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Tantalum compounds as heterogeneous catalysts for saccharide dehydration to 5-hydroxymethylfurfural†

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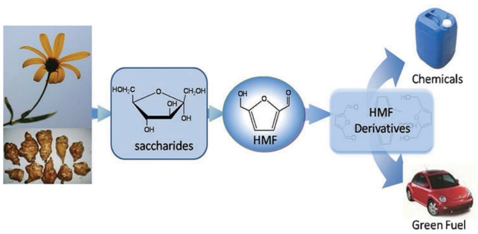
A new solid acid, based on tantalum hydroxide, was used to catalyze saccharide dehydration into 5-hydroxymethylfurfural (HMF) with high catalytic activity and excellent stability in a water–2-butanol biphasic system. Furthermore, good results were also obtained from Jerusalem artichoke juice with the catalyst under the same conditions.

With the rapid decrease in fossil resources, much attention has been paid to find sustainable sources for the production of chemicals and fuels in recent decades. Biomass, one of the most abundant renewable resources, has been regarded as an alternative carbon resource for bio-fuels and platform chemicals.[1] 5-Hydroxymethylfurfural (HMF) is a versatile and key platform chemical,[2] which can be obtained from biomass-based carbohydrate chemistry and further converted into high quality fuels and valuable chemicals (Scheme 1). Thus simple and effective routes to transform biomass into HMF would be of great significance.

Many efforts have been made to produce HMF efficiently from various sustainable reactants.[1–3] Many reaction systems have been studied, such as organic solvents,[4] ionic liquids[5] or aqueous systems.[6] However, all these processes have some disadvantages, such as significant energy input for high temperature organic solvent (*e.g.* DMSO) and subcritical or supercritical solvents, high cost of expensive ionic liquids, and corrosion from homogeneous acids, which make it difficult to produce HMF in large scale. Heterogeneously catalytic processes are more desired for industrial applications in view of facile catalyst separation and catalyst regeneration, and relatively low cost compared with homogeneous catalysts and ionic liquids. Therefore, it remains a challenge to catalyze the dehydration of saccharides into HMF in a heterogeneous catalytic process.[7–9] One-pot reaction using heterogeneous catalysts to transform polysaccharides and biomass into useful chemicals affords unique and environment-friendly benefits, including avoidance of isolation and purification of intermediate compounds, which saves time, energy and solvent.[1] In addition, water is a green and convenient reaction medium, so it is favorable to use water as solvent in the production. Unfortunately, most heterogeneous catalysts for HMF production require high reaction temperature[7] (>200 °C), and the HMF yield is low (<36%), besides, their catalytic activity is unstable in aqueous systems.[4] Qi *et al.* studied the reaction in aqueous system at 200 °C with sulfated zirconia catalyst, but the HMF yield was only 36%,[4] and the catalyst was unstable in this reaction system. Asghari *et al.* carried out the reaction in a batch-type reactor with sub-critical water in the presence of zirconium phosphate at 240 °C, and the HMF yield was 50%.[10] HMF yield of 47.6% was obtained from glucose using SO_4^{2-}/ZrO_2 and $SO_4^{2-}/ZrO_2–Al_2O_3$ catalyst.[11] Watanabe *et al.* studied the reaction in aqueous system at 200 °C with TiO_2 and ZrO_2 catalysts, but HMF yields were below 30%.[12] In this respect, it will be of significance to find an effective heterogeneous catalyst to produce HMF in aqueous system for future industrial applications.



Scheme 1 Biomass-based feedstock such as Jerusalem artichoke can be converted to 5-hydroxymethylfurfural, a versatile chemical, which can be further used for preparation of chemicals and green fuel.

We have found niobium compounds had good activity on monosaccharide dehydration.[13] Some experiments using analogous tantalum compounds as catalysts were thus also conducted. The results showed that the tantalum catalysts had better stability than the niobium catalysts (Table 1). Most importantly, the Ta catalysts are water-tolerant solid acids which show excellent stability in water-containing systems. Modified hydrated tantalum oxide (TA-p) can be reused multiple times without any substantial decrease in the product selectivity, which is highly favorable for biomass conversion since biomass contains much water. Although the hydrated tantalum oxide ($Ta_2O_5 \cdot nH_2O$, TA), "tantalum hydroxide", displays strong acid properties in the amorphous form and has good catalytic activity for some acid-catalyzed reactions,[14] to our knowledge there are no

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Table 1 Properties of different catalysts tested

			Fructose		JA[c]		
Catalyst[a]	BET/$m^2\ g^{-1}$	NH_3-TPD[b]/mmol g^{-1}	C[e] (%)	Y[f] (%)	C (%)	Y (%)	Catalyst life[d]
NA	69.6	3.5	79	46	72	17	—
TA	41.6	0.9	81	62	76	28	—
NA-p	214.9	4.4	90	89	46	22	7[g]
TA-p	141.5	1.5	94	90	90	50	15[h]

[a] Catalyst: NA: niobium hydroxide, TA: tantalum hydroxide, NA-p and TA-p correspond to NA and TA treated with 1 M phosphoric acid and calcined at 300 °C. [b] Acid density was measured by NH_3-adsorption. [c] JA: enzymatic hydrolysis of the juice of Jerusalem artichoke tuber by exoinulinase; conversion was based on total saccharides. [d] Catalyst life based on fructose. [e] C: conversion. [f] Y: HMF yield. [g] The activity decreased at the 8th recycle. [h] TA-p retains good activity for fifteen runs.

reports about this tantalum compound as catalyst to catalyze saccharides to HMF. Moreover, the current knowledge of the physical and chemical properties of TA is rather limited. Thus, besides the studies in the catalytic performance on saccharide dehydration, we also performed physicochemical characterizations, *i.e.* acidity–basicity properties and other surface properties by Brunauer–Emmett–Teller (BET) measurements, temperature programmed desorption of ammonia and carbon dioxide (NH_3-TPD, CO_2-TPD), X-ray diffraction (XRD), thermogravimetry–differential scanning calorimetry (TG-DSC) and Fourier-transform infrared spectroscopy (FTIR) techniques. We found that hydrated tantalum oxide treated with 1 M H_3PO_4 and calcined at 300 °C for 3 h (abbreviated as TA-p) had larger surface area and more acid sites, and its catalytic activity in saccharide dehydration was improved greatly after treatment (62% and 90% of HMF yield from fructose was obtained using TA and TA-p as catalyst at 160 °C, respectively).

First, experiments were performed to determine the optimal catalyst dosage and reaction temperature. It has been found that HMF yield and fructose conversion increased with increase of catalyst amount (Fig. S1†). HMF yield of 90% was obtained when the ratio of the catalyst amount to the reactant was 0.1 : 1.2 at 160 °C. Such high HMF yield has not been reported in aqueous heterogeneous catalytic systems. Moreover, the reaction temperature exhibits great influence on HMF yield and selectivity. HMF yield increased from 50 to 90% when the reaction temperature was increased from 140 to 160 °C (Fig. S2†). Reaction temperatures higher than 160 °C were not applied since high temperatures are energy-consuming and difficult on control. Accordingly, a reaction temperature of 160 °C and ratio of catalyst to reactant loading at 0.1 : 1.2 were employed as the reaction conditions in the following.

Converting different reactants to HMF were carried out using the TA-p catalyst in the biphasic system. Fructose, one of the best raw materials for HMF production,[4] was first catalyzed. In addition, glucose is one of the most abundant monosaccharides, and therefore this substrate was also investigated for the production of HMF catalyzed by TA-p. HMF yields of 90 and 58% were reached at 160 °C when fructose and glucose were reactants, respectively (Fig. 1). For glucose and fructose, the selectivity had the same changing trend as the yield, increasing initially and then decreasing, which suggests that fructose or glucose was first converted to unknown intermediate(s) and the intermediate(s) subsequently converted to HMF and other byproducts.[15] Additionally, a small amount of isomerization products were found, some basic sites may also exist on this catalyst as isomerization reactions of glucose and fructose are usually catalyzed by base.[1] Moreover, the catalyst showed excellent stability of fructose dehydration to HMF (Fig. 2). The catalyst was simply recovered by decantation, washing with deionized water and drying at 65 °C for 12 h. The results revealed that TA-p retained a good performance after being used 15 times at 160 °C (180 min reaction time for each run). The fructose conversions and HMF yields were always about 95% and 85%, respectively. Therefore, it can be concluded that the catalyst is stable in this biphasic system.

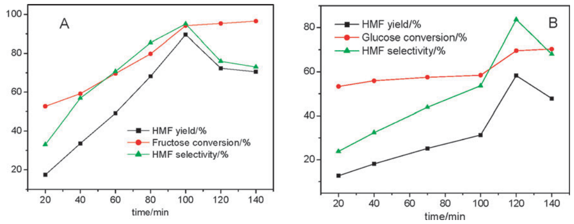

Fig. 1 Transformation of HMF from fructose (A) and glucose (B) over TA-p catalyst. Reaction conditions: fructose (A) or glucose (B): 1.2 g, catalyst: 0.1 g, 20 ml of water, 30 ml of 2-butanol, 160 °C, 800 rpm. Yields were determined by HPLC analysis.

Direct formation of HMF from polysaccharides, such as inulin, and Jerusalem artichoke juice, was also tested using the TA-p catalyst under the same reaction conditions. Remarkably, exciting results (Table 2) were obtained, demonstrating the tantalum compound is effective for polysaccharide hydrolysis and monosaccharide dehydration. The highest HMF yield is 87%, which was obtained at 150 min using inulin, a polymer of fructose, as the reactant. Compared with fructose as reactant, a longer reaction time (150 min) was needed to achieve the maximum yield. The reason might be that the hydrolysis of inulin was slow in this heterogeneous catalyzed system. Jerusalem artichoke is a potential energy crop, and has many desired features, such as easy cultivation, low input requirements, good tolerance for cold and drought and high resistance to wind and sand, thus avoiding the competition for land with food. Most importantly, the yield of its tuber is higher (typically 16-20 t/ha)[16] than other crops, such as corn, potato, sweet potato, *etc.* This desirable nonfood feedstock has been considered as one of the greatest potential raw materials for production of bio-fuels and chemicals by Chinese and German

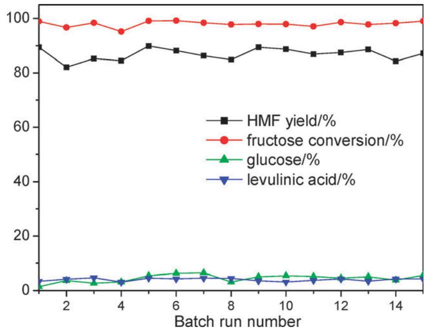

Fig. 2 Recycling of the catalyst system in the dehydration of fructose. Reaction conditions for each batch: fructose (1.2 g), water (20 ml), 2-butanol (30 ml), 160 °C, 800 rpm. Yields were determined by HPLC analysis.

Table 2 Conversion of saccharides individually in the biphasic system[a]

Saccharide	t/min	Yield (%)	Conv. (%)	TOF[b]
Fructose	100	90	94	36.1
Glucose	140	58	70	16.7
Inulin	150	87	95	23.4
JA1[c]	150	50	91	13.5
JA2[d]	120	79	91	16.3

[a] Reaction conditions: saccharide: 1.2 g, TA-p: 0.1 g, 20 ml of water, 30 ml of 2-butanol, 160 °C, 800 rpm. Yields were determined by HPLC analysis. [b] Turnover frequency (TOF): expressed as mmol of HMF/(g of catalyst × h). [c] JA1: juice of Jerusalem artichoke tuber. [d] JA2: juice of Jerusalem artichoke tuber processed by ultrafiltration dialysis, to remove protein, and pretreated by cation and anion exchange resin to remove ions.

governments.[16] Now the main challenge is how to convert it into fuels and useful building blocks. Thus the Jerusalem artichoke juice was used as reactant to produce HMF, and the HMF yield reached to 50% when Jerusalem artichoke juice was hydrolyzed by exoinulinase without other pretreatment. Considering that a certain amount of ions are in Jerusalem artichoke juice, they might be disadvantageous to the activity of the catalyst. Therefore, further treatment was applied to eliminate the ions in the Jerusalem artichoke juice through cation and anion exchange resins. An improved HMF yield of 79% was obtained (Table 2) using hydrolysed ion-free Jerusalem artichoke juice as reactant.

In order to have a better understanding of the catalyst, surface properties, BET, CO_2- and NH_3-TPD, XRD and FTIR measurements were performed. The untreated sample TA had a surface area of 41.6 $m^2 g^{-1}$, while the surface area of TA-p was found to increase dramatically to 141.5 $m^2 g^{-1}$ after treatment. Thus the treatment with phosphoric acid and calcination were effective for maintaining large surface area. This might be the reason for TA-p showing higher catalytic activity for saccharide dehydration, since catalytic behavior occurred on the surface of heterogeneous catalyst. However, too large surface area and too high acidity is likely to facilitate side reactions, such as with the niobium compounds, resulting in lower HMF yields (Table 1). A P–O vibration appeared in the FTIR spectra at 1100 cm^{-1} (Fig. S3†), indicating that a certain amount of phosphate groups was on the catalyst surface, which may be advantageous for the activity of TA-p. The acid sites existing on TA-p and TA are mainly Lewis acids according to pyridine-FTIR spectra (Fig. S4†).

There was a broad desorption profile over the range 100–550 °C in the NH_3-TPD profiles, suggesting a wide distribution of heterogeneous acid sites existing on the solid acid surface. The number of acid sites of the tantalum compound increased from 0.92 to 1.54 mmol g^{-1} after treatment (see Table 1), while the acid strength did not present any significant change because the desorption temperature of the adsorbed NH_3 showed little change. Most of the acid sites were weak or moderate.[17] CO_2-TPD showed that there were some basic sites on the TA-p, and the highest peak was over the range of 250–550 °C (Fig. S6†), which indicated the presence of mainly medium strength basic sites, which may be active for the isomerization of glucose and fructose. XRD and TG-DSC showed that the TA-p was more stable than TA at high temperature (Fig. S7 and S8†), confirming that treatment with phosphoric acid is helpful to prevent crystallization, and the amorphous form displays strong acid properties which increases the catalytic activity.[14]

The catalyst upon treatment of 1 M H_3PO_4 and calcination at 300 °C had larger surface area and more acid sites which led to the polysaccharide hydrolysis and monosaccharide dehydration to occur smoothly. As for polysaccharides, it seems that the glucosidic bond was weakened by the acid sites of the catalyst, thus producing fructose and glucose, which would dehydrate into HMF at the acidic sites of TA-p. A putative pathway for glucose as reactant catalyzed by TA-p is that the basic sites of TA-p catalyzed the isomerization of glucose into fructose which was then converted into HMF catalyzed by acidic sites of TA-p.

In conclusion, HMF, the most important intermediate between bio-based chemicals and petroleum-based chemicals, was efficiently obtained from monosaccharides, polysaccharides and Jerusalem artichoke juice by a simple heterogeneous catalyst. The catalyst made the process favorable so facilitating environment-friendly and cost effective conversion of biomass into bio-fuels and chemicals.

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