

Electronic Supplementary Information for

Tantalum compound as solid acid catalyst for saccharides dehydration to 5-hydroxymethylfurfural

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1 Experimental Section

1.1 Material

HMF and fructose was purchased from Aldrich (99% purity) and Salarbio ($\geq 99\%$ purity) respectively, and glucose (99%) and 2-butanol (chemical pure reagent) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Tantalum hydroxide ($\text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O}$, TA sample) was supplied by HKXC (China).

1.2 Catalyst preparation and characterization

The catalyst (TA-p) was prepared by mixing 3 g of TA in 40 ml of 1 M H_3PO_4 and stirring at room temperature for 52 h. The mixture was aged at ambient condition for 12 h. The precipitate was washed 3 or 4 times with deionized water until the pH was neutral and dried overnight at 65 °C in dry chamber, followed by drying at 110 °C in vacuum oven for 2 h and calcining in air at 300 °C with slow heating rate for 3 h.

As catalysts characterization, the surface areas were determined by

Brunauer-Emmett-Teller (BET) isotherms of N₂ adsorption at -196 °C. The acidity-basicity properties of the catalyst was determined by temperature programmed desorption of ammonia (NH₃-TPD) and carbon dioxide (CO₂-TPD). As for NH₃-TPD, catalyst samples (~100mg) were loaded into a glass flow through cell, and ammonia was adsorbed onto the catalyst for 1.5 h at 150 °C. The samples were heated at a ramp of 10 °C /min up to 700 °C and desorbed at 150 °C. CO₂-TPD was performed similarly to NH₃-TPD with adsorption at 80 °C, and the TPD curve was recorded from 50 to 700 °C.

Thermal analysis (TG-DSC, Thermogravimetric-Differential Scanning Calorimeter) of TA and TA-p was conducted with a NETZSCH STA 449F3 thermal analyzer. The sample was placed in a crucible and heated in flowing N₂ (50ml/min) from room temperature to 800 °C at rate of 10 °C /min. FTIR spectra were recorded on a Fourier transform instrument Burker VECTOR22, using pressed disks of KBr, and pyridine-FTIR used the pure power pressed disks after outgassing at 300 °C and following contact with pyridine vapors. The X-ray diffraction (XRD) patterns of the TA-p and the TA were obtained with an X'pert (PANalytical) diffractometer operated at 40 kV and 40 mA, using Ni-filtered Cu-K α radiation.

1.3 Reaction testing

A biphasic reaction system was employed to take advantage of water being green and convenient solvent for dehydration of saccharides to HMF. HMF was prone to decompose to levulinic acid, formic acid, humin or other byproducts in the presence of water. Thus, 2-butanol was introduced to promote the dehydration reaction by

shifting the equilibrium as well as suppressing HMF hydration with H₂O by separating HMF immediately from reaction medium as it formed, thus higher yield of HMF was assumed to be obtained in this biphasic system. In this biphasic system, saccharides were dehydrated in the aqueous phase in the presence of TA-p, and 2-butanol was utilized to extract HMF immediately by stirring.

The batch catalytic assay in biphasic system was performed in a 100ml stainless steel at 160 °C. The amount of catalyst and reaction time were pre-determined. Intermediate samplings from the reaction mixture were taken. In the analysis, zero time was taken when the temperature reached 160 °C. As for the catalyst recycle experiments, TA-p was collected and washed 3-4 times with deionized water and dried in 65 °C for 12 h for the next use.

1.4 Product analysis

Reactants disappearance was performed by HPLC (esa) equipped with DIONEX CarboPac™ PA1 column at 30 °C and Coulochem □ detector, using 8:2v/v water: NaOH (0.5 M) as the mobile phase at a flow rate of 1.0 ml/min. HMF in the aqueous and organic phase was quantified by HPLC equipped with Hypersil BDS-C8 (5µm) reverse phase column and UV230 detector (320 nm). The mobile phase was 2:8v/v methanol: water at a flow rate of 0.7 ml/min. Each sample was diluted with ultra pure water before analysis. Levulinic acid was determined by ion chromatography equipped with DIONEX IonPac® AS11-HC column at 30 °C and conductivity detector, using NaOH (1 mM) as the mobile phase at a flow rate of 1.0 ml/min.

Reactants conversion and HMF yield were calculated from the product of the

aqueous and organic phase concentration obtained in the HPLC and their corresponding volumes after reaction since the value of $V_{\text{org}}/V_{\text{aq}}$ changed after reaction.

Reactant conversion (mol %), products yield (mol %) and product selectivity (%) was defined as follows:

$$\text{Conversion (mol \%)} = (\text{moles of x reacted}) / (\text{moles of x initial}) \times 100\%$$

$$\text{Yield (mol \%)} = (\text{moles of y produced}) / (\text{moles of x initial}) \times 100\%$$

$$\text{Selectivity (\%)} = (\text{moles of y produced}) / (\text{moles of x reacted}) \times 100\%$$

2. Supporting Figures

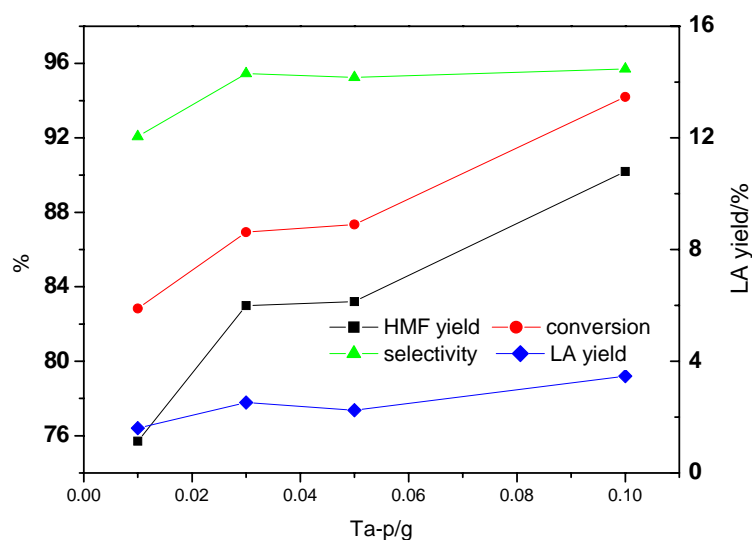


Fig. S1 Effect of catalyst dosage on fructose conversion and HMF yield and selectivity. TA-p as catalyst, 20ml of water, 30ml of 2-butanol, 160 °C, 800rpm. Yields were determined by HPLC analysis (LA: levulinic acid).

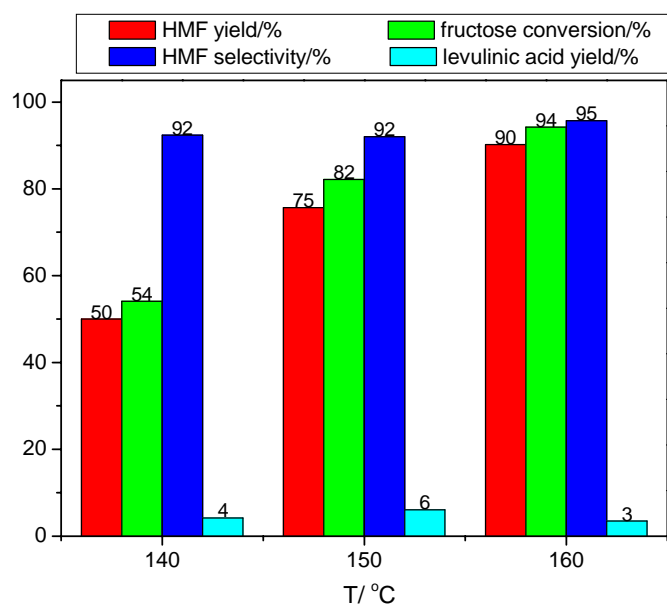


Fig. S2: Effect of temperature on the fructose conversion and HMF yield and selectivity. Reaction conditions: 1.2 g of fructose, 0.1 g TA-p, 20 ml of water, 30 ml of 2-butanol, 800 rpm. Yields were determined by HPLC analysis.

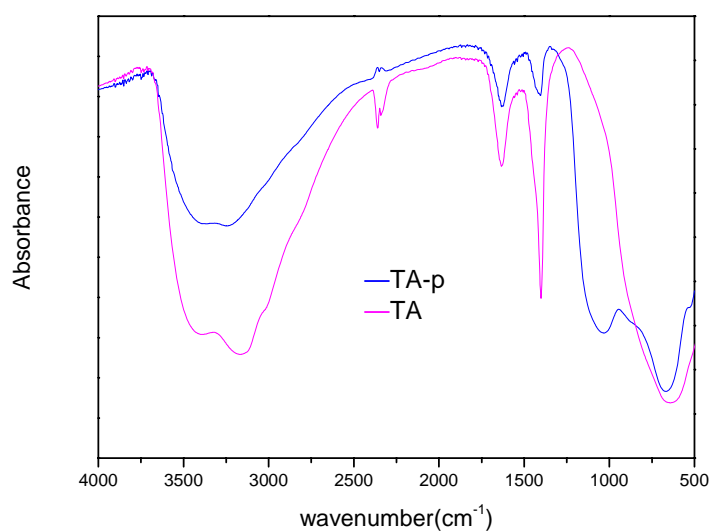


Fig. S3. FTIR spectra (KBr pressed disks) of TA and TA-p

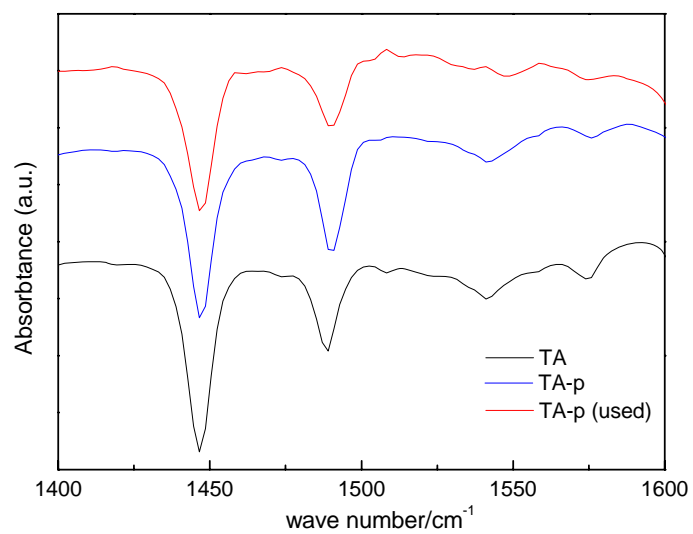


Fig. S4. Pyridine-FTIR spectra (pure power pressed disks) of TA and TA-p

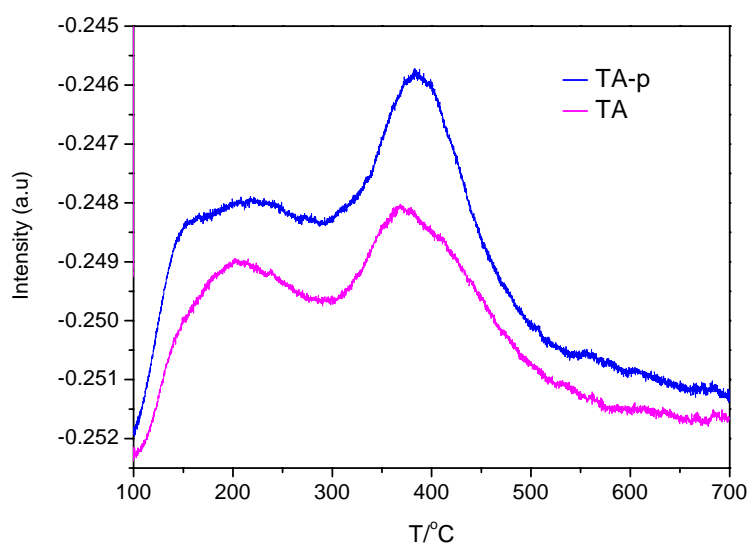


Fig. S5. NH₃-TPD profiles of samples TA-p and TA

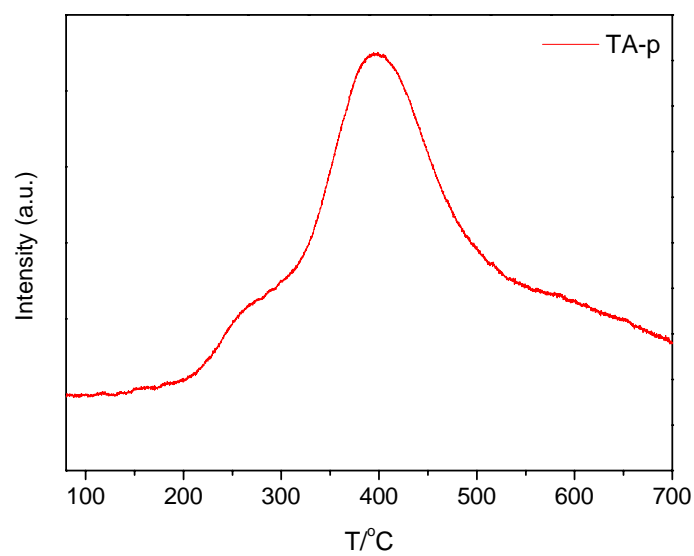


Fig. S6. CO₂-TPD profile of the TA-p catalyst.

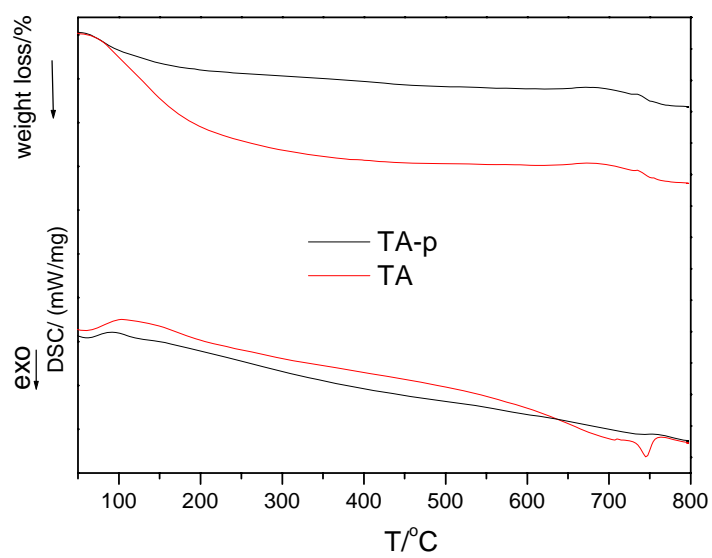


Fig. S7. TG-DSC profiles of the TA-p and TA catalyst

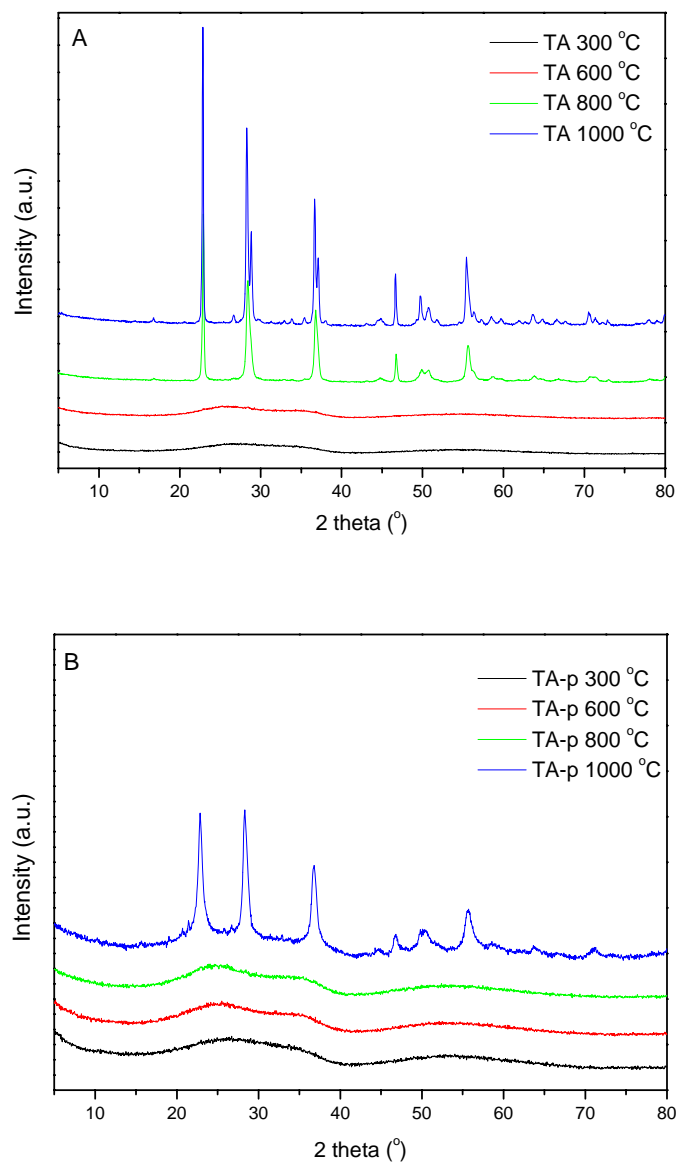


Fig. S8. X-ray diffraction patterns of the TA (A) and TA-p (B) catalyst calcinated at different temperatures