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Protonated and layered transition metal oxides as solid acids for dehydration of biomass-based fructose into 5-hydroxymethylfurfural

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ABSTRACT

A series of protonated and layered transition metal oxides, including layered HTaWO₆, HNbMoO₆ as well as HNbWO₆, were synthesized by solid-state reaction and ion-exchange. The layered HTaWO₆ has been systematically studied as a solid acid to realize the dehydration of fructose to 5-hydroxymethylfurfural (HMF). The transition metal oxide samples were characterized with ICP-OES, EDS, XRD, XPS, SEM, TGA, FT-IR, N₂ adsorption-desorption and NH₃-TPD. The influential factors such as reaction temperature, reaction time, solvent, catalyst amount and substrate concentration were deeply investigated. The optimized fructose conversion rate of 99% with HMF yield of 67% were achieved after 30 min at 140 °C in dimethyl-sulfoxide.

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1. Introduction

With the exhaustion of fossil fuel resources and the aggravation of global warming, considerable effort has been devoted to the chemical transformations of renewable biomass into fuels and chemicals [1]. Among all the biomass-derived chemicals, 5-hydroxymethylfurfural (HMF) is recognized as a key platform compound, since a variety of value added chemicals such as 2,5-dimethylfuran, 2,5-diformylfuran, 2,5-furandicarboxylic acid and γ -valerolactone can be synthesized from HMF [2–5].

HMF is mainly prepared from the acid-catalyzed dehydration of carbohydrate, in particular, monosaccharide [6–8]. It is widely acknowledged that homogeneous acids contain the drawbacks such as the high cost of separation and the potential corrosion to equipment. To date, from the viewpoint of green chemistry, a variety of heterogeneous acids have been explored, including zeolites, ion-exchange resins, heteropoly acids, phosphates, sulfated materials, sulfonated materials and supported ionic liquids [9–14]. In addition, so as to facilitate the product separation, ever-increasing interests have been focused on the biphasic systems, including water-tetrahydrofuran (THF), water-isopropyl alcohol (IPA), and water-methyl isobutylketone (MIBK) [15].

In recent years, ion-exchangeable layered metal oxides and the derived exfoliated nanosheets have been deeply investigated as strong, water-tolerant solid acid catalysts [16]. For instance, Dias et al. investigated the dehydration of xylose into furfural with HTiNbO₅, HTi₂NbO₇, HNb₃O₈, H₄Nb₆O₁₇ and H₂Ti₃O₇ nanosheets [17]. Takagaki and co-workers delved into the dehydration of 2-propanol, esterification of acetic acid, and cracking of cumene with HTiNbO₅ nanosheet [18]. Their group also investigated the catalytic performance of layered HNbMoO₆·*n*H₂O in friedel-crafts alkylation [19], esterification of hydrocarboxylic acid [20], acetalization, hydration [21] and hydrolysis of saccharides [22,23]. Additionally, their group demonstrated that the catalytic activity for friedel-crafts alkylation of anisole decreases in the order HMWO₆ nanosheet (M=Ta, Nb) > HNb₃O₈ nanosheet > HTiNbO₅ nanosheet [24]. Similarly, He et al. found that the catalytic activity for esterification increase in the order layered HTiNbO₅ < layered HNbWO₆·1.5H₂O < layered HNbMoO₆·H₂O [25]. Morita et al. adopted layered HNbMoO₆ for the dehydration of sorbitol into 1,4-sorbitan [26]. Yang and colleagues demonstrated that layered HNb₃O₈ with in situ self-exfoliation behavior shows excellent catalytic activity in the hydration of ethylene oxide [27]. More recently, their team achieved HMF yield of 55.9% with in situ exfoliated layered HNb₃O₈ under microwave irradiation [28].

However, the preparation of the precursors of HTiNbO₅, HTi₂NbO₇, HNb₃O₈ and H₄Nb₆O₁₇ mentioned above require high temperature (1050–1200 °C). Moreover, the traditional exfoliation aggregation through a soft-solution process is costly (the

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49 adoption of expensive agent tetrabutylammonium hydroxide) and
50 time-consuming (1–3 weeks for pre-exfoliation) [17,19,28]. As for
51 the microwave irradiation, it seems still difficult to be applied into
52 large-scaled industrial fields. Therefore, the exploration of proto-
53 nated, layered transition metal oxides whose precursors require
54 relatively lower calcination temperature in acid-catalyzed reaction
55 is of great significance.

56 Notably, tantalum-based oxides were demonstrated to exhibit
57 higher performance in acid-catalyzed reactions than the niobium-
58 substituted oxides [24,29,30]. Nevertheless, to the best of our
59 knowledge, there are limited papers in literature dealing with the
60 synthesis of HMF with tantalum-based oxides [31,2]. Herein, in the
61 present study, the selective conversion of fructose to HMF was ex-
62 amined with protonated, layered transition metal oxides HTaWO₆,
63 HNbMoO₆ and HNbWO₆. Under the optimal condition, a HMF yield
64 of 67% with 99% fructose conversion were obtained using layered
65 HTaWO₆ in DMSO after 30 min at 140 °C.

66 2. Experimental

67 2.1. Materials

68 5-Hydroxymethylfurfural (98%), D-fructose, Li₂CO₃, Ta₂O₅,
69 Nb₂O₅, WO₃, MoO₃, tetra(n-butylammonium) hydroxide
70 (TBA⁺OH⁻) were obtained from Aladdin Industrial Inc. (Shanghai,
71 PR China). Dimethylsulfoxide, tetrahydrofuran, isopropyl alcohol, n-
72 propyl alcohol were purchased from Sinopharm Chemical Reagent
73 Co. Ltd (Shanghai, PR China). H-Beta (Si/Al = 12.5), HY-zeolite
74 (Si/Al ≥ 5.2) and HZSM-5 (Si/Al = 25) were purchased from
75 Nankai University Co. Ltd. (Tianjin, PR China).

76 2.2. Synthesis of catalyst

77 2.2.1. Preparation of layered transition metal oxides [20,26]

78 Layered LiTaWO₆, LiNbMoO₆ and LiNbWO₆ were obtained by
79 the calcination of stoichiometric mixtures of Li₂CO₃ and metal ox-
80 ides (Ta₂O₅ and WO₃, Nb₂O₅ and MoO₃, Nb₂O₅ and WO₃) for 24 h
81 with one intermediate grinding. The calcination temperature was
82 1073, 853 and 1073 K, respectively. Layered HTaWO₆, HNbMoO₆
83 and HNbWO₆ were prepared by proton exchange of the precu-
84 sors. The proton-exchange reaction was conducted by shaking 2.0 g
85 of the lithium precursors in 150 mL of 1 M HNO₃ aqueous solution
86 at room temperature for 1 week with 2 intermediate exchange of
87 HNO₃ solution. The as-prepared samples were washed with dis-
88 tilled water and dried at 323 K.

89 2.2.2. Preparation of exfoliated nanosheets

90 25 wt% TBA⁺OH⁻ solution was added to 150 mL of distilled
91 water containing 2.0 g of the protonated compound until the pH
92 reached 9.5–10.0, the resulting solution was shaken for 1 week.
93 The insertion of voluminous and hydrophilic TBA⁺ cations into the
94 interlayer expanded the interlayer spaces, leading to the delamina-
95 tion of the layered samples into nanosheets. The nonexfoliated par-
96 ticles were removed from the supernatant solution through cen-
97 trifugation. 30 mL of HNO₃ aqueous solution (0.1 M) was added to
98 150 mL of the supernatant solution, leading to immediate aggre-
99 gation of the nanosheets. The aggregated nanosheets were rinsed
100 with distilled water and dried at 323 K.

101 2.3. Characterization of catalyst

102 Inductively coupled plasma-Optical Emission Spectroscopy (ICP-
103 OES) analysis was performed with Perkin-Elmer Optima 8000 in-
104 strument. X-ray diffraction (XRD) patterns were obtained with
105 PANalytical X'pert Pro multipurpose diffractometer at 40 KV and

40 mA, using Ni-filtered Cu-K α radiation ($\lambda = 1.5418$). X-ray photo- 106
electron spectroscopy (XPS) data was obtained with Kratos Axis Ultra 107
Ultra (DLD) photoelectron spectrometer operated at 15 kV and 5 mA 108
at a pressure of about 5×10^{-9} torr using Al K α as the exciting 109
source. The binding energies were referenced to the C 1s pho- 110
toelectron peak (284.6 eV). Scanning electron microscopy (SEM) 111
images were recorded by Hitachi S-4800 instrument operated at 112
10 KV. Brunauer-Emmett-Teller (BET) surface area measurements 113
were performed with N₂ adsorption-desorption isotherms at 77 K 114
(SI-MP-10/PoreMaster 33, Quantachrome), after degassed under 115
vacuum at 423 K for 12 h. The specific BET surface areas were evalu- 116
ated using the method in the p/p_0 range from 0.05 to 0.3. Ther- 117
mal gravimetric analysis (TGA) was performed using TA Q50 from 118
room temperature to 500 °C with a scan rate of 10 K/min under 119
a stream of nitrogen gas. Fourier transform infrared (FT-IR) spec- 120
tra of KBr pellets were recorded at room temperature in the 400– 121
1100 cm⁻¹ region with a Bruker Tensor 27 spectrometer equipped 122
with a Data Station. Temperature-programmed desorption of am- 123
monia (NH₃-TPD) was carried out using ASIQAIV200-2 with ther- 124
mal conduction detector. The samples were heated at 423 K for 1 h 125
under He flow, exposed to NH₃ at 373 K for adsorption until it was 126
saturated, exposed to He flow at 373 K for 1 h to remove excess 127
NH₃, and heated in a N₂ flow with temperature raised from 373 K 128
to 923 K at a rate of 10 K/min. 129

130 2.4. Fructose conversion into HMF

131 In a typical run, fructose (150 mg), layered HTaWO₆ (120 mg) 131
and DMSO (3 mL) were added to an Ace Pressure Tube. The tube 132
was placed in a preheated oil bath at 140 °C with vigorous stir- 133
ring for 30 min, and then quenched in ice bath. The liquid mix- 134
ture were decanted into a volumetric flask after filtration with de- 135
ionized water as diluents, and analyzed with high-performance liq- 136
uid chromatography (HPLC). 137

138 2.5. Reusability of the catalyst

139 After reaction, the catalyst was filtrated from the reaction mix- 139
ture and washed with de-ionized water. The powder was then 140
dried at 323 K until it attained constant weight. A minority of fresh 141
catalyst was added to compensate the loss in the recycle process. 142
The reaction conditions were the same as those described above. 143

144 2.6. Analysis of product

145 The HPLC analysis was performed on Shimadzu LC-20AT 145
equipped with a refractive index/UV-vis detector and Shodex Sugar 146
SH-1011 column ($\varnothing 8 \times 300$ mm). The fructose conversion is tested 147
with refractive index detector, while the yield of HMF is tested 148
with UV-vis detector. H₂SO₄ (0.005 M) solution was used as the 149
mobile phase at a flow rate of 0.5 mL/min, and the column temper- 150
ature was maintained at 50 °C. The amounts of fructose and HMF 151
were calculated based on external standard curves constructed 152
with authentic standards. 153

154 3. Results and discussion

155 3.1. Catalyst characterization

156 According to ICP-OES, after the acid exchange, the lithium 156
amount in layered HTaWO₆, HNbMoO₆ and HNbWO₆ is 0.11%, 157
0.18% and 0.23%, respectively, which indicates that the precursors 158
are basically full proton-exchanged. While according to EDS, the 159
amounts of Ta, W, C and O in the layered HTaWO₆ are 37.2%, 160
36.1%, 5.6% and 21.1%, respectively, which is in accordance with 161

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