

## Preparation and Photocatalysis of Ordered Mesoporous Mg-Ta Mixed Oxide

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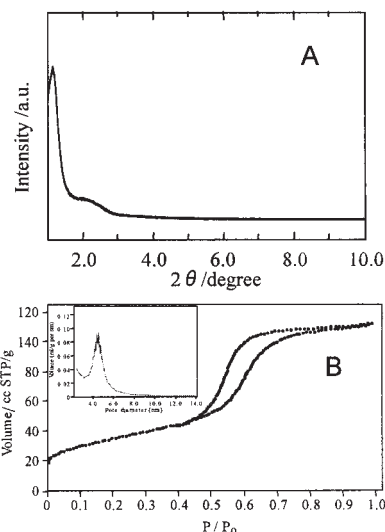
An ordered mesoporous Mg-Ta mixed oxide ( $123 \text{ m}^2 \cdot \text{g}^{-1}$  BET surface area, *ca.* 5.0 nm mesopore size and 3.6 nm wall thickness), which was stable after calcination at  $500^\circ\text{C}$  for 30 h, showed stable and high photo-catalytic activity for overall water decomposition.

$\text{Ta}_2\text{O}_5$  and various Ta mixed oxides (tantalates) are known to be active photo-catalysts for overall water decomposition under UV irradiation.<sup>1,2</sup> We previously synthesized and studied the photo-catalysis of a mesoporous  $\text{Ta}_2\text{O}_5$ , and the stable activity for overall water decomposition was observed even though the  $\text{Ta}_2\text{O}_5$  wall was amorphous.<sup>3</sup> The high photo-activity of mesoporous  $\text{Ta}_2\text{O}_5$  was attributable to the short distance of migration of the excited electrons to the surface due to the porous structure. The problems of the previous study were its wormhole structure and poor thermal stability. Therefore, mesoporous structures are expected to be advantageous for photocatalytic reactions. In this study, a mesoporous tantalate was prepared by mixing Mg and Ta at 3 : 7 molar ratio, which showed ordered mesoporous structure stable after calcination at  $500^\circ\text{C}$  for 30 h. The photo-catalytic activity of the prepared Mg-Ta mixed oxide for the water decomposition into stoichiometric  $\text{H}_2$  and  $\text{O}_2$  was studied.

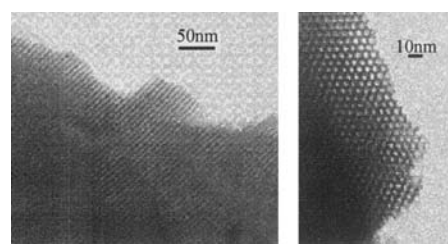
Tantalum chloride ( $\text{TaCl}_5$ , 0.007 mol) and magnesium chloride ( $\text{MgCl}_2$ , 0.003 mol) were dissolved in ethanol (10 g) containing 1 g of poly(alkylene oxide) block copolymer  $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_{20}(\text{CH}_2\text{CH}(\text{CH}_3)\text{O})_{70}(\text{CH}_2\text{CH}_2\text{O})_{20}\text{H}$  (Pluronic P-123). After vigorous stirring for 30 min, the resulting sol solution was aged at  $40^\circ\text{C}$  for 7–10 days. The sample was then calcinated at  $500^\circ\text{C}$  for 30 h to completely remove the template. The photo-catalytic activity for overall water decomposition was studied on as- prepared and NiO loaded samples.

A low-angle XRD pattern (A) and  $\text{N}_2$  adsorption-desorption isotherm (B) of mesoporous Mg-Ta mixed oxide is shown in Figure 1. The presence of a diffraction peak at around  $2\theta = 1.3$  degree together with a broad band at  $2\theta = 1.8\text{--}2.8$  degree suggests an ordered mesoporous structure. The  $d(100)$  was 7.5 nm, and the repeat distance was estimated as 8.6 nm assuming a 2D hexagonal mesoporous structure. The type IV isotherm in Figure 1 is also characteristic to mesoporous material, and the pore size distribution was centered at 5.0 nm. Therefore, the wall thickness is estimated as 3.6 nm, which is thick and typical to the mesoporous oxides prepared with neutral block co-polymer templates.<sup>4,5</sup> BET surface area was obtained as  $123 \text{ m}^2 \cdot \text{g}^{-1}$ . The complete removal of the template from mesoporous Mg-Ta mixed oxide after calcination at  $500^\circ\text{C}$  for 20 h was confirmed by elemental (CHN) analysis.

The ordered mesoporous structure was also observed by TEM. In Figure 2 two TEM images from different directions are



**Figure 1.** (A) Powder X-ray diffraction pattern (XRD) of the mesoporous Mg-Ta mixed oxide obtained on a RIGAKU RINT 2000 diffractometer using  $\text{Cu-K}\alpha$  radiation (40 kV, 40 mA) at a 0.02 step size and 1 s step time over the range  $1.5^\circ < 2\theta < 15^\circ$ . (B)  $\text{N}_2$  adsorption-desorption isotherm of mesoporous Mg-Ta mixed oxide measured using a Micromeritics COULTER OMNISORP 100CX system after degassing at  $100^\circ\text{C}$ . BET surface areas were estimated over a relative pressure ( $P/P_0$ ) ranging from 0.05 to 0.30, and BJH (Barrett-Joyner-Halenda) method was employed for the estimation of the pore size distribution.

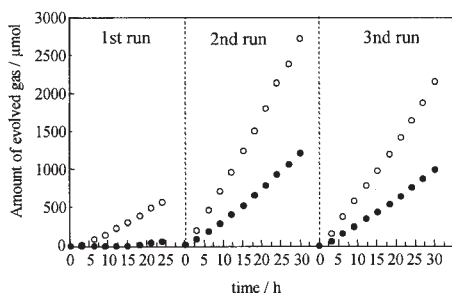


**Figure 2.** Transmission electron microscopy (TEM) images of the mesoporous Mg-Ta mixed oxide obtained on a JEOL 2010F electron microscope operated at 200 keV.

shown. In the left image straight and parallel mesopores running in the same direction are observed, while the well ordered pore arrangement is clearly found in the right image when the electron

beam transmits in the direction of mesopores. The bundle of mesopores consists of some ordered domains: Aberrations are observed in the right image. The small size of the ordered mesopore domains is probably responsible for the lack of clear observation of the XRD peaks at 1.8–2.8 degree. The observed pore size and wall thickness in the TEM image are in agreement with the values estimated by XRD and  $N_2$  adsorption-desorption isotherm in Figure 2, indicating that the particle shown in Figure 2 is a representative of the whole sample. An energy dispersive X-ray (EDX) analysis using the TEM apparatus at several spots (<5 nm in diameter) of several particles confirmed the presence of Mg and Ta at the preparation ratio (3 : 7). Therefore, Mg and Ta atoms are mixed homogeneously in the amorphous oxide wall structure.

The photo-catalytic activity of mesoporous Mg-Ta mixed oxide is demonstrated in Figure 3. Although some induction period was observed in the first run, which is sometimes observed in photo-catalytic water decomposition,<sup>6</sup> stable activity for overall water decomposition into stoichiometric  $H_2$  and  $O_2$  was obtained in the successive runs. The activity was about 100 and  $50 \mu\text{mol}\cdot\text{h}^{-1}$  for  $H_2$  and  $O_2$ , respectively. Even in the absence of NiO co-catalyst working as active sites for  $H_2$  evolution, 57 and



**Figure 3.** Photocatalytic activity of NiO (0.1 wt%)-loaded mesoporous Mg-Ta mixed oxide for overall decomposition of water under UV irradiation. Open and close symbols indicate the amount of evolved  $H_2$  and  $O_2$ , respectively. NiO was loaded from nickel aqueous nitrate solution by impregnation, followed by calcination at 600 K for 1 h. 0.3 g of the sample was suspended in 420 mL of pure water and irradiated by a high pressure Hg lamp (450 W). Amounts of evolved gases were analyzed by a gas chromatography directly connected to the reaction system.

$25 \mu\text{mol}\cdot\text{h}^{-1}$  of  $H_2$  and  $O_2$  evolved.

As was found in the previous study, mesoporous  $Ta_2O_5$  was more active than the crystallized bulk  $Ta_2O_5$ , even though the wall around the mesopores consisted with amorphous  $Ta_2O_5$ .<sup>3</sup> In the case of Mg-Ta mixed oxide, the crystallized  $MgTa_2O_6$  prepared by solid state reaction is known to be one of the inactive photo-catalysts in the series of tantalates,<sup>1</sup> and in fact, did not evolved  $H_2$  and  $O_2$  in the stoichiometric ratio: only  $15 \mu\text{mol}\cdot\text{h}^{-1}$  of  $H_2$  and  $1 \mu\text{mol}\cdot\text{h}^{-1}$  of  $O_2$  were evolved at maximum when 0.1 wt% of NiO was loaded. For photo-catalytic reactions, crystallized lattice structure is preferable due to the better mobility of the excited electrons and holes. However, mesoporous  $Ta_2O_5$  and Mg-Ta mixed oxide both resulted in higher photo-catalytic activity for overall water decomposition than the corresponding crystallized materials. It should be noted that the band gaps of mesoporous  $Ta_2O_5$  and Mg-Ta Mixed oxide were the same as those of the corresponding crystallized bulk materials ( $>4.0 \text{ eV}$ ). Therefore, mesoporous structure is expected to be advantageous to the photo-catalytic reactions, even though the wall structure is amorphous, most probably due to the short distance of migration of the excited electrons in bulk to the surface. We recently have succeeded in the preparation of crystallized mesoporous Nb-Ta mixed oxide (NbTa-TIT-1),<sup>7,8</sup> which consists of mesoporous single crystal particles. If the prepared mesoporous  $Ta_2O_5$  and Mg-Ta mixed oxide are crystallized with maintaining the mesoporous structure, much higher photo-catalytic activity would be obtained. Such materials are the target for the further study together with the preparation of other mesoporous transition metal oxides.

#### References and Notes

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