

# Synthesis and Characterization of Mesoporous Ta–W Oxides as **Strong Solid Acid Catalysts**

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Several mesoporous  $Ta_x W_{10-x}$  mixed oxides prepared from  $TaCl_5$  and  $WCl_6$  in the presence of poly block copolymer surfactant Pluronic P-123 were examined as potential solid acid catalysts. Amorphous wormhole-type mesopores were observed in samples with x values from 3 to 10, whereas W-rich samples (x = 0-2) formed nonmesoporous structures with crystallized tungsten oxide (WO<sub>3</sub>). The acid strength increased with addition of W for mesoporous  $Ta_x W_{10-x}$  oxides, and mesoporous Ta<sub>3</sub>W<sub>7</sub> oxide exhibited the highest acid catalytic activity for the Friedel-Crafts alkylation of anisole and the hydrolysis of disaccharides. The results are compared with those of nonporous Ta<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>, HTaWO<sub>6</sub> nanosheets, which were a solid acid obtained by exfoliation and aggregation of layered HTaWO<sub>6</sub> with strong Brønsted acid sites in the interlayer, and a range of conventional solid acid catalysts. Mesoporous Ta-W oxides exhibited a turnover rate higher than that of nonporous  $Ta_2O_5$ -WO<sub>3</sub> and HTaWO<sub>6</sub> nanosheets, indicating that the mesoporous structure is an advantageous environment for the strong acid sites, because of the high surface area and easy reactant accessibility.

## 1. Introduction

Solid acid catalysts, which are reusable and readily separable from reaction products, have been widely investigated as direct replacements for liquid acids to reduce the impact on the environment and to decrease costs.<sup>1</sup> These new concepts for designing industrial reactions, maximizing the amount of raw material that ends up in a product, minimizing the environmental impact, and substituting renewable sources for depleting sources called "green chemistry" or sustainable chemistry<sup>2,3</sup> have been widely applied in organic chemistry, inorganic chemistry, biochemistry, analytical chemistry, and physical chemistry.

The use of mesoporous transition metal oxides as solid acid catalysts is an interesting approach to developing a

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solid acid catalyst with enhanced activity.<sup>4–6</sup> Mesopores in the oxide enable the reactants to access additional active acid sites, resulting in improved rates of acid catalysis. Sulfated mesoporous niobium<sup>5</sup> and tantalum oxides<sup>6</sup> have been reported to exhibit remarkable activity and selectivity in acid-catalyzed Friedel-Crafts alkylation and isomerization. However, the use of a recycled catalyst remains difficult, because of leaching of sulfate species, as reported for mesoporous silica and organosilicas bearing sulfonic acid groups. Previous studies on mesoporous Nb-W oxide solid acids<sup>7</sup> have revealed that wormhole-type mesoporous Nb-W oxides can be applied as recyclable and highly active solid acid catalysts for Friedel-Crafts alkylation, hydrolysis of disaccharides, and esterification. The reaction rate and the acid strength increased gradually with the addition of W, reaching the highest reaction rate with mesoporous Nb<sub>3</sub>W<sub>7</sub> oxide, which exceeded the reaction rate of ion-exchange resins, zeolites, and nonmesoporous metal oxides.

In this study, mesoporous Ta–W mixed oxides with different Ta and W concentrations were examined as novel solid acid catalysts. Our previous study demonstrated that isomorphous replacement of Nb5+ with higher-valence W<sup>6+</sup> cations formed strong Brønsted acid sites in W-enriched samples, resulting in a highly active mesoporous solid acid.<sup>7</sup>

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#### Article

Therefore, the mesoporous Ta-W mixed oxide was tested in an attempt to obtain a solid acid more effective than nonmesoporous  $Ta_2O_5$ -WO<sub>3</sub> oxide and HTaWO<sub>6</sub> nanosheet aggregate, which is a two-dimensional crystalline oxide obtained from exfoliation of cation-exchangeable layered oxide.<sup>8</sup> The acid properties of mesoporous Ta-W oxides were evaluated by NH<sub>3</sub> temperature-programmed desorption (NH<sub>3</sub>-TPD), coloration using Hammett indicators, and Fourier transform infrared (FT-IR) spectroscopy. The acid catalytic activities of mesoporous Ta-W oxides with different Ta-W concentrations were examined during liquidphase Friedel-Crafts alkylation of anisole and hydrolysis of disaccharides, and the results are compared with those of conventional solid acids.

### 2. Experimental Section

**2.1. Preparation of Mesoporous Metal Oxides.** Mesoporous  $Ta_x W_{10-x}$  and Ta oxides were prepared from tantalum pentachloride (TaCl<sub>5</sub>) (99.99%, Kojundo Chemical Laboratory Co., Ltd.) and tungsten hexachloride (WCl<sub>6</sub>) (99.99%, Kojundo Chemical Laboratory Co., Ltd.). Poly block copolymer surfactant Pluronic P-123 {[HO(CH<sub>2</sub>CH<sub>2</sub>O)<sub>20</sub>-[CH<sub>2</sub>CH(CH<sub>3</sub>)O]<sub>70</sub>-(CH<sub>2</sub>CH<sub>2</sub>O)<sub>20</sub>H (Aldrich)} was used as a structure-directing agent (SDA). We synthesized mesoporous  $Ta_x W_{10-x}$  oxide by dissolving 1 g of P-123 in 10 g of dehydrated 1-propanol and adding TaCl<sub>5</sub> and WCl<sub>6</sub> (total of 6 mmol of metal chloride) for mesoporous  $Ta_x W_{10-x}$  and 7 mmol of TaCl<sub>5</sub> for mesoporous Ta oxide with vigorous stirring. Water (30 mmol) was added to the solution with further stirring. The resulting sol was gelled in a Petri dish at 313 K for 10–14 days. The aged gel samples were then treated at 773 K for 5 h in static air to remove the SDA.

**2.2.** Characterization. Samples were characterized by  $N_2$  desorption (BEL Japan, BELSORP-miniII), X-ray diffraction (XRD) (RINT-UltimaIII, Rigaku), and scanning electron microscopy (SEM) (S-4700, Hitachi). The Brunauer-Emmett-Teller (BET) surface area was 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 branches of the isotherms using the Barrett-Joyner-Halenda (BJH) method and the small-angle powder X-ray diffraction pattern.

The acid properties of the samples were determined by NH<sub>3</sub>-TPD (acid strength and concentration of sites) using a TPD-1-AT instrument (BEL Japan) equipped with a quadrupole mass spectrometer, Hammett indicators (acid strength), and FT-IR (acid type, Brønsted and Lewis acid) spectroscopy (Jasco, FT/ IR-6200). For TPD measurement, a 20 mg sample was heated at 423 K for 1 h under a helium flow, exposed to NH<sub>3</sub> at 373 K for adsorption, and finally heated at a rate of 2 K/min. For coloration using Hammett indicators, a 0.1 g sample was heated at 423 K for 1 h under a helium flow and then introduced in a 3 mL dehydrated benzene solution under stirring. Finally, 0.5 mL of a benzene solution with Hammett indicators (1%), including dicinnnamalacetone, chalcone, anthraquinone, 4-nitrotoluene, and 2,4-dinitrotoluene, was added to observe the coloration. For IR spectroscopic measurements, the samples were evacuated in a conventional gas circulation system at 423 K for 1 h, and then pyridine was introduced into the system to be adsorbed on the acid sites for the study of the acid properties.

**2.3. Acid-Catalyzed Reactions.** For Friedel-Crafts alkylation, the reaction was performed using 0.2 g of catalyst,



**Figure 1.** (A) Low and (B) wide-angle powder XRD patterns for mesoporous (a) Ta, (b)  $Ta_9W_1$ , (c)  $Ta_8W_2$ , (d)  $Ta_7W_3$ , (e)  $Ta_6W_4$ , (f)  $Ta_5W_5$ , (g)  $Ta_4W_6$ , (h)  $Ta_3W_7$ , and (i)  $Ta_2W_8$  oxides and nonmesoporous (j)  $Ta_1W_9$ and (k) W oxides.

100 mmol of anisole, and 10 mmol of benzyl alcohol in an oil bath at 373 K for 1 h. The products (*o*-benzylanisole, *p*-benzylanisole, and dibenzyl ether) were analyzed by flame ionization gas chromatography (GC-2014, Shimadzu), using a capillary column (J&W Scientific, DB-FFAP, length of 30 m, inside diameter of 0.25 mm, and film of 0.25  $\mu$ m).

For hydrolysis, the reaction was performed using 0.1 g of catalyst, 0.5 g of sucrose (1.46 mmol) or cellobiose, and water (10 or 5 mL, respectively) in an oil bath at 353 or 373 K, respectively, for 3 h. The rates of glucose production (millimoles per gram per hour) were obtained from the yields (percent) of glucose obtained after 1 h reactions. The products (glucose and fructose) were analyzed by high-performance liquid chromatography (HPLC) (LC-2000 plus, Jasco) using a Shodex Asahipak NH2P-50 column. A Bio-Rad Aminex HPX-87H column was also used for analysis of 5-hydroxymethylfurfural, levulinic acid, and formic acid.

The activities of niobic acid (Nb<sub>2</sub>O<sub>5</sub>·*n*H<sub>2</sub>O), Ta<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>, ion-exchange resins (Amberlyst-15 and Nafion NR50), and H-type zeolites [H-Beta, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 25; JRC-Z-HB25 and H-ZSM5, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 90; JRC-Z-5-90H supplied by the Catalysis Society of Japan (Japan Reference Catalyst)] were used for comparison. Ta<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub> was prepared as follows. Ta<sub>2</sub>O<sub>5</sub> and (NH<sub>4</sub>)<sub>10</sub>W<sub>12</sub>O<sub>41</sub>·5H<sub>2</sub>O were dissolved in an oxalic acid solution and distilled water, respectively, at 353 K. The solutions were then mixed and stirred vigorously at 353 K. After drying, the obtained materials were calcined at 773 K for 3 h to yield Ta-W mixed oxides. The TOF (inverse hours) was calculated from the rate of production (millimoles per gram per hour) and acid site concentration (millimoles per gram) obtained by NH<sub>3</sub>-TPD.

#### 3. Results and Discussion

**3.1.** Structure of Mesoporous  $Ta_x W_{10-x}$  Metal Oxides. The presence of a mesoporous structure was evaluated from XRD patterns (Figure 1), SEM images (Figure 2), and N<sub>2</sub> sorption isotherms (Figure 3). The small-angle XRD patterns (Figure 1) contained peaks attributable to mesopores for  $Ta_x W_{10-x}$  oxides with x values from 3 to 10. The small-angle XRD peaks for W-enriched samples (x = 3-7) were broader than those of Ta-concentrated samples (x = 8-10), indicating the formation of more randomly sized mesopores. Wide-angle powder XRD patterns revealed the presence of an amorphous structure in

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Figure 2. SEM images of mesoporous (a) Ta, (b) Ta<sub>7</sub>W<sub>3</sub>, (c) Ta<sub>5</sub>W<sub>5</sub>, and (d) Ta<sub>3</sub>W<sub>7</sub> oxides and (e) nonmesoporous W oxides.



Figure 3.  $N_2$  sorption isotherms of (a) Ta, (b) Ta<sub>9</sub>W<sub>1</sub>, (c) Ta<sub>8</sub>W<sub>2</sub>, (d) Ta<sub>7</sub>W<sub>3</sub>, (e) Ta<sub>6</sub>W<sub>4</sub>, (f) Ta<sub>5</sub>W<sub>5</sub>, (g) Ta<sub>4</sub>W<sub>6</sub>, (h) Ta<sub>3</sub>W<sub>7</sub>, and (i) Ta<sub>2</sub>W<sub>8</sub> oxides and nonmesoporous (j) Ta<sub>1</sub>W<sub>9</sub> and (k) W oxides.

samples for which x = 3-10, and crystallized tungsten oxide (WO<sub>3</sub>) in W-rich samples (x = 0-2). SEM images of the prepared porous oxides are shown in Figure 2. Mesoporous Ta, Ta<sub>7</sub>W<sub>3</sub>, Ta<sub>5</sub>W<sub>5</sub>, and Ta<sub>3</sub>W<sub>7</sub> oxides had wormholetype mesopores, but no mesoporous structure was observed in the W oxides, supporting the XRD results. N<sub>2</sub> sorption isotherms (Figure 3) indicated the presence of mesoporous structures in samples for which x = 3-10. These exhibited a typical type IV pattern with an H1-type hysteresis loop at high relative pressures for mesopores with high Ta (x =8-10) concentrations. In W-enriched samples (x = 3-7), hysteresis loops similar to the H2 type were observed, confirming the XRD and SEM results.

Characterization of the mesopores was conducted by both Brunauer–Emmett–Teller (BET) (surface area estimation) and Barrett–Joyner–Halenda (BJH) (pore size distributions) methods. Figure 4 shows the variation in surface area and pore volume versus W concentration. The BET surface area decreased gradually from 196 (mesoporous Ta oxide) to 52 m<sup>2</sup>/g (nonmesoporous W oxide) with increasing W content, up to x = 0, due to the formation of crystallized W oxide in the W-rich samples. Aggregation and crystallization resulted in the destruction of the original mesoporous structure and the development of larger pores (between 4.8 and 21.5 nm) for W-rich  $Ta_x W_{10-x}$  oxides (x = 0-2) due to interparticle voids. The addition of the transition metal Ta to the W oxide should have improved the thermal stability of the material in the amorphous phase by elevating the crystallization temperature beyond that required for complete removal of the mesoporous template.9 The pore volume obtained by BJH decreased up to x = 3, and then the pore volumes increased in the nonmesoporous W-rich oxides (x = 0-2) due to the formation of void spaces between particles, which can be observed in the SEM image of nonporous W oxide (Figure 3). The BJH pore size distributions of samples with different concentrations are presented in Figure 5, and the corresponding structural properties obtained from N<sub>2</sub> sorption isotherms and XRD patterns are summarized in Table 1. The BJH pore size distributions indicate the formation of mesopores in

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Figure 4. BET surface areas (square meters per gram) and mesopore volumes (microliters per gram) of mesoporous  $Ta_x W_{10-x}$  oxides.



**Figure 5.** Pore size distributions of mesoporous (a) Ta, (b)  $Ta_7W_3$ , (c)  $Ta_5W_5$ , and (d)  $Ta_3W_7$  oxides and (e) nonmesoporous  $Ta_1W_9$  oxide.

Table 1. Structural Properties of Mesoporous  $Ta_xW_{10-x}$  Oxides

mesoporous $Ta_x W_{10-x}$ oxides	$S_{\rm BET} \over ({ m m}^2/{ m g})$	pore size (nm)	pore volume (mL/g)	D(100) (nm)
TaoW10	52	21.5	0.20	_
$Ta_1W_9$	68	8	0.16	_
$Ta_2W_8$	89	4.8	0.14	_
$Ta_3W_7$	110	4.2	0.12	7.2
$Ta_4W_6$	120	3.7	0.12	7.4
$Ta_5W_5$	128	3.7	0.12	7.1
$Ta_6W_4$	142	3.7	0.13	6.5
$Ta_7W_3$	152	3.7	0.15	6.4
$Ta_8W_2$	168	3.7	0.19	6.3
$Ta_9W_1$	179	3.7	0.19	6.0
$Ta_{10}W_0$	196	3.7	0.20	5.7

 $Ta_x W_{10-x}$  oxides with x values from 3 to 10 and exhibited decreased levels of mesopore formation in W-enriched samples. The BJH pore size distribution peaks also showed a small increase in the W-enriched samples.

**3.2.** Characterization of Acid Sites. The acid properties of mesoporous  $Ta_xW_{10-x}$  oxides (x = 3, 5, 7, and 10) were evaluated by NH<sub>3</sub> temperature-programmed desorption (NH<sub>3</sub>-TPD) and Fourier transform infrared (FT-IR) spectroscopic measurements of adsorbed pyridine. The NH<sub>3</sub>-TPD profiles for mesoporous  $Ta_xW_{10-x}$  (x = 3-10) exhibited a broad main peak at 495–520 K and a shoulder peak above 560 K (Figure 6). The order of acid strength of the mesoporous  $Ta_xW_{10-x}$  oxides (x = 3-10) increased with an increasing W oxide concentration. The shoulder peak was observed at 520 K for mesoporous Ta oxide, at 560 K for mesoporous  $Ta_5W_5$  oxide, and at 575 K for mesoporous  $Ta_3W_7$  oxide. The acid concentrations, both Brønsted



**Figure 6.** NH<sub>3</sub>-TPD (m/e 16, 2 K/min) curves for mesoporous (a) Ta, (b) Ta<sub>7</sub>W<sub>3</sub>, (c) Ta<sub>5</sub>W<sub>5</sub>, and (d) Ta<sub>3</sub>W<sub>7</sub> oxides.

and Lewis acid sites together, obtained from NH<sub>3</sub>-TPD were 0.20 (mesoporous Ta<sub>3</sub>W<sub>7</sub> oxide), 0.21 (mesoporous  $Ta_5W_5$  oxide), 0.23 (mesoporous  $Ta_7W_3$  oxide), and 0.12 mmol/g (mesoporous Ta oxide). The acid strength was also evaluated by Hammett indicators. The coloration obtained with each indicator reagent is summarized in Table 2. For mesoporous Ta oxide, a yellow color developed in chalcone ( $pK_a = -5.6$ ) could be observed, indicating that the acidity of the sample corresponds to  $\geq$  71% sulfuric acid. The addition of W to the mesoporous Ta oxide increased the  $pK_a$  value, yielding acidic coloration of anthraquinone for mesoporous Ta7W3 oxide  $(pK_a = -8.2)$  and of 4-nitrotoluene for mesoporous Ta<sub>5</sub>W<sub>5</sub> oxide. The coloration could not be clearly observed for mesoporous Ta<sub>3</sub>W<sub>7</sub> oxide because of the dark green coloration of the catalyst. The ranking of catalyst acidity increased with addition of W, reaffirming the acid strength order obtained from NH<sub>3</sub>-TPD.

We evaluated the acid properties of mesoporous  $Ta_xW_{10-x}$  oxides (x = 3, 5, 7, and 10) also by probing the vibrational spectra of adsorbed pyridine using IR spectroscopic measurements, as shown in Figure 7. For comparison, nonporous  $Ta_2O_5$ – $WO_3$  (1:1 Ta:W ratio) was also included. Both mesoporous  $Ta_xW_{10-x}$  oxide and nonporous  $Ta_5W_5$  oxide were confirmed to possess the Lewis (LAS) acid site at 1435 cm<sup>-1</sup> and the Brønsted (BAS) acid site at 1532 (BAS) cm<sup>-1</sup>. The W-containing samples had both Brønsted acid sites and Lewis acid sites, whereas the Ta oxide sample had a negligible number of Brønsted acid sites. The IR spectroscopic measurements indicated that the peak intensity of the bond at  $1532 \text{ cm}^{-1}$ , attributed to pyridinium ions formed on Brønsted acid sites,  $^{10,11}$  was enhanced with an increase in W content. The IR spectroscopic

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Table 2. Coloration by Color Indicator Reagents for Mesoporous  $Ta_x W_{10-x}$  Oxides

			coloration	
indicator reagent	pK <sub>a</sub>	Та	$Ta_7W_3$	Ta <sub>5</sub> W <sub>5</sub>
dicinnamalacetone	-3.0	+	+	+
chalcone	-5.6	+	+	+
anthraquinone	-8.2	_	+	+
4-nitrotoluene	-11.4	_	_	+
2,4-dinitrotoluene	-12.8	_	_	_

measurement peak observed in nonporous  $Ta_2O_5-WO_3$ oxide was very similar to that of mesoporous  $Ta_5W_5$  oxide, indicating that the acid sites formed in both mesoporous and nonporous  $Ta_5W_5$  are similar, with differences only in the formation of mesoporous structure. The increase in the number of Brønsted acid sites corresponded to the increasing number of desorption peaks observed in W-enriched mesoporous  $Ta_xW_{10-x}$  oxides by NH<sub>3</sub>-TPD.

3.3. Acid-Catalyzed Reactions. The acid-catalyzed reactions were first tested on mesoporous  $Ta_x W_{10-x}$  oxides using liquid-phase Friedel-Crafts alkylation of anisole with benzyl alcohol, and hydrolysis of sucrose (a disaccharide composed of glucose and fructose) in water. A plot of the product yield for different Ta and W contents in the Friedel-Crafts alkylation of anisole and the hydrolysis of sucrose, reacted for 1 h at 373 and 353 K, respectively, is shown in Figure 8. Variation of the Ta and W contents resulted in remarkably different reaction rates of benzylanisole formation in alkylation and hydrolysis. The reaction rates increased gradually with an increase in W content, starting from 0% yield for mesoporous Ta oxide and reaching the highest alkylation yield (59% of benzylanisole) for mesoporous Ta<sub>3</sub>W<sub>7</sub> oxide. The yield decreased drastically for nonmesoporous oxide samples with x values from 2 to 0, reaching 0% for W oxide. A similar curve was plotted for the hydrolysis of sucrose, where the highest yield (24%) was obtained for mesoporous Ta<sub>3</sub>W<sub>7</sub> oxide. These results demonstrate the importance of the mesoporous structure to the reaction and indicate drastic changes in the nature of the acid sites. The reaction yield increased for W-enriched mesoporous  $Ta_x W_{10-x}$  oxide samples, consistent with the acid strength determined by NH<sub>3</sub>-TPD, with Hammett indicators, and with the increase in the number of Brønsted acid sites, which promotes the reaction,<sup>12</sup> observed by IR spectroscopic measurements.

The acid catalytic activities of mesoporous Ta–W oxides for Friedel–Crafts alkylation were also compared to those of conventional solid acids. The acid concentration and surface area of the tested solid acids and the results of the Friedel–Crafts alkylation of anisole are summarized in Table 3. Nonmesoporous  $Ta_2O_5$ –WO<sub>3</sub> and HTaWO<sub>6</sub> nanosheet aggregates, obtained by exfoliation of layered HTaWO<sub>6</sub>,<sup>8</sup> were also used for comparison. Mesoporous  $Ta_3W_7$  oxide also exhibited the best performance in this Friedel–Crafts alkylation reaction, producing the highest yield and turnover frequency (147 h<sup>-1</sup>).



**Figure 7.** FT-IR spectra for pyridine-adsorbed mesoporous (a) Ta, (b)  $Ta_7W_3$ , (c)  $Ta_5W_5$ , and (d)  $Ta_3W_7$  oxides and (e) nonmesoporous  $Ta_5W_5$  oxide (B for the Brønsted acid site; L for the Lewis acid site). Assignments: 1532 cm<sup>-1</sup> (Brønsted acid site) and 1435 cm<sup>-1</sup> (Lewis acid site).



**Figure 8.** (a) Friedel–Crafts alkylation of anisole and (b) hydrolysis of sucrose over mesoporous  $Ta_x W_{10-x}$  oxides. Reaction conditions: anisole (100 mmol), benzyl alcohol (10 mmol), and catalyst (0.2 g) at 373 K for 1 h or sucrose (0.5 g, 1.46 mmol), H<sub>2</sub>O (10 mL, 556 mmol), and catalyst (0.1 g) at 353 K for 1 h.

Mesoporous Ta<sub>5</sub>W<sub>5</sub> oxide also exhibited a turnover frequency (53  $h^{-1}$ ) higher than those of bulk Ta<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub> oxide (47  $h^{-1}$ ) and HTaWO<sub>6</sub> nanosheets (28  $h^{-1}$ ), indicating that the mesoporous structure enhanced the reaction rate of the accessible acid sites. After the reaction, o-benzylanisole, p-benzylanisole, and dibenzyl ether were formed. The selectivity of o-benzylanisole via *p*-benzylanisole observed for mesoporous  $Nb_xW_{10-x}$  oxides for Friedel-Crafts alkylation gradually increased with an increase in W content (36.9, 39.8, and 42.2% for mesoporous Ta<sub>7</sub>W<sub>3</sub>, Ta<sub>5</sub>W<sub>5</sub>, and Ta<sub>3</sub>W<sub>7</sub> oxides, respectively). The same selectivity of *o*-benzylanisole was observed for bulk Ta<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub> (Ta<sub>5</sub>W<sub>5</sub>) oxide (39.3%). The variation of selectivity was probably not caused by the mesoporous structure, but by variations of the acid properties (Brønsted acid and Lewis acid sites) due to changing Ta and W concentrations.<sup>7</sup> The selectivity for dibenzyl ether, a byproduct of benzyl alcohol, was 20, 17, and 15% for mesoporous Ta7W3, Ta5W5, and Ta3W7 oxides, respectively. These results are consistent with the IR spectroscopic measurements, which increase as the Brønsted acid site at 1532 cm<sup>-1</sup> promotes a decrease in the selectivity of dibenzyl ether, a byproduct formed by

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Table 3. Friedel-Crafts Alk	vlation of Anisole over S	Several Solid Acid C	atalysts

			alkylation of anisole <sup>a</sup>			
catalyst	$S_{\rm BET}~({\rm m^2/g})$	acid site concentration (mmol/g)	yield (%)	TOF $(h^{-1})^b$	selectivity of <i>o</i> -benzylanisole (%) <sup><i>c</i></sup>	
mesoporous Ta <sub>3</sub> W <sub>7</sub>	110	$0.20^e$	58.6	168	42.2	
mesoporous Ta <sub>5</sub> W <sub>5</sub>	128	$0.21^{e}$	22.1	70	39.8	
mesoporous Ta <sub>7</sub> W <sub>3</sub>	152	$0.23^{e}$	9.3	21	36.9	
mesoporous Ta	196	$0.12^{e}$	not detected	not detected	not detected	
bulk Ta <sub>5</sub> W <sub>5</sub>	38	$0.11^{e}$	10.4	62	39.3	
HTaWO <sub>6</sub> nanosheets	47	$0.48^{e}$	27.0	29	33.1	
H-Beta <sup>d</sup>	420	$1.0^{f}$	30.6	19	42.1	
Amberlyst-15	50	$4.8^{f}$	42.1	9	45.0	
Nafion NR50	0.02	$0.9^{f}$	42.3	27	49.2	

<sup>*a*</sup> Reaction conditions: anisole (100 mmol), benzyl alcohol (10 mmol), and catalyst (0.2 g) at 373 K for 1 h. <sup>*b*</sup> Calculated from the rate of produced benzylanisole (30 min) and acid site concentration. <sup>*c*</sup> Selectivity (%) = (*o*-benzylanisole)/(*o*-benzylanisole + *p*-benzylanisole) × 100. <sup>*d*</sup> SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 25, JRC-Z-HB25. <sup>*e*</sup> Determined by NH<sub>3</sub>-TPD. <sup>*f*</sup> From ref 17.

		hydrolysis of sucrose <sup>a</sup>		hydrolysis of cellobiose <sup>b</sup>	
catalyst	acid site concentration (mmol/g)	rate of glucose production $(\text{mmol g}^{-1} \text{ h}^{-1})$	TOF $(h^{-1})^f$	rate of glucose production (mmol $g^{-1} h^{-1}$ )	$TOF(h^{-1})^f$
mesoporous Ta <sub>3</sub> W <sub>7</sub>	$0.20^{d}$	7.0	35.0	0.15	0.75
mesoporous Ta <sub>5</sub> W <sub>5</sub>	$0.21^{d}$	5.6	26.7	0.11	0.52
mesoporous Ta <sub>7</sub> W <sub>3</sub>	$0.23^{d}$	2.7	11.7	0.04	0.17
bulk Ta <sub>5</sub> W <sub>5</sub>	$0.11^{d}$	1.2	10.9	0.01	0.09
HTaWO <sub>6</sub> nanosheets	$0.48^{d}$	5.2	10.8	0.09	0.19
Nb <sub>2</sub> O <sub>5</sub> · <i>n</i> H <sub>2</sub> O	$0.4^e$	0.3	0.6	0	0
H-ZSM5 <sup>c</sup>	$0.2^e$	0.1	0.7	0	0
Amberlyst-15	$4.8^e$	6.1	1.4	0.51	0.11
Nafion SAC 13	$0.1^{e}$	1.2	8.5	0.03	0.34
Nafion NR50	$0.9^{e}$	2.0	2.4	0.44	0.48
$H_2SO_4$	20.4	45.6	2.2	6.73	0.33

<sup>*a*</sup> Reaction conditions: sucrose (0.5 g, 1.46 mmol), H<sub>2</sub>O (10 mL, 556 mmol), and catalyst (0.1 g) at 353 K. <sup>*b*</sup> Reaction conditions: cellobiose (0.5 g, 1.46 mmol), water (5 mL, 278 mmol), and catalyst (0.1 g) at 373 K. <sup>*c*</sup> SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 90, JRC-Z-5-90H. <sup>*d*</sup> Determined by NH<sub>3</sub>-TPD. <sup>*e*</sup> From ref 17. <sup>*f*</sup> Calculated from the rate of glucose production and acid site concentration.

the Lewis acids. However, dibenzyl ether is also a good alkylating agent, and its concentration decreased as it was consumed, along with the benzyl alcohol, at the end of the alkylation reaction.

Mesoporous  $Ta_x W_{10-x}$  oxides were also tested for hydrolysis of disaccharides (sucrose and cellobiose). The hydrolysis of saccharides requires sufficient acid strength and water-tolerant acid sites and is an important class of reaction, used to convert biomass into sugars, important raw materials for obtaining bioethanol and other useful chemicals with minimal environmental impact.<sup>13,14</sup> The rate of glucose production and turnover frequency (TOF) for hydrolysis of sucrose and cellobiose over several solid acid catalysts are listed in Table 4. Ion-exchange resins like Amberlyst-15<sup>13e</sup> are powerful catalysts for the hydrolysis of saccharides because of the strong sulfonic acid sites, and niobic acid is a unique solid acid with water-tolerant acid sites.<sup>15,16</sup> The activity of mesoporous Ta<sub>3</sub>W<sub>7</sub> oxide, however, substantially exceeded the performance of all other materials tested, achieving a glucose formation rate of 7.0 mmol  $g^{-1} h^{-1}$ for sucrose hydrolysis. This reaction rate was significantly higher than that of niobic acid or H-ZSM5, and 3 times that of Nafion NR50. Moreover, the turnover frequency of mesoporous Ta<sub>3</sub>W<sub>7</sub> oxide was more than 15 times that of Nafion NR50 and Amberlyst-15. Mesoporous Ta<sub>5</sub>W<sub>5</sub> oxide also exhibited a reaction rate and turnover frequency more than 3 times greater than that of bulk  $Ta_2O_5$ -WO<sub>3</sub> oxide; this considerable difference between mesopore and bulk Ta<sub>5</sub>W<sub>5</sub> cannot be explained in the view of acid properties, once they were very similar at IR spectroscopic measurements. This increase in the TOF indicates that the mesoporous structure enhanced the reaction rate at the accessible acid sites of mesoporous Ta<sub>5</sub>W<sub>5</sub> oxide. The high surface area should have helped in the usage of acid sites by optimization of the contacts between acid sites and reactants. The low acid site density helps in the effective usage of all acid sites and would

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prevent the formation of polymerization of reactants. Cellobiose is the subunit of cellulose composed of  $\beta$ -1,4glycosidic bonds, which are much more stable than the  $\alpha$ -1,2-glycosidic bonds comprising sucrose and are thus more resistant to hydrolysis.<sup>13</sup> Accordingly, the rate of production of glucose from the hydrolysis of cellobiose was much lower than that of sucrose over all of the acid catalysts tested, because of the  $\beta$ -1,4-glycosidic bonds. Nevertheless, mesoporous Ta<sub>3</sub>W<sub>7</sub> oxide exhibited the highest TOF (0.75  $h^{-1}$ ) of glucose production among the solid acids tested, including ion-exchange resins, niobic acid, and zeolites, and achieved twice the turnover frequency of sulfuric acid. The total production of glucose for mesoporous Ta<sub>3</sub> $W_7$  oxide for the 3 h reaction was estimated to be 0.4 mmol, corresponding to a turnover number of 2.0. We have confirmed that no product was observed by decomposition of glucose or fructose, including 5-(hydroxymethyl)furfural (HMF), levulinic acid, and formic acid for all samples after the 3 h hydrolysis reaction of sucrose and cellobiose, which is determined by using a Bio-Rad Aminex HPX-87H column for HPLC.

The very high level of catalytic performance of mesoporous  $Ta_3W_7$  oxide was due to a high-surface area mesoporous structure and the formation of strong Brønsted acid sites by the isomorphous replacement of  $Ta^{5+}$  by higher-valence  $W^{6+}$  cations in these W-enriched samples like that observed at WO<sub>3</sub>/ZrO<sub>2</sub>.<sup>18</sup> It is reported that replacement of ZrO<sub>2</sub> with WO<sub>3</sub> forms acids sites similar to that of  $SO_4/ZrO_2^{-18}$  with strong acid sites. The highest activity of WO<sub>3</sub>/ZrO<sub>2</sub> has been obtained over a range of surface tungsten densities, which maximizes the quantity of amorphous surface polytungstate species relative to isolated surface  $WO_x$  and crystallized  $WO_3$ .<sup>19</sup> Similar to WO<sub>3</sub>/ZrO<sub>2</sub>, formation of strong Brønsted acid sites could be observed in IR spectroscopic measurement results of mesoporous  $Ta_x W_{10-x}$  oxides. The Brønsted acid sites could have formed which led to the high surface tungsten densities in the tantalum matrix with no crystallized WO<sub>3</sub>. Higher concentrations of W oxide deformed the mesoporous structure, forming the crystallized WO<sub>3</sub> and decreasing the reaction rate.

#### 4. Conclusion

Wormhole-type mesoporous  $Ta_x W_{10-x}$  oxides were found to function as highly active mixed metal oxide solid acid catalysts for Friedel-Crafts alkylation and hydrolysis, exceeding the reaction rate of nonporous  $Ta_2O_5-WO_3$ oxide and HTaWO<sub>6</sub> nanosheets. The formation of crystallized WO<sub>3</sub> was observed in W-rich samples (x = 0-2), which formed a nonmesoporous structure with a low reaction activity. The reaction rate and acid strength increased gradually with the addition of W, reaching the highest reaction rate with mesoporous Ta<sub>3</sub>W<sub>7</sub> oxide, which exceeded the TOF of ion-exchange resins, zeolites, and nonmesoporous metal oxides. The very high level of catalytic performance of mesoporous Ta<sub>3</sub>W<sub>7</sub> oxide was due to a high-surface area mesoporous structure and the formation of strong Brønsted acid sites.

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