



## Microwave-assisted hydrolysis of polysaccharides over polyoxometalate clusters



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### HIGHLIGHTS

- Phosphotungstic acid effectively hydrolyzed starch and cellulose during microwaving.
- Clusters of phosphotungstic acid were stable and recyclable after hydrolysis.
- The dielectric property of phosphotungstic acid could conserve microwave energy.

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### ABSTRACT

Polyoxometalate (POM) clusters were utilized as recyclable acid catalysts and microwave-absorbing agents for the microwave-assisted hydrolysis of corn starch and crystalline cellulose. Phosphotungstic (PW) and silicotungstic (SiW) acids showed high hydrolyzing activity, while phosphomolybdic acid (PMo) showed lower glucose stability. The PW catalyst could be recycled by ether extraction at least 4 times without changing its catalytic activity. The addition of PW could reduce the energy demand required for running the hydrolysis by 17–23%. The dielectric property of the aqueous PW solution was important for increasing the microwave-absorption capability of the reaction system and reducing the energy consumption.

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### 1. Introduction

Biorefinery is a key technology for the reduction of carbon dioxide emissions and the establishment of sustainable industries and a recycling-based society. As a biorefinery technology, microwave-assisted hydrolysis can provide fast energy transfer into recalcitrant biomass and can encourage catalytic activity as a result of its direct and internal heating properties (Tsubaki and Azuma, 2011). A microwave is an electromagnetic wave with a frequency between 300 MHz and 300 GHz. Microwave has been utilized in radar and telecommunication as well for heating ovens in domestic kitchens. Irradiation with microwaves induces the dipole rotation of water molecules to follow the change in the electric field, and the delay in molecular motion is converted to heat. The unique

heating properties of microwave have been effectively applied to organic and inorganic chemical reactions (Kappe, 2008). Microwave irradiation is also applicable to the pretreatment of lignocellulosic material (Azuma et al., 1984), the extraction of useful chemicals from waste biomass (Tsubaki et al., 2008; Yoshida et al., 2010), the solvent-free hydrodistillation of essential oils (Lucchesi et al., 2004), the extraction of oil from microalgae (Balasubramanian et al., 2011) and the pyrolysis of lignocellulosic materials (Salema and Ani, 2012).

Additionally, electrolytic and ferromagnetic materials significantly absorb microwave energy. Halide ions absorb microwave energy and also act to accelerate biomass hydrolysis (Li et al., 2001; Xing et al., 2005; Tsubaki et al., 2010). The addition of an electrolyte also decreases the energy demand for the hydrothermal hydrolysis of cellobiose by 33–41% (Tsubaki et al., 2012). Catalysts such as NaOH and peroxomolybdate were reported to be microwave sensitizers in addition to their catalytic activity (Muley and Boldor, 2013; Verma et al. 2011). Activated carbon also performs

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as a microwave absorber for the hydrothermal hydrolysis of polysaccharides (Matsumoto et al., 2011).

In this study, we have employed polyoxometalate (POM) clusters as acid catalysts as well as microwave-absorbing electrolytes. POMs are high-molecular-weight metallic clusters, which typically have a Keggin-type structure ( $[XM_{12}O_{40}]^-$ ) consisting of hetero atoms (X) of P or Si, addenda atoms (M) of Mo or W and oxygen atoms (terminal, edge-bridging and corner-bridging) (Kozhevnikov, 1999). POMs have an advantage in their very strong Brønsted acidity and oxidative activity with fairly high thermal stability and recyclability. The hydrolytic activities of POMs were previously investigated for crystalline cellulose, and the results demonstrated the high catalytic activities and environmental friendliness of homogeneous POMs (Tian et al., 2010), micellar POMs (Cheng et al., 2011), cesium salt (Tian et al., 2011) and metal salts (Shimizu et al., 2009).

In this study, we have characterized the catalytic activities of POMs on the hydrolysis of corn starch and crystalline celluloses under the application of an electromagnetic field with emphasis on the microwave-absorbing properties of POMs.

## 2. Methods

### 2.1. Materials

Corn starch, Avicel cellulose, cotton linter and fibrous  $\alpha$ -cellulose were purchased from Wako Pure Chemical Industries, Ltd., Merck KGaA; Sigma–Aldrich Co., LLC and Nakarai Tesque, Inc., respectively. Samples of Avicel cellulose with different crystallinities were prepared by ball milling with zirconia balls for 2–24 h. The native and ball-milled crystalline-cellulose powders were analyzed by wide-angle X-ray diffraction (Rigaku Ultima IV diffractometer) operating at 40 kV and 20 mA using  $CuK\alpha$  radiation, and the crystallinity indices (C.I.) were calculated from the following equation;

$$C.I. = (I_{200} - I_{18.5^\circ}) / I_{200} \times 100 (\%)$$

where  $I_{200}$  and  $I_{18.5^\circ}$  are the reflection intensity at the 200 plane and the intensity at  $2\theta = 18.5^\circ$ , respectively. The scanning electron microscopic images of the native crystalline celluloses and the ball-milled Avicel celluloses were generated by using a VE-9800 (Keyence Co., Osaka, Japan).

Phosphotungstic acid-30H<sub>2</sub>O (PW), phosphomolybdic acid-29H<sub>2</sub>O (PMo) and silicotungstic acid-26H<sub>2</sub>O (SiW) were purchased from Wako Pure Chemical Industries, Ltd. The amount of water hydrated on the POM clusters was determined by thermogravimetric analysis using a Seiko SII TGDTA6300. The ion-exchange resins Dowex 50 W  $\times$  8 and Amberlyst TM 15 were purchased from Dow Chemical Co. and Organo Co., respectively. All other reagents used were analytical grade.

### 2.2. Microwave-heating hydrolysis

Microwave heating was performed with a START D multimode microwave oven (frequency: 2.45 GHz; maximum output: 1 kW; Milestone Inc., Shelton, CT, USA) and an HPR-100 TFM reactor (100 mL closed reactor made of Teflon). The reaction temperature was controlled by PID with a direct temperature measurement of the reactant using a thermocouple thermometer. The distributions of the microwaves and the reactant were kept homogeneous by using a diffuser, a rotation table and a stirrer bar. One gram of corn starch or crystalline cellulose was suspended in 20 mL of distilled water or an aqueous solution of POM clusters (1–15 mM) and heated with microwave irradiation in a closed system. For the corn starch, the thermal history consisted of 4 min of come-up time and

10 min of reaction time at the desired temperature, which ranged from 120 to 220 °C. For the crystalline cellulose, 8 min of come-up time and 5 min of reaction time were used. After the reaction, the reactor was immediately cooled in an ice bath (approximately 15 min). The reactants were then centrifuged to remove insoluble materials. The POM clusters in the solubilized fraction were removed after precipitation by the addition of tetra ammonium bromide. The recycling of the PW was conducted by extraction of the precipitate with diethyl ether after acidification with concentrated hydrochloric acid. The PW was obtained from the bottom layer. The extracted materials were evaporated to dryness to recover the PW, which was then dissolved in distilled water and added to new substrates. The weight loss (%) after hydrolysis was calculated by dividing the weight of the solubilized material by the initial substrate load and multiplying by 100.

### 2.3. Induction-heating hydrolysis

Induction heating was conducted by using an SSN-400 (Shikoku Rika Co., Kochi, Japan) with a hastelloy-C-lined iron autoclave (50 mL). The temperature was measured by a thermocouple thermometer placed in the autoclave and controlled by PID to follow the same thermal history as the microwave heating. The reactant was mixed by rocking the entire induction-coil unit, including the autoclave. After the reaction, the autoclave was immediately air-cooled by a fan for the same duration as the cooling performed in the microwave experiments (approximately 15 min). The initial concentrations of corn starch and crystalline cellulose as well as the volume of the PW solution were the same as those in the microwave experiments.

### 2.4. Chemical analyses

The amounts of reducing sugars and glucose were determined by the dinitrosalicylic acid (DNS) method and by the Glucose CII kit Wako based on the mutarotase-GOD method (Wako Pure Chemical Industries, Ltd., Osaka, Japan), respectively. The reducing-sugar and glucose yields were calculated as percentages of the glucose yields times 0.9 over the initial substrate load. The glucose selectivity was determined by dividing the glucose yield by the reducing-sugar yield and multiplying by 100. The yields of 5-hydroxymethyl furfural and furfural were determined by HPLC equipped with a column of Aminex HPX-87H (300  $\times$  7.8 mm, Bio-rad Laboratories, Inc., CA, USA) at 40 °C. The elution was carried out with 0.008 N sulfuric acid at a flow rate of 0.6 mL/min, and the detections were performed at 280 nm. The concentrations of tungsten after recycling the PW 1–4 times were determined by inductively coupled plasma measurements (ICP; ICPE-9000 Shimadzu Co.). <sup>31</sup>P NMR measurements were made on a JEOL Model JNM-LA400 spectrometer at 161.70 MHz. D<sub>2</sub>O contained in an inner tube was used as an instrumental lock. The chemical shifts were referenced to 85% H<sub>3</sub>PO<sub>4</sub>.

### 2.5. Measurement of microwave-absorption properties

The energy consumption was calculated from the total microwave output monitored by a power monitor equipped on the microwave oven (START D) using distilled water, 1–5 mM solutions of POM clusters and 1 g/20 mL of ion-exchange resin in suspension. The permittivity, the dielectric loss and the dissipation factor were measured by the dielectric-probe method using an Agilent Technologies HP-85070B Network Analyzer and an Agilent dielectric high-temperature probe (Agilent Technologies Inc.). The electrical conductivities of the solutions were measured with an electrical conductivity meter (ES-51, Horiba, Ltd., Kyoto, Japan).

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