figure 3. The 2D-hexagonal arrangement of mesopores can be clearly seen. This ordered structure was obtained by calcination at 673–773 K for 10–30 h, which also demonstrates that the material is thermally stable. Thus, the NiO-loaded mesoporous Mg-Ta mixed oxide is sufficiently stable to survive thermal activation treatment for use as a photocatalyst.

2. Formation of Highly Ordered Mesoporous Structure. Although organic templates are usually removed by calcination in air, such templates may also be removed by simple washing in water after aging, because the block copolymer templates have weaker interaction with inorganic sources compared to ionic surfactants. This method of surfactant removal was employed successfully in the preparation of supermicroporous Nb oxide with pores 1.5 nm in size.¹¹ Thus, the pore structure and size are strongly dependent on the template-removal method, whether calcination or water-washing. From this result, it is suspected that the structure of the template micelles changes during the calcination procedure for removal of the template. It is expected that the structure of template micelles in template-containing materials can be revealed by removing the micelles from the aged sample prior to calcination. Figure 4 compares the adsorption–desorption isotherms (Ar or N₂) of the calcined and water-washed materials. The N₂ adsorption isotherm of the calcined Mg-Ta oxide agrees with that in Figure 1, with a BET surface area of 146 m² g⁻¹ and pore size of 5.5 nm, while the washed sample is microporous. An Ar isotherm is shown in Figure 4b for the washed sample. The BET surface area was estimated to be 424 m² g⁻¹. These results indicate that the material was microporous but that the 2D-hexagonal mesoporous structure had not yet formed. TEM images of the washed sample shown in Figure 5 confirm the microporous features of the washed sample. Although a small region of less ordered cylindrical pores is observed in the left part of the particle in Figure 5A, wormhole-like micropores are dominant (Figure 5A,B). Thus, it is considered that a drastic rearrangement of the pore structure occurs during calcination. This is consistent with

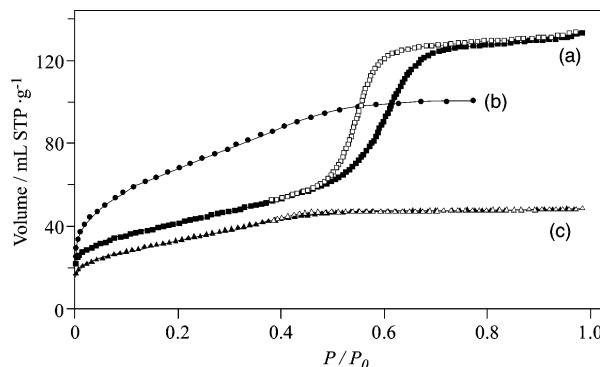


Figure 4. (a) N₂ adsorption–desorption isotherm of mesoporous Mg-Ta oxide calcined at 773 K for 30 h, (b) Ar adsorption–desorption isotherm of water-washed sample, and (c) N₂ adsorption–desorption isotherm of the sample from panel b after calcination at 773 K for 30 h. Open and closed symbols correspond to adsorption and desorption branches, respectively.

the XRD pattern of the washed sample, where no clear peak was observed.

To investigate this further, the washed sample was then calcined under the same conditions as for template removal. The N₂ adsorption–desorption isotherm of this sample is shown in Figure 4c. N₂ uptake is not obvious at any relative pressure, in contrast to Figure 4a. The BET surface area was 120 m² g⁻¹. In TEM images of the washed–calcined sample (Figure 5C,D), the pore shape is distorted and no longer round, but the pore arrangement was slightly better than before calcination. These results indicate that the presence of the block copolymer template is indispensable for the formation of the 2D-hexagonal mesoporous structure in Mg-Ta mixed oxide during the calcination process. In other words, micropores in the aged sample are converted to mesopores accompanying the progress of condensation and rearrangement of the inorganic phase in the presence of the template during thermal treatment.

The changes in carbon content, BET surface area, and morphology of the Mg-Ta oxide during calcination were studied by elemental analysis, N₂ adsorption isotherm, and TEM observation. The aged sample was divided and each portion was calcined at 423, 523, 573, or 773 K. The carbon content (wt %) and BET surface area of samples calcined at different temperatures are plotted in Figure 6 together with the carbon content of the as-prepared Mg-Ta oxide. Calcination at 423 K did not remove the surfactant in the as-prepared sample, whereas more than half of the organic template was successfully removed by calcination at 523 K. By increasing the calcination temperature, the carbon content in the sample gradually decreased simultaneously with an increase in the BET surface area. The slight decrease in the BET surface for the 773 K calcined Mg-Ta oxide is most probably due to an increase in the density of the amorphous Mg-Ta oxide phase or decrease of the template-derived surface area.

The change in the organic–inorganic mesostructure was observed by TEM (Figure 7). As shown in Figure 7A,B, the ordered mesostructure was present in the Mg-Ta oxide calcined at 423 K, in which more than 95% of the template still remained a composite (Figure 6). Therefore, the nonordered organic–inorganic microstructure of the as-prepared Mg-Ta mixed oxide is

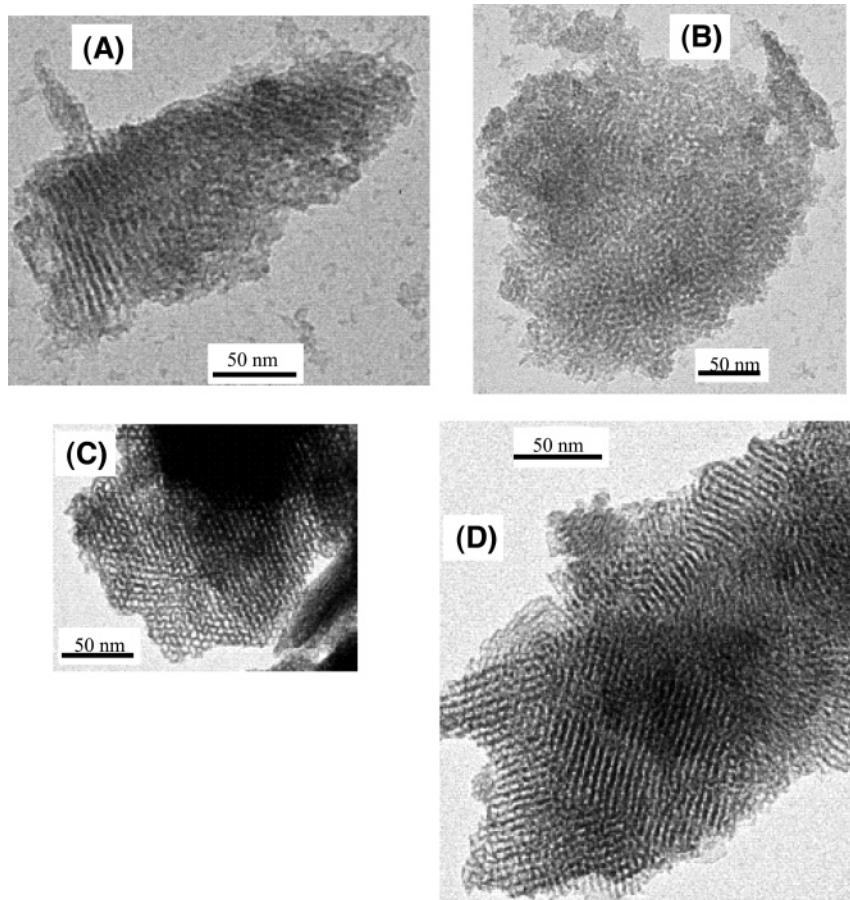


Figure 5. TEM images of mesoporous Mg-Ta oxide: (A and B) washed sample, (C and D) washed and calcined (773 K for 30 h) sample.

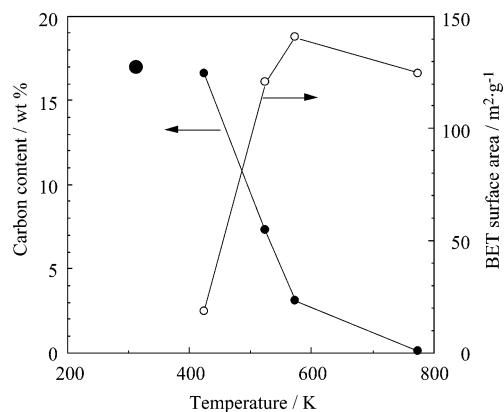


Figure 6. Changes in carbon content (closed circles) and BET surface area (open circles) of mesoporous Mg-Ta oxide with calcination temperature. The large closed circle indicates the carbon content of the as-prepared sample.

reorganized into an ordered mesostructure below 423 K in the presence of the template. The poor contrast in TEM images in Figure 7A,B is due to the remaining organic template. The contrast appears more sharply in a similar TEM image of the sample calcined at 523 K (Figure 7(C)), where ca. 60% of the organic template had been removed. Since no structural difference was observed between Mg-Ta oxides calcined at 423 and 523 K, the ordered mesoporous structure is regarded not to undergo further changes at higher temperature. The Mg-Ta mixed oxide once calcined at 523 K was further calcined at 773 K and observed by TEM for confirmation of this point. As shown in Figure 7D, the

ordered mesoporous structure was clearly observed at the edge (thin area) of a particle. Therefore, no structural change occurred during the removal of the remaining organic species at 773 K. Small-angle XRD patterns of the samples calcined at 423, 523, 673, and 773 K after aging are shown in Figure 8. As in good agreement with the TEM observation, gradual formation of the ordered mesoporous structure by increasing the calcinations temperature is evidenced. Therefore, rearrangement of less ordered pores to the ordered mesopores occurs in the presence of template.

3. Photocatalytic Water Decomposition over Mesoporous Mg-Ta Mixed Oxide. The ordered mesoporous Mg-Ta mixed oxide calcined at 773 K exhibits high photocatalytic activity for overall water decomposition under UV irradiation, despite the presence of an amorphous inorganic oxide phase.³ The improved photocatalytic activity achieved by loading with NiO is compared with that of crystallized MgTa₂O₆ with NiO loading in Figure 9, which shows the progress of the photocatalytic decomposition of water over NiO-loaded (0.1 wt %) mesoporous Mg-Ta mixed oxide (amorphous) and crystallized MgTa₂O₆. In general, the highly crystallized structure of inorganic materials is advantageous for photocatalytic reactions compared to amorphous structures due to the higher mobility of excited electrons and holes. However, as clearly observed in Figure 9, mesoporous Mg-Ta oxide exhibits much higher activity than the crystallized MgTa₂O₆ with stoichiometric production of H₂ and O₂. The effect of the degree of NiO loading on the photocatalytic water decomposition over

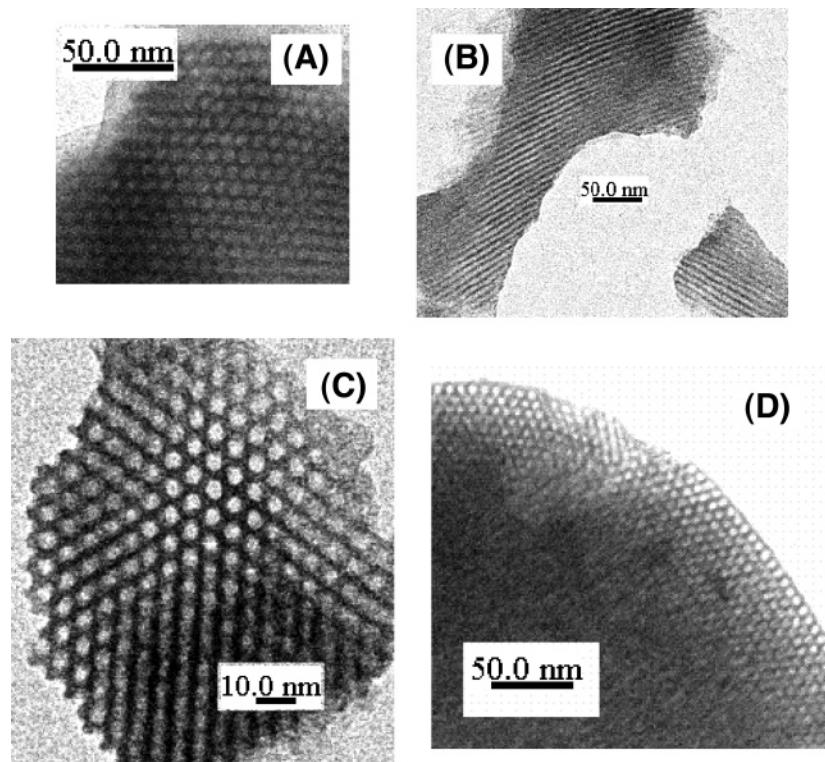


Figure 7. TEM images of mesoporous Mg-Ta oxide calcined at (A and B) 423 K, (C) 523 K, and (D) 523 K followed by 773 K.

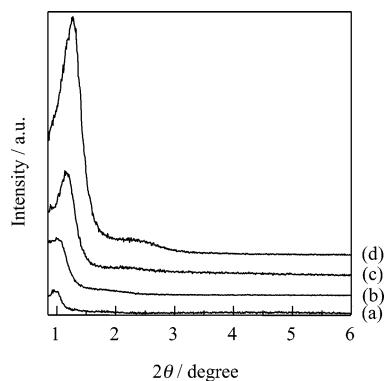


Figure 8. Small-angle XRD patterns of Mg-Ta oxide calcined at 423 K (a), 523 K (b), 573 K (c) and 773 K (d).

both mesoporous Mg-Ta mixed oxide and MgTa_2O_6 is summarized in Table 1. Over mesoporous Mg-Ta oxide, 0.1 wt % NiO loading was found to be optimal, whereas there was no obviously optimal NiO content for MgTa_2O_6 . In addition, only a small amount of O_2 evolved over MgTa_2O_6 , whereas stoichiometric H_2 and O_2 were generated from H_2O over mesoporous Mg-Ta mixed oxide. Among the various Ta mixed oxides, which all exhibit comparatively high photocatalytic activity for water decomposition under UV irradiation, MgTa_2O_6 is reported to be one of the exceptions.⁵ Therefore, the results for crystallized MgTa_2O_6 in the present study are reasonable. On the other hand, mesoporous Mg-Ta mixed oxide consisting of an amorphous inorganic phase is a photocatalyst with unexpectedly high activity. This high activity is considered to be due to the thin walls of the mesopores, which provide a short distance for the excited electrons and holes to travel to the surface.

It is known that reduction and reoxidation of the NiO loaded on photocatalysts enhance the activities of photo-

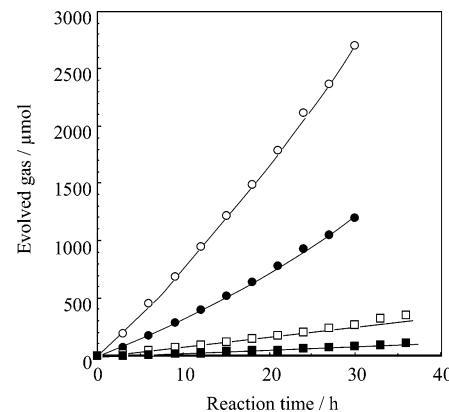


Figure 9. Progress of H_2 and O_2 evolution from water under UV irradiation. Circles and squares denote gas evolution catalyzed by mesoporous Mg-Ta oxide and crystallized MgTa_2O_6 , and open and closed symbols indicate H_2 and O_2 evolution, respectively.

Table 1. Dependence of Photocatalytic Activity for Water Decomposition on the Amount of NiO Loading

loading/wt %	evolved gases/ $\mu\text{mol}\cdot\text{h}^{-1}$			
	mesoporous Mg-Ta oxide		MgTa_2O_6	
	H_2	O_2	H_2	O_2
0	57	25	6	1
0.1	90	41	10	3
0.5	58	25	5	1
1.0	15	4	15	1
2.0	8	2	11	3
0.1 ^a	102	51	8	2

^a After reduction and reoxidation treatment.

tocatalysts such as SrTiO_3 and $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$.^{15–18} NiO pretreatment results in Ni metal particles covered with

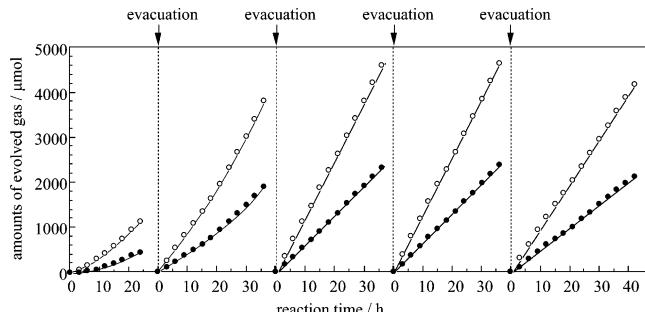


Figure 10. Progress of H_2 and O_2 evolution from water under UV irradiation over mesoporous NiO-loaded (0.1 wt %) Mg-Ta oxide after reduction and reoxidation treatment. Open and closed circles indicate H_2 and O_2 evolution, respectively.

NiO on the main photocatalyst. 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 particles. The Ni metal then comes into ohmic contact between the oxide photocatalyst and NiO. In this way, 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 observed enhancement of photocatalytic activity.^{15,18} The same pretreatment is not necessary for most tantalates because of the relatively high conduction band bottom, which makes it possible to inject conduction-band electrons directly into the conduction band of NiO.⁴⁻⁸

Following from the distinct improvement in the photocatalytic activity observed in the case of mesoporous pure Ta_2O_5 ,² reduction and reoxidation treatment for NiO-loaded Mg-Ta mixed oxide and MgTa_2O_6 was also attempted here. Reduction was carried out at 773 K for 2 h followed by oxidation at 473 K for 1 h. In the case of mesoporous Ta_2O_5 , which has lower thermal stability, the reduction temperature was limited to 723 K. Preservation of the ordered mesoporous structure of Mg-Ta mixed oxide after this treatment was confirmed from the N_2 adsorption isotherms (data not shown) and TEM images shown below. The photocatalytic activities over NiO-loaded (0.1 wt %) and pretreated catalysts are compared in Table 1. Similar to the bulk Ta mixed-oxide materials, only a slight improvement was observed for the mesoporous Mg-Ta oxide by this pretreatment, while no improvement was observed for crystallized MgTa_2O_6 .

The stable photocatalytic activity for water decomposition over NiO-loaded and treated mesoporous Mg-Ta mixed oxide can be seen in the progress of the reaction shown in Figure 10. Stoichiometric H_2 and O_2 evolution for more than 170 h was confirmed with regular evacuation. Considering these results and the results of the previous study on mesoporous Ta_2O_5 , it is concluded that mesoporous tantalates are stable photocatalysts for overall water splitting. The meso-

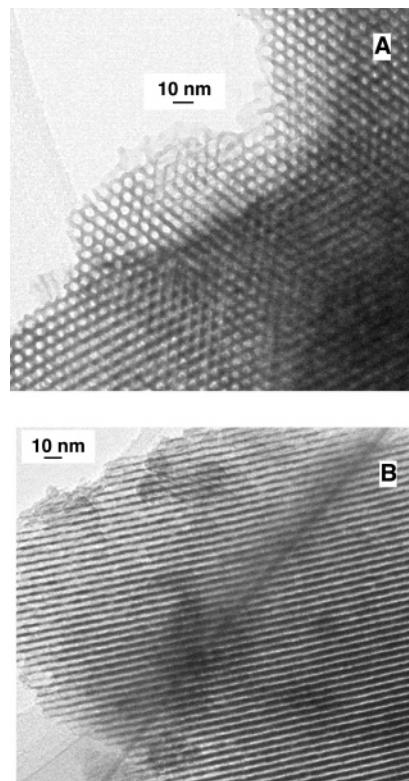


Figure 11. TEM images of NiO-loaded (0.1 wt %) and pretreated mesoporous Mg-Ta oxide observed (A) perpendicular and (B) vertical to the channel direction.

porous structure itself therefore appears to be advantageous for Photocatalytic reaction, despite the amorphous inorganic structure of these materials.

4. Characterization of NiO-Loaded and Pretreated Mesoporous Mg-Ta Mixed Oxide. The optimal level of NiO-loading on mesoporous Mg-Ta mixed oxide is 0.1 wt %, which is much lower than for the previously reported mesoporous Ta_2O_5 (4.0 wt %). Therefore, good dispersion of the loaded NiO is regarded as an important factor in enhancing the photocatalytic activity. This was investigated through TEM observation and energy-dispersive X-ray analysis. TEM images of NiO-loaded (0.1 wt %) and pretreated mesoporous Mg-Ta oxide are shown in Figure 11. The absence of NiO particles and lack of structural destruction are clearly observed. In contrast, NiO particles of various sizes were evident in TEM images of NiO-loaded (5 wt %) and pretreated mesoporous Ta oxide in the previous study.² Energy-dispersive X-ray analysis of ~ 5 nm spots was performed to examine the presence and dispersion of the loaded NiO. A total of four to six spots in nine different particles were analyzed, and the results are summarized in Figure 12. The atomic Ni concentration in comparison to the standard amounts of Mg, Ta, and Ni was estimated (0.1 wt % NiO corresponds to 0.2 atom %). The spots examined were selected in extremely dark and bright places, and the results are distinguished from other particles by dotted lines in Figure 12. The particles shown in parts A and B of Figure 11 correspond to the fourth and third groups from the left in Figure 12. Although some small dark particles overlap the ordered mesoporous structure in the top left of the TEM image in Figure 11B, the elemental analysis revealed a quite homogeneous dispersion of NiO (third

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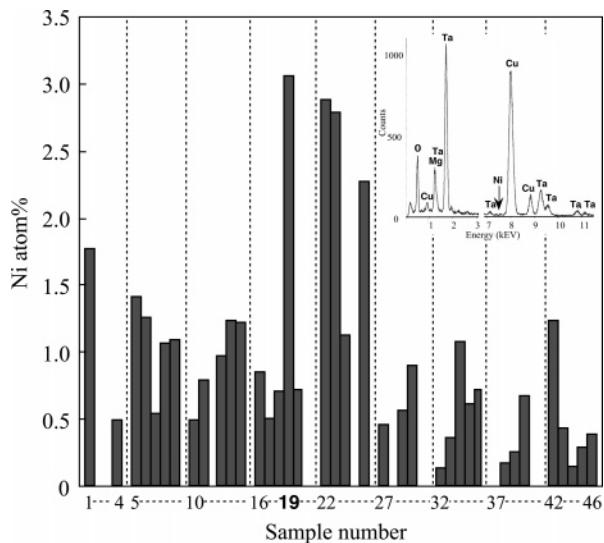


Figure 12. Ni content in NiO loaded (0.1 wt %) and pre-treated mesoporous Mg–Ta oxide, as measured by energy-dispersive X-ray analysis. A typical spectrum (for sample 19) is shown.

group from the left in Figure 12). Moreover, the intensity of the peak due to Ni for sample number 19 (maximum detected amount of Ni) was very small, as shown in the inset of Figure 12. Therefore, although the values themselves are not reliable for quantification of the ideal amount of NiO (0.2 atom %), the results demonstrate the uniform presence of loaded NiO at low concentration.

The optimal degree of NiO loading on mesoporous Mg–Ta oxide for photocatalytic water decomposition is 0.1 wt %, and at this concentration the dispersion of NiO is very uniform. Therefore, surplus NiO would become recombination centers, rather than active sites, or form larger NiO particle consuming active small NiO particles, with a resultant decrease in catalytic activity (Table 1).

Conclusions

The detailed processes of the formation of 2D hexagonal mesoporous Mg–Ta oxide using a neutral block copolymer template were studied. The ordered mesoporous structure was found to be completed in the initial stage of calcination (ca. 423 K) for template removal and is not formed by aging alone. The photocatalytic activity of mesoporous Mg–Ta oxide for overall water splitting was improved by loading with 0.1% NiO and pretreatment. The optimized catalyst provided evolution rates of $100 \mu\text{mol h}^{-1} \text{H}_2$ and $50 \mu\text{mol h}^{-1} \text{O}_2$, with considerable stability for repetition. TEM observation and energy-dispersive X-ray analysis revealed the highly uniform dispersion of loaded NiO (0.1 wt %) on the mesoporous Mg–Ta.

Acknowledgment. This work was supported by the Core Research for Evolutional Science and Technology (CREST) program of the Japan Science and Technology (JST).

CM030355S