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Conversion of saccharides into levulinic acid and 5-hydroxymethylfurfural over WO3-Ta2O5 catalysts

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Bimetallic oxide catalysts WO_3-Ta_2O_5 are active in converting saccharides into 5-hydroxymethylfurfural(HMF) and levulinic acid(LA) in one-pot reactions. The product selectivity varies at different WO_3 to Ta_2O_5 ratios. FTIR measurements indicate the presence of Lewis acid sites and the strength of the Lewis acid sites varies when the WO_3 to Ta_2O_5 ratio changes. The result suggests that conversion of carbohydrates into HMF and LA can be realized using a single catalytic system by adjusting the catalyst's acidic properties.

Introduction

Future supplies of chemicals, materials, and energy depend on developing renewable alternatives to petroleum. Carbohydrates are a key renewable biomass component and an important potential source of chemical intermediates, however, selectively converting carbohydrates to desired platform chemicals is difficult. Therefore, it is particularly important to develop new catalysts for that purpose.

5-Hydroxymethylfurfural (HMF) and levulinic acid (LA) are key platform chemicals; both can be obtained from biomass-based carbohydrate chemistry and further upgraded to high quality fuels and value-added chemicals.[2-5] LA is considered as one of top 12 bio-derived feedstocks by the United States Department of Energy (DOE) for its applications as fuel additives, polymers, and resin precursors.[6, 7] It is well accepted that HMF is a product of facile acid-catalyzed dehydration of carbohydrates while LA is a product of subsequent rehydration of HMF.[8] The reaction pathway is shown in Scheme 1.
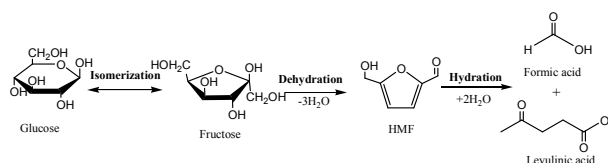
Scheme 1: Conversion of saccharides into HMF or LA

Direct conversion of carbohydrates into HMF and LA involves multiple steps including but not limited to hydrolysis, isomerization, dehydration, and rehydration. Several homogeneous and heterogenous catalytic systems containing Brønsted or Lewis acid catalysts for the conversion of biomass into HMF have been reported.[9-12] Most of the reported LA preparation methods use mineral acids(HCl, H_2SO_4, H_3PO_4, etc.) as catalysts at higher temperatures (about 250^oC).[13] Although homogeneous Brønsted acid-catalyzed conversion of saccharides into LA is a well-established process with many large scale units in operation, the harsh reaction conditions, difficulties in handling the liquid acidic waste, as well as the low product selectivity makes this process undesirable.

Processes using heterogeneous catalysts are generally more environmentally friendly than those which use mineral acids as the catalyst.[14, 15] Nevertheless, the yield of LA is generally lower when heterogeneous acid catalysts are used.[16, 17] For example, the highest yield of LA reported in the literature is 43% when a LZY zeolite catalyst was used in converting fructose.[18] Zhang et al. utilised MFI-type zeolite with different SiO_2/Al_2O_3 ratios as catalysts in the dehydration of glucose to LA, reporting the highest LA yield of 35.8%.[19] Zhang et al. also found that the strength of acidic sites and the mesoporosity of the zeolites had a significant effect on LA formation.[19]

We have reported that tantalum compounds are water-tolerant solid acids which exhibit unique acidic properties and good stability in water-containing system.[20] Furthermore, WO_3 is an efficient catalyst for the dehydration of alcohols.[21] However, research on WO_3-Ta_2O_5 has not been widely published. We report within this paper that tungsten-tantalum mixed oxides (hereinafter WO_3-Ta_2O_5), prepared by co-precipitation, is a reusable heterogeneous catalyst for the

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conversion of saccharides into value-added chemicals. Furthermore, WO_3-Ta_2O_5 is active in one-pot synthesis of LA from Jerusalem artichoke juice.

Results and Discussion

The effect of WO_3 ratio on the yield of LA and HMF

The catalytic activity of WO_3-Ta_2O_5 at different WO_3 to Ta_2O_5 ratios was investigated. The results show that WO_3-Ta_2O_5 at all ratios are catalytic active in the conversion of monosaccharidesto HMF and LA. The yield of products (HMF and LA) varies at different WO_3 to Ta_2O_5 ratios (see Fig.1). The HMF yield increases when WO_3 to Ta_2O_5 decreases. The HMF yield reached 61% using 0.5% WO_3 in WO_3-Ta_2O_5 as the catalyst (hereinafter "0.5% WO3-Ta_2O_5"). It has been previously reported that the HMF yield reached 90% using fructose as a reactant and a tantalum catalyst containing no WO_3,[11] which suggests that the presence of WO_3 may be unfavourable to HMF. As for LA—the product of HMF rehydration—its yield increased initially and then decreased when WO_3 was increased in the ratio. The highest LA yield is 89%, which was achieved when fructose was used as a reactant and catalyzed by 5% WO_3-Ta_2O_5. Such a high LA yield has not been reported in aqueous heterogeneous catalytic systems. Therefore, more WO_3 in WO_3-Ta_2O_5 decreases the LA yield. E.g., the LA yield was 76% using 20% WO_3-Ta_2O_5, indicating that too high a content of WO_3 is unfavorable for the formation of LA.

It is commonly understood that the acidic property of heterogeneous catalysts is important for saccharide dehydration. The WO_3-Ta_2O_5 catalyst was characterized using pyridine-FTIR. The pyridine-FTIR spectra show that the peak intensity at 1450 cm^{-1}(attributed to pyridinium ions formed on Lewis acid sites) became weaker when the percentage of WO_3 increased. This suggested that the formation of HMF was stimulated by the Lewis acid, which is consistent with Nakajima's findings.[22] With more WO_3 added,the formation of HMF was inhibited. Conversely, a suitable ratio of WO_3 was favorable in forming levulinc acid—the rehydration product of HMF—indicating that the role of WO_3 is similar to homogeneous acid, such as H_2SO_4.[22, 23]
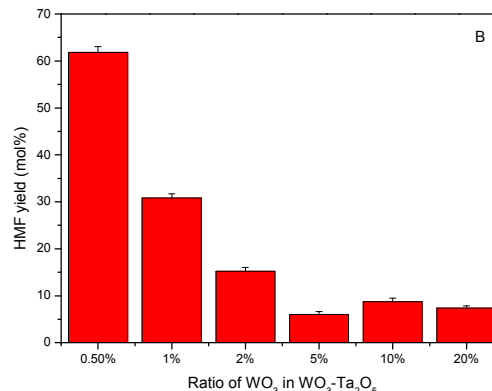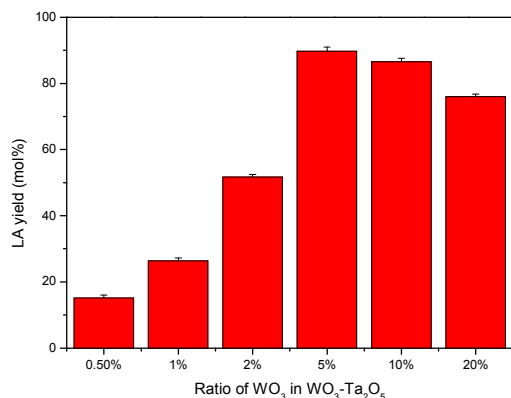

Fig. 1.The effect of WO_3 on LA yields (A) and HMF yields (B).

Reaction condition：fructose (F) :1.2 g, WO_3-Ta_2O_5: 0.1 g, 20 ml of water, 30 ml of 2-butanol, 180 ^{o}C, 800 rpm Yields were determined by HPLC analysis.Glucose, such as aldohexose is more difficult to convert into HMF or LA than fructose. But it would be significant to use glucose as reactant to convert into chemicals and platforms on a larger scale. Results using glucose as a reactant were shown in Fig. S1 and Fig. S2. It can be seen that the trends of LA and HMF yields are similar to that of conversion of fructose. 5% WO_3-Ta_2O_5 showed the best selectivity to LA. The highest LA yield was 21%. The highest HMF yield (39%) was obtained using 0.5% WO_3-Ta_2O_5 as the catalyst. In addition, all the reactant conversion rates are more than 95% catalyzed by WO_3-Ta_2O_5 with different WO_3 to Ta_2O_5 ratio, indicating formation of byproducts (i.e. humins, insoluble products etc.) in these reactions.[24, 25]

In addition to pyridine-FTIR, characterizations were carried out using X-ray diffraction, TEM, and NH_3-TPD. The morphology of the samples was studied using TEM. Fig. S4 is a TEM micrograph. The images reveal that the catalysts are amorphous at different WO_3 to Ta_2O_5 ratios, which is consistent with the XRD results (see Fig. S5).Tantalum oxide in this form contains mainly Lewis acids and displays better acidic properties on saccharide dehydration into HMF.[26] The addition of WO_3 may inhibit the Lewis acid sites from binding with pyridine thus weakening the peak intensity of 1450 cm^{-1}.There were two desorption profiles (50-300°C, 300-600°C) over the temperature range of 50-600°C in the NH_3-TPD profiles (Fig S6), suggesting the catalyst contains weak, moderate, and strong acid sites on its surface. In order to ensure that the catalyst remains amorphous, all the samples were treated at 300°C, thus the profiles at 50-300°C are important to our experiments. and the 5% WO_3-Ta_2O_5 catalyst has the maximum amount of acid sites within this temperature range, which could be the reason why the 5% WO_3-Ta_2O_5 ratio has a better catalytic performance than catalysts at other ratios.

The effect of temperature on the LA and HMF yields

Fig. 2 shows the effect of temperature on the LA and HMF yields when using the ratio of 5% WO_3-Ta_2O_5. The LA yield is directly related to the reaction temperature. The LA yield was

89% at the reaction temperature of 180°C. When the reaction temperature was 160°C, the highest LA yield was 69%,with an extended reaction time. Conversely, the yield of HMF is lower at a higher reaction temperature. The HMF yield was 10% of HMF at the reaction temperature of 180°C and 23% of HMF at 160°C, using 5% WO_3-Ta_2O_5 as the catalyst for both temperatures. This indicates that HMF was converted into LA more quickly at a lower temperature. Additionally, the HMF yield decreased when the reaction time was increased due to the rehydration of HMF into LA or other by-products. These results show that a higher temperature promotes the formation of LA. The reaction temperature is modest relative to the reaction temperature required when using homogeneous acids as catalysts.
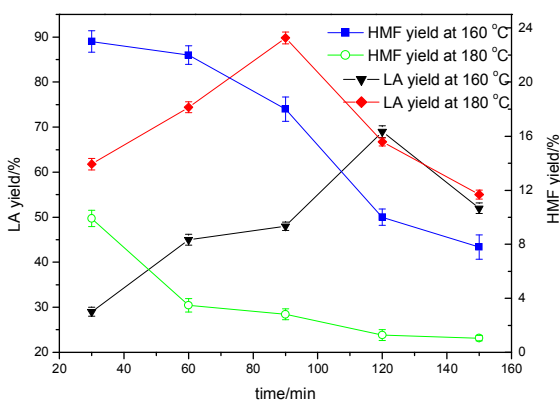

Fig.2. Effect of reaction temperature on LA and HMF yields.

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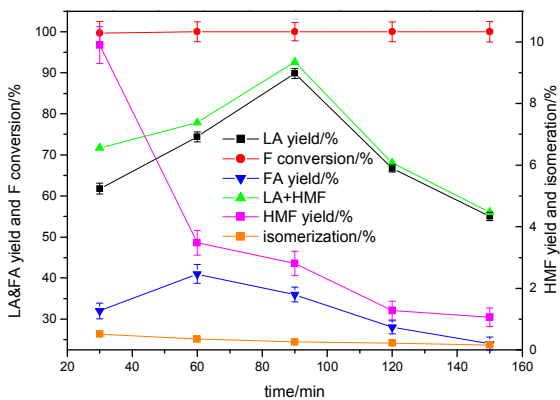

Fig.3. Product yields from fructose catalyzed by 5%WO_3-Ta_2O_5 .

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

Saccharides as the reactant

Fructose was first catalyzed by 5% WO_3-Ta_2O_5 and the products were analysed by HPLC. The highest LA yield of 89% was obtained (see Fig.3), which was much higher than the reported LA yield using other solid acids as the catalyst.[27] The yield of LA increased initially and then decreased; which suggests that the generated LA was converted into other by-products. Furthermore, the amount of HMF was small with the longer reaction time directly affecting the decrease in the HMF yield. The rehydration of HMF also produced formic acid, and its molar yield should have been equivalent to that of LA. Incongruously, the yield of formic acid was less than that of LA. This discrepancy may be caused by the formic acid generated as Brønsted acid catalyst consumed by hydrogenation with HMF, or as a reagent for other reactions.[28] Glucose or fructose as isomerization products were also detected when fructose and glucose as reactants (see Fig.3 and Fig.S7), indicating that the isomerization occurred in this reaction system. The similar phenomena were obtained when glucose was catalyzed by these catalysts.
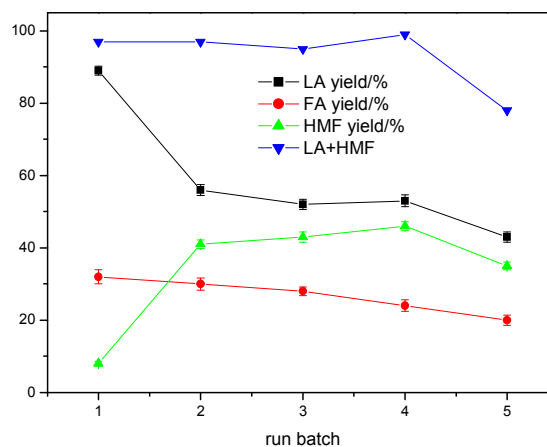

Fig. 4 WO_3-Ta_2O_5 (5%) recycling experiments.

Reaction condition for each batch: fructose: 1.2 g, 20ml of water, 30ml of 2-butanol, 180°C, 800rpm. Yields were determined by HPLC analysis.

Jerusalem artichoke juice was also used as the reactant in addition to glucose and fructose. This non-food feedstock grows well on marginal lands and has high tolerance for cold and drought as well as resistance to wind and sand, and the easy cultivation and relatively low input requirements make Jerusalem artichoke juice a promising feedstock for biofuels and intermediates chemicals. Therefore, the Jerusalem artichoke has been considered as one of the greatest potential raw materials for production of biofuels and chemicals.[29] The total saccharide (main components were fructose and glucose with ratios of 3.75:1)concentration of Jerusalem artichoke was 6% after pre-treatment (including membrane process, resin

exchange methods, and enzymatic hydrolysis method) as the protein and ions might be disadvantageous for the activity of the catalyst.[30] The LA yield was 82% using pre-treated Jerusalem artichoke juice catalyzed by 5% WO_3-Ta_2O_5 (see Fig.S8). The results confirm that the heterogeneous catalysts are effective to produce HMF and LA from biomass in a single catalytic system, which is a challenge.[31] It provides new ideas for transformation biomass into biochemicals by heterogenous catalysts.

Catalyst recycling

Recycling of catalyst is very important in green chemistry so that the catalyst stability and reusability were tested. In the case of 5% WO_3-Ta_2O_5 after each reaction, the catalyst was separated, washed with deionized water, and dried at 60^oC for 12 hours prior to being reused in the next run. As shown in Fig.4, the reaction using the fresh 5% WO_3-Ta_2O_5 proceeds efficiently produced a LA yield of 89%. The reused catalyst has not shown significant loss of activity. The yield of LA was 56% in the second use, 52% in the third use, and 53% in the fourth use. In addition, the HMF yield was 8% in the first use, which increased sharply to 41% in the second use, 43% in the third use, and 46% in the fourth use. Moreover, the sum of the LA and HMF yields little changed in the first four uses but decreased in the fifth uses, which may be attributed to catalyst deactivation. The exact mechanism of catalyst deactivation requires further studies.

Conclusions

The WO_3-Ta_2O_5 catalyst at different WO_3 to Ta_2O_5 ratios and different acid strengths was synthesized and evaluated in the conversion of monosaccharide and Jerusalem artichoke juice into HMF and LA in a water-containing biphasic system. There apparently are few Brønsted acid sites on the tungsten oxide incorporated in the tantalum compound and the Lewis acid declined with the increase in WO_3. The ratio of WO_3 influenced the products distribution while 5% WO_3-Ta_2O_5 showed the best activity and selectivity to LA. The catalyst is also active in the conversion of Jerusalem artichoke juice. Experiments using recycled catalysts indicate that the WO_3-Ta_2O_5 catalyst can be recycled and reused. It is believed that the carbohydrate dehydration into HMF and HMF rehydration into LA continues in the presence of the acid sites on the catalyst. Further studies are in progress.

Acknowledgements

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