Supporting Information

Conversion of saccharides into 5-hydroxymethylfurfural and levulinic acid by WO_3-Ta_2O_5 catalyst

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Experimental Section

1.1 Material

HMF and fructose was purchased from Aldrich (99% purity) and Salarbio (≥99% purity) respectively, and glucose (99%) and 2-butanol (chemical pure reagent) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Tantalum pentaethoxide was purchased from Alfa Aesar (99% purity). The total saccharides concentration of Jerusalem artichoke was 6% (main component were fructose and glucose with fructose to glucose ratio of 3.75:1) after some pretreatment to eliminate the possible unfavorable factors, such as ions (Cl^-, Br^-, K^+, and so on), protein and other component might be harmful to the activity of the heterogeneous catalysts. And the pretreatments include an ultrafiltration procedure to remove protein, resin exchange methods to eliminate the ions in the Jerusalem artichoke juice.

1.2 Catalyst preparation and characterization

The catalyst (WO_3-Ta_2O_5) was prepared by the sol-gel method as following: by mixing ammonium metatungstate aqueous and tantalum pentaethoxide. Different concentrations of ammonium metatungstate aqueous were prepared, and then tantalum pentaethoxide was slowly dropped under stirring after the ammonium metatungstate totally dissolved, the precipitate was generated immediately when the tantalum pentaethoxide was added. The mixture was stirred vigorously at room temperature for 48 h, then aged at ambient condition for 12 h, and dried overnight at 65 ^oC in dry chamber, followed by drying at 110 ^oC in vacuum oven for 2 h and calcining in air at 300 ^oC with slow heating rate for 3 h.

As catalysts characterization, the concentration of acid sites per gram of the catalyst was quantified by temperature programmed desorption of ammonia (NH_3-TPD). Catalyst samples (~100mg) were loaded into a glass flow through cell, and ammonia was adsorbed onto the catalyst for 1.5h at 150 ^oC. The samples were heated at a ramp of 10 ^oC /min up to 700 ^oC and desorbed at 150 ^oC. The X-ray diffraction (XRD) patterns of the WO_3-Ta_2O_5 were obtained with an X'pert (PANalytical) diffractometer operated at 40 kV and 40 mA, using Ni-filtered Cu-Kα radiation. Pyridine-FTIR used the pure power pressed disks after outgassing at 300 ^oC and following contact with pyridine vapors. Transmission electron microscope (TEM) analysis of the sample was performed on a JEM-2100 (acceleration voltage: 200kV) instrument by dispersing sample power on a Cu grid pre-coated with a thin carbon film.

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, and HMF was hydrolyzed to levulinic acid and formic acid in the presence of water under acidic condition. 2-butanol was introduced to

promote the dehydration reaction of saccharides to HMF by shifting the equilibrium. The batch catalytic assay in biphasic system was performed in a 100ml stainless steel at 180 ^{o}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 180 ^{o}C.

1.4 Product analysis

Reactants disappearance was performed by HPLC (esa) equipped with DIONEX CarboPac ™ PA10 column at 30 ^{o}C and IntAmp detector, using 82:18v/v water: NaOH (0.1 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 ^{o}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_{org}/V_{aq} changed after reaction.

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

Conversion (mol %) = (moles of x reacted) / (moles of x initial) ×100%

Yield (mol %) = (moles of y produced) / (moles of x initial) ×100%

Selectivity (%) = (moles of y produced) / (moles of x reacted) ×100%

2. Supporting Figures

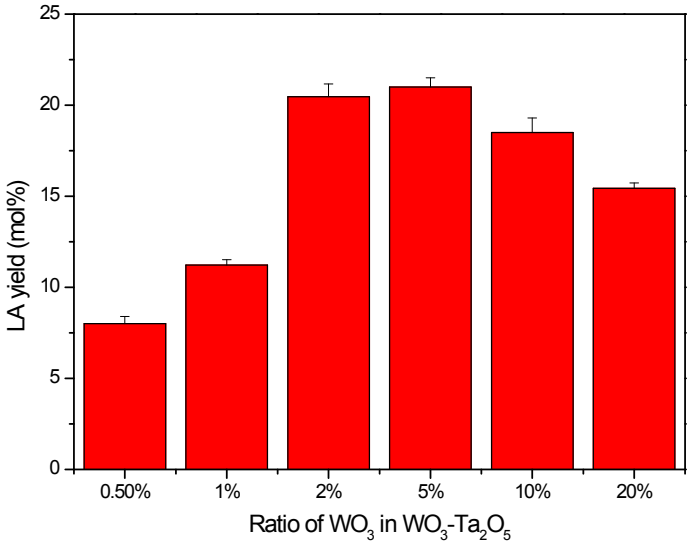

Fig. S1.The effect of the ratio of WO_3 on LA yields.

Reaction condition：glucose:1.2 g, WO_3-Ta_2O_5: 0.1 g, 20 ml of water, 30 ml of 2-butanol, 180 ^oC, 800 rpm Yields were determined by HPLC analysis**.**

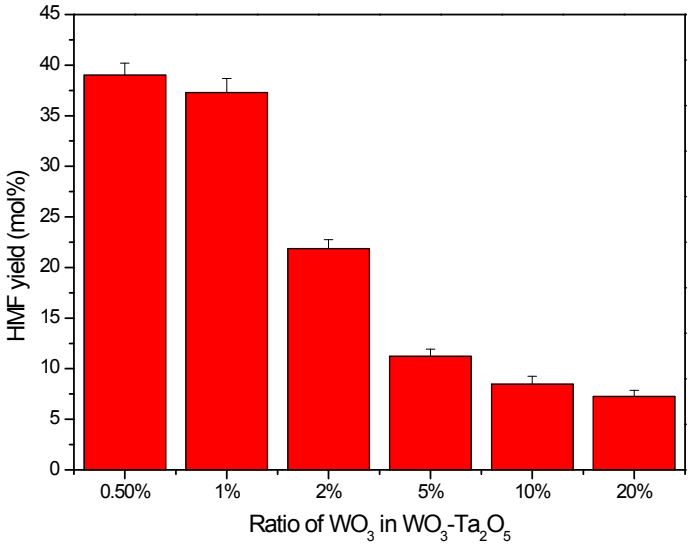

Fig. S2.The effect of the ratio of WO_3 on HMF yields.

Reaction condition：glucose:1.2 g, WO_3-Ta_2O_5: 0.1 g, 20 ml of water, 30 ml of 2-butanol, 180 °C, 800 rpm Yields were determined by HPLC analysis.

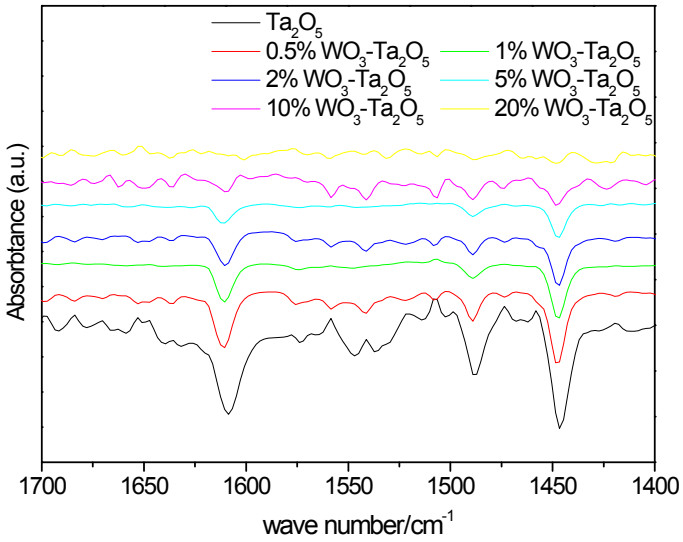

Fig. S3. Pyridine-FTIR spectra (pure power pressed disks) of WO_3-Ta_2O_5

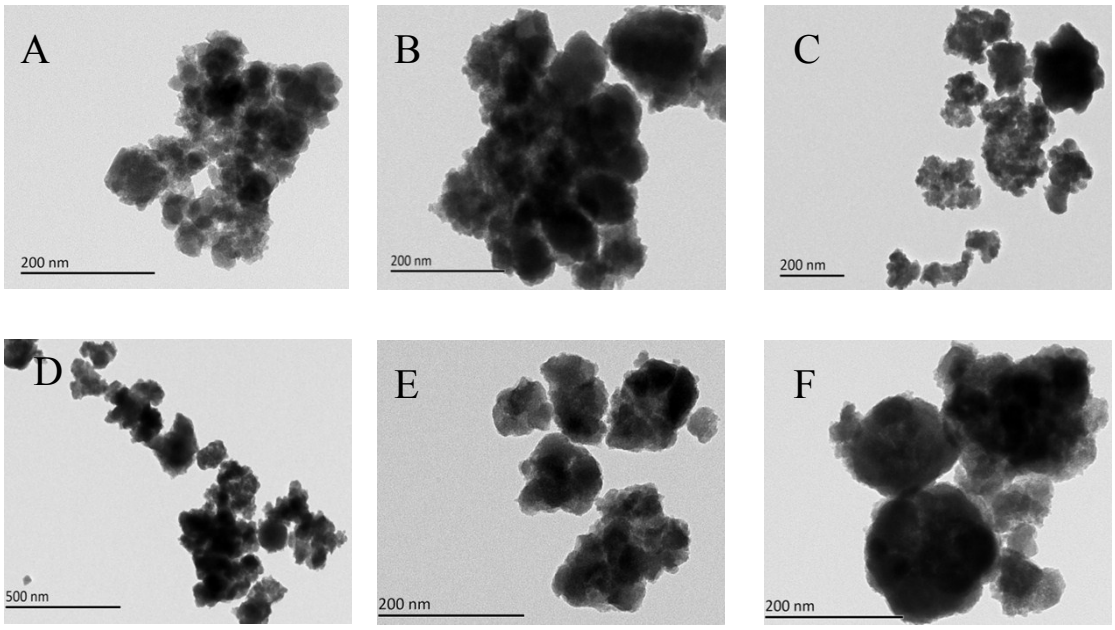

Fig. S4. Representation and TEM images of A) 0.5% WO_3-Ta_2O_5, B) 1% WO_3-Ta_2O_5, C) 2% WO_3-Ta_2O_5, D) 5% WO_3-Ta_2O_5, E) 10% WO_3-Ta_2O_5, F) 20% WO_3-Ta_2O_5

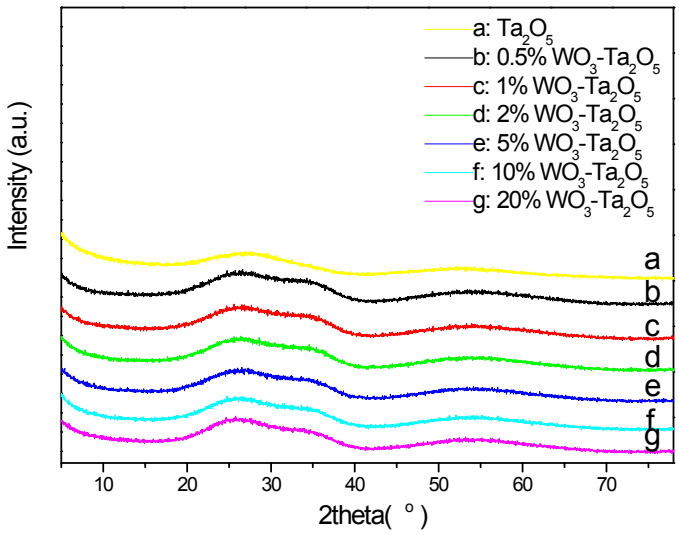

Fig. S5. X-ray diffraction patterns of WO_3-Ta_2O_5 with different ratio

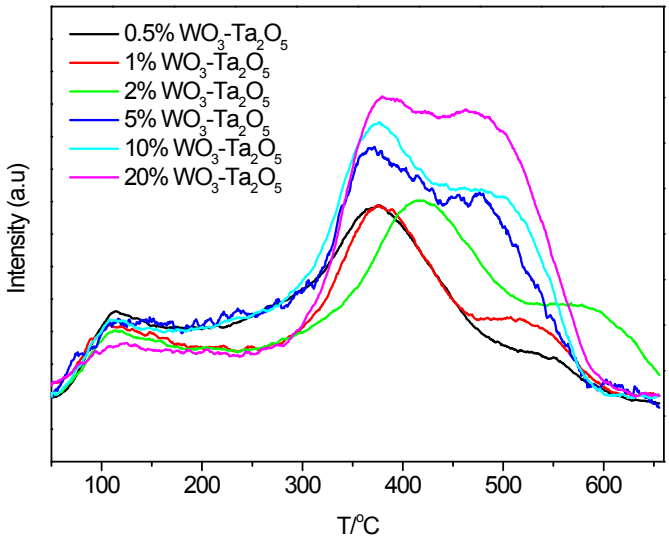

Fig. S6 NH_3-TPD profiles of samples WO_3-Ta_2O_5 with different ratio.

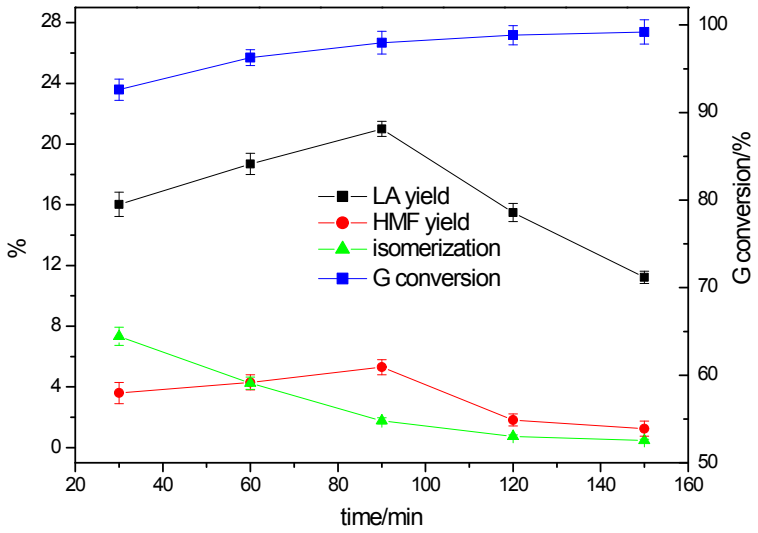

Fig.S7. Products yields from glucose catalyzed by 5%WO_3-Ta_2O_5 .

Reaction condition：Glucose:1.2 g, WO_3-Ta_2O_5 (5%): 0.1 g, 20 ml of water, 30 ml of 2-butanol, 180 ^oC, 800 rpm. Yields were determined by HPLC analysis.

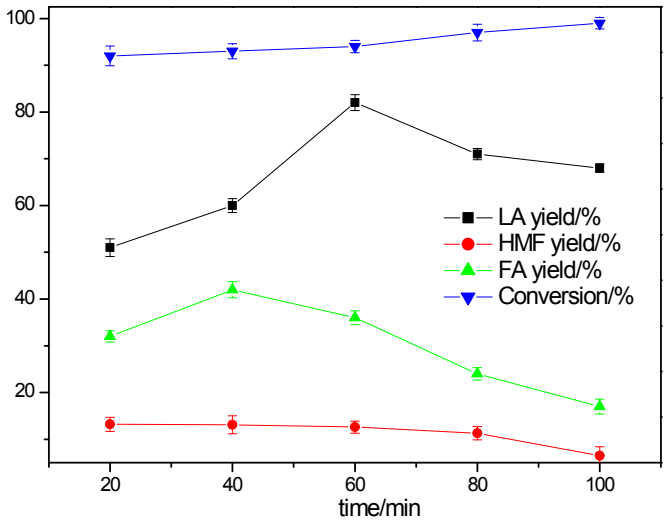

Fig.S8. Products yields from Jerusalem artichoke juice catalyzed by 5% WO_3-Ta_2O_5 .

Reaction condition：the concentration of total saccharides of Jerusalem artichoke:6(wt)% (the

ratio of fructose and glucose is 3.75:1), 20ml, WO_3-Ta_2O_5 (5%): 0.1 g, 30 ml of 2-butanol, 180 ^oC, 800 rpm. Yields were determined by HPLC analysis**.**

The Jerusalem artichoke juice hydrolyzed by exoinulinase was processed by ultrafiltration dialysis and exchange resin to remove unfavorable factors, such as protein, ions and so on.