One-dimensional γ-Al₂O₃ nanofibers were modified with Nb₂O₅ to be used as an efficient heterogeneous catalyst to catalyze biomass into 5-hydroxymethylfurfural (5-HMF). At low Nb₂O₅ loading, the niobia species were well dispersed on γ-Al₂O₃ nanofiber through Nb–O–Al bridge bonds. The interaction between Nb₂O₅ precursor and γ-Al₂O₃ nanofiber results in the niobia species with strong Lewis acid sites and intensive Brønsted acid sites, which made 5-HMF yield from glucose to reach the maximum 55.9~59.0% over Nb₂O₅-γ-Al₂O₃ nanofiber with a loading of 0.5~1 wt% Nb₂O₅ at 150 °C for 4 h in dimethyl sulfoxide. However, increasing Nb₂O₅ loading could lead to the formation of two-dimensional polymerized niobia species, three-dimensional polymerized niobia species and crystallization, which significantly influenced the distribution and quantity of the Lewis acid sites and Brønsted acid sites over Nb₂O₅-γ-Al₂O₃ nanofiber. Lewis acid site Nb⁺δ played a key role on the isomerization of glucose to fructose, while Brønsted acid sites are more active for the dehydration of generated fructose to 5-HMF. In addition, the heterogeneous Nb₂O₅-γ-Al₂O₃ nanofiber catalyst with suitable ratio of Lewis acid to Brønsted sites should display an more excellent catalytic performance in the conversion of glucose to 5-HMF.

Fossil-based resources such as petroleum, coal and natural gas are deemed as the dominant raw materials to be used for energy and synthesis of organic chemicals. Nevertheless, the mismatch between the increasing demand for and sharply diminishing supply of fossil-based resources implies that the search for alternative raw material sources is critically important. Renewable biomass is the most suitable candidate for alternative raw material sources since they are abundant, easy to obtain and rich of carbohydrates which can be converted to valuable chemicals. Consequently, the conversion of renewable biomass to fuels and chemicals has received wide attention.

Cellulose as an important branch of biomass is composed of the basic glucose unit building blocks that can be transformed to the useful platform molecule 5-HMF. 5-HMF can acts as the raw material to be used to synthesize chemicals, liquid fuels and so on ref. 5 and 6. Hence, developing an approach to efficiently synthesize 5-HMF from rich and cheap glucose resources under mild conditions is extremely desirable.

5-HMF synthesis from glucose is difficult due to the high stability of the glucose ring, making the dehydration process more difficult. In order to overcome this disadvantage, the catalysts were paid more attention to reduce the activation energy of this reaction. Catalysts used for glucose dehydration to 5-HMF are classified into heterogeneous and homogeneous catalysts which play the different performance in different reaction solvents such as aqueous, organic solvents and ionic liquids. Homogeneous catalysts like ionic liquids and metal salts employed for 5-HMF conversion from glucose are limited due to several drawbacks including the high cost, toxicity, difficult separation and recovery. In contrast, heterogeneous catalysts avoided aforementioned disadvantage.

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have been widely utilized for biomass conversion into 5-HMF, e.g. oxides, phosphates, ion exchange resins and heteropolyacids. As for the heterogeneous catalysts, besides the main catalytic active sites like metal oxides such as WO₃, TiO₂, and ZrO₂, the supports also play a very important role on catalytic process. Generally, the conventional porous materials were used as supports because of their large surface areas. But the porosity and surface area will be reduced during the loading of active sites. Recently, various one-dimensional (1D) oxide nanofibers have been reported as the efficient heterogeneous catalyst supports, which can realize the loading of active sites without declining surface area.

Herein, the active sites (acidic Nb₂O₅) were loaded on the surface of 1D γ-Al₂O₃ nanofibers by facile incipient-wetness impregnation method. Nb₂O₅-γ-Al₂O₃ nanofibers displayed the high catalytic activity in glucose conversion to 5-HMF with dimethyl sulfoxide as solvent, and it was found that Lewis acid site Nb⁵⁺ promoted the isomerization of glucose to fructose, while Brønsted acid sites catalyzed the dehydration of generated fructose to 5-HMF.

**Results and Discussion**

**Nb₂O₅-γ-Al₂O₃ nanofiber characterization.** 1D γ-Al₂O₃ nanofiber with different Nb₂O₅ loading of 0, 1, 3, 3.4, 4.7, 9.4, 26.6 and 33.9 wt% was prepared by facile incipient-wetness impregnation method. Nb₂O₅-γ-Al₂O₃ nanofibers displayed the high catalytic activity in glucose conversion to 5-HMF with dimethyl sulfoxide as solvent, and it was found that Lewis acid site Nb⁵⁺ promoted the isomerization of glucose to fructose, while Brønsted acid sites catalyzed the dehydration of generated fructose to 5-HMF.

| Catalyst      | Nb⁺ concentration (mg/L) | Nb₂O₅ content controlled (wt%) | Nb₂O₅ real content (wt%) |
|---------------|--------------------------|-------------------------------|--------------------------|
| 1 wt%Nb₂O₅-γ-Al₂O₃ | 0.046                    | 1                            | 1.0                      |
| 3 wt%Nb₂O₅-γ-Al₂O₃ | 0.014                    | 3                            | 3.0                      |
| 5 wt%Nb₂O₅-γ-Al₂O₃ | 0.016                    | 5                            | 3.4                      |
| 10 wt%Nb₂O₅-γ-Al₂O₃ | 0.022                    | 10                           | 4.7                      |
| 15 wt%Nb₂O₅-γ-Al₂O₃ | 0.044                    | 15                           | 9.4                      |
| 30 wt%Nb₂O₅-γ-Al₂O₃ | 0.124                    | 30                           | 26.6                     |
| 40 wt%Nb₂O₅-γ-Al₂O₃ | 0.158                    | 40                           | 33.9                     |

Table 1. The Nb₂O₅ contents of Nb₂O₅-γ-Al₂O₃ by ICP-AES.
diameter of 30–50 nm, which indicates Nb2O5 loading do not influence the morphology and structure of γ-Al2O3 nanofibers. However, the particles are observed to aggregate together when Nb2O5 loading reaches 4.7 wt%, due to the surface tension\textsuperscript{21,22}. Moreover, the characterization of γ-Al2O3 and 1 wt% Nb2O5-γ-Al2O3 by transmission electron microscopy (TEM) was also performed. As shown in Fig. 4a,b, the average size and the morphology of these particles are similar. Elemental mapping by EDS was used to study the distribution of the Al, O, and Nb elements in nanofiber based samples (Fig. 4d). The abundant Al and O elements distribute homogeneously in a single nanofiber, however the content of Nb element is comparably smaller and Nb element mainly distributes on the surface of γ-Al2O3.

As shown in Fig. 5, γ-Al2O3 nanofiber exhibits the very weak Raman bands in the region of 200–2000 cm\textsuperscript{-1} due to the low polarizability of light atoms and the ionic character of Al–O bonds\textsuperscript{23}. As for Nb2O5-γ-Al2O3 nanofiber with 1~9.4 wt % load, the intensive Raman bands in the region of 1000–2000 cm\textsuperscript{-1} appeared due to the polarizability of Nb–O–Al species\textsuperscript{24}.

### Effects of different Nb2O5 loading on biomass selectivity conversion.

Under the condition of 150 °C for 4 hours, 5-HMF yield from glucose is in the range of 32.5% to 59.0% with the different Nb2O5 loading (Fig. 6A), and the best 5-HMF yield is about 59.0% over the catalyst with 0.5 wt% Nb2O5 loading, while the yield is only 33.5% with 33.9 wt% Nb2O5 loading. 59.0% 5-HMF yield over 0.5 wt% Nb2O5-γ-Al2O3 nanofiber is significant which is higher than those reported in literatures\textsuperscript{20,25,26}. Nb2O5-γ-Al2O3 nanofiber can well catalyze...
the conversion of fructose and xylose to 5-HMF and furfural, which is not as significant as glucose conversion (Fig. 6B,C). As Nb$_2$O$_5$ loading increased from 3 wt% to 33.9 wt%, 5-HMF yields from fructose conversion raised from 67.4% to 76.8%, but 3 wt% Nb$_2$O$_5$ loading resulted in the minimum 5-HMF yield. When xylose was dehydrated, the maximum 56.1% furfural yield was obtained over 1 wt% Nb$_2$O$_5$-γ-Al$_2$O$_3$ nanofiber, but furfural yield declined to 36.9% when Nb$_2$O$_5$ loading reached 33.9 wt%. Those results indicated that the niobia species existed on the γ-Al$_2$O$_3$ nanofiber support played the key role on biomass conversion or dehydration.

As shown in Fig. 7, the states of niobia species dispersed on the γ-Al$_2$O$_3$ nanofibers can be expressed in such three kinds of structure as a single NbO$_6$ unit, two-dimensional aggregation and three-dimensional aggregation$^{27-30}$. If the niobia species exist in the form of a highly dispersed monomer NbO$_6$ unit, Lewis acid sites are originated from Nb$^{5+}$ ion. At low Nb$_2$O$_5$ loading, the niobia species dispersed on the γ-Al$_2$O$_3$ nanofiber support through Nb–O–Al bridge bonds. γ-Al$_2$O$_3$ has Lewis acid sites with different acid strengths and weak Brønsted acid sites, and the reaction between Nb$_2$O$_5$ precursor and hydroxyl groups on the surface of γ-Al$_2$O$_3$ nanofiber results in strong metal-support interaction, generating Nb$_2$O$_5$-γ-Al$_2$O$_3$ nanofiber with both strong Lewis acid sites and relatively intensive Bronsted acid sites$^{14}$. With the increase of Nb$_2$O$_5$ loading, the interaction between the isolated niobia species and their nearest neighbors (either isolated or polymerized species) resulted in the formation of Nb–O–Nb bridge bonds. The Bronsted acid sites originated from the Nb–OH–Nb bridge bonds$^{27-29}$, and the abundance and intensity of Bronsted acid sites could be raised obviously because Nb$_2$O$_5$ loading increase could lead to the formation of three-dimensional polymerized niobia species. Nb$_2$O$_5$ crystallization caused a rapid decline of the L and B acid sites of Nb$_2$O$_5$-γ-Al$_2$O$_3$ nanofiber, which indicated that the crystalline phase Nb$_2$O$_5$ has few L and B acid sites$^{30}$.

It is known that the conversion of glucose to 5-HMF is a two-step reaction. The first step is the isomerization of glucose to fructose catalyzed by Lewis acid and the second step is the dehydration of generated fructose from glucose to 5-HMF under Bronsted acid conditions$^{31}$. Herein, Nb$_2$O$_5$ loading increase could lead to the formation of two-dimensional polymerized niobia species, three-dimensional polymerized niobia species and crystallization, which influenced the distribution and quantity of the Lewis acid sites and Bronsted acid sites. On one hand, the Lewis acid site Nb$^{5+}$ play a key role on the isomerization of glucose to fructose, and Bronsted acid sites are more active in the dehydration of generated fructose to 5-HMF$^{14,32}$. The heterogeneous catalyst with the suitable ratio of Lewis acid sites to Bronsted sites should display an more excellent catalytic performance in the conversion of glucose to 5-HMF in organic solvents$^{33}$. Herein, the γ-Al$_2$O$_3$ nanofibers loaded with 0.5~1 wt% Nb$_2$O$_5$ offers the optimum ratio of Lewis acid sites to Bronsted acid sites, thus they exhibits the best performance in 5-HMF (or furfural) yield from glucose (or xylose) (see Fig. 8). On the other hand, the 1D γ-Al$_2$O$_3$ nanofiber support may play an important role on improving 5-HMF yield. For instance, the active Nb$_2$O$_5$ catalytic centers are decorated on the external surface of γ-Al$_2$O$_3$ fibers, improving the direct interaction between the active sites and glucose. The randomly oriented niobia species form a large interconnected void (10~20 nm), which made glucose to well contact with the active sites$^{34}$.

The catalyst re-usability was studied using 1 wt% Nb$_2$O$_5$-γ-Al$_2$O$_3$ nanofibers. After reaction, the catalyst was separated from DMSO by centrifugation, and then washed with deionized water and ethanol, dried at 80 ℃ under vacuum before the next run. From Figs 9 and 10, it is found that the XRD pattern and morphology of catalyst well maintain after one recycle. However, the color of catalyst changed from white to brown, which maybe result from an accumulation of humans on the surface of catalyst$^{12}$, which caused some decrease of catalytic performance.

Figure 3. SEM images of γ-Al$_2$O$_3$ with different Nb$_2$O$_5$ loadings: (a) 0 wt%; (b) 1 wt%; (c) 3 wt%; (d) 3.4 wt%; (e) 4.7 wt%; (f) 9.4 wt%; (g) 26.6 wt%; (h) 33.9 wt%.
Conclusions

Nb$_2$O$_5$-γ-Al$_2$O$_3$ nanofibers have been prepared by facile incipient-wetness impregnation method to catalyze the conversion of glucose (fructose and xylose as well) into 5-HMF. It is found that Nb$_2$O$_5$-γ-Al$_2$O$_3$ nanofibers...
can efficiently promote the dehydration of glucose, fructose and xylose. The sample with 0.5~1 wt% Nb$_2$O$_5$ load exhibits the best performance in glucose conversion into 5-HMF, and 5-HMF yield come up to 55.9~55.9%. This

**Figure 6.** Effect of different Nb$_2$O$_5$ loadings on γ-Al$_2$O$_3$ on the yield of: 5-HMF from the dehydration of glucose at for 4 hours (A) and fructose for 5 hours (B), furfural from the dehydration of xylose for 6 hours (C) at 150 °C.

**Figure 7.** The states of niobia species dispersed on the γ-Al$_2$O$_3$ nanofibers.
excellent performance of 0.5~1 wt% Nb₂O₅-γ-Al₂O₃ nanofibers in glucose conversion into 5-HMF is ascribed to the synergistic effect of suitable ratio of Lewis acid sites to Brønsted acid sites on Nb₂O₅-γ-Al₂O₃ nanofibers.

**Methods**

**Synthesis of supports.** All commercially available chemicals and solvents are of reagent grade and were used as received without further purification. The γ-Al₂O₃ nanofibers were prepared by the hydrothermal method. A buffer solution prepared by diluting ammonia (40 mL, 25%) with deionized water to 10%, was used as the precipitation agent. Besides, 30 g Al(NO₃)₃·9H₂O was dissolved in 50 mL deionized water. The buffer solution was loaded into the solution of Al(NO₃)₃ by dropwise under vigorous stirring until the solution became milky and the initial pH of the mixture ranged from 2.0 to 5.0. The resulting uniform solution was then transferred into a PTFE-lined autoclave and heated in an oven at 200 °C for 48 h. Thereafter, the obtained precipitate was washed several times with deionized water and ethanol by centrifugation, and the obtained precipitate was dried overnight at 55°C and subsequently calcined in air at 600°C for 5 h to obtain γ-Al₂O₃ nanofibers.
Preparation of catalysts. Nb$_2$O$_5$-\(\gamma\)-Al$_2$O$_3$ nanofibers were prepared by the incipient-wetness impregnation method where NbCl$_5$ was selected as the niobium precursor and incorporated into \(\gamma\)-Al$_2$O$_3$ nanofibers. Firstly, the appropriate amount of NbCl$_5$ was mixed together with the prepared \(\gamma\)-Al$_2$O$_3$ nanofibers (0.5 g) in order to obtain catalysts with the controlled Nb$_2$O$_5$ loading (wt% = Nb$_2$O$_5$/[Nb$_2$O$_5$ + Al$_2$O$_3$]) equal to 1, 3, 5, 10, 15, 30 and 40, respectively. Secondly, the deionized water containing the oxalate with the mole about five times of the mole of NbCl$_5$ was introduced and then the mixture was kept at room temperature for 48 h. Thirdly, the mixture was dried at 100 °C for 24 h to obtain the different Nb$_2$O$_5$-\(\gamma\)-Al$_2$O$_3$ catalysts.

Catalytic activity. The glucose, fructose and xylose dehydration reactions were performed in a 15 mL sealed tube (thick walled pressure bottle from Beijing synthware glass) under magnetic stirring. In a typical run, glucose (450 mg), catalyst (45 mg) and DMSO (2.5 ml) were loaded into sealed tube which was then immersed into the preheated oil bath and stirred for a required time. After reaction, the mixture cooled to room temperature naturally, and then the internal standard substances (1-chloronaphthalene) was added into reaction mixture which was further diluted by methanol. The filtered solution was analyzed by HPLC. The dehydration reaction procedures of fructose and xylose were similar to that of glucose, and the glucose (450 mg) was replaced by fructose (450 mg) or xylose (375 mg), respectively.

General Information. The surface morphology and composition of catalysts were characterized by field emission scanning electron microscopy (SEM, JSM-7001F, JEOL, Tokyo, Japan). High-resolution transmission electron microscopy (HRTEM) images were taken on a JEOL JEM-2100F field emission electron microscope under an accelerating voltage of 200 kV equipped with an energy-dispersive X-ray spectroscopy (EDX) instrument (Quantax-STEM, Bruker). The phases structures of catalysts were characterized by powder X-ray diffraction (XRD) analysis using an X-ray diffractometer (DX-2700, China) with Ni-filtered Cu K$_\lambda$ under an accelerating voltage of 200 kV equipped with an energy-dispersive X-ray spectroscopy. Electron microscopy (HRTEM) images were taken on a JEOL JEM-2100F field emission electron microscope. The surface morphology and composition of catalysts were characterized by field emission scanning electron microscopy (SEM, JSM-7001F, JEOL, Tokyo, Japan). High-resolution transmission electron microscopy (HRTEM) images were taken on a JEOL JEM-2100F field emission electron microscope under an accelerating voltage of 200 kV equipped with an energy-dispersive X-ray spectroscopy (EDX) instrument (Quantax-STEM, Bruker). The phases structures of catalysts were characterized by powder X-ray diffraction (XRD) analysis using an X-ray diffractometer (DX-2700, China) with Ni-filtered Cu K$_\lambda$ radiation (\(\lambda = 1.5406 \text{Å}\)) at 40 kV and 30 mA with a fixed slit, ranging from 10 to 80°. Surface areas were determined by low temperature N$_2$ adsorption performed at 77 K, on a 3H-2000PS2 analysis instrument, after pretreatment performed for 8 h at 150 °C under vacuum. The BET (Brunauer-Emmet-Teller) method was used to derive surface areas from the resulting isotherms. Pore size distributions were obtained from analysis of the adsorption branch of the isotherms using Barrette Joiner Halenda (BJH) method. The Raman spectra of these catalysts were determined by Renishaw inVia plus from 200 to 2000 cm$^{-1}$. The Nb$_2$O$_5$ contents of Nb$_2$O$_5$-\(\gamma\)-Al$_2$O$_3$ nanofibers were characterized by Optima 8000 (ICP-AES). The 5-HMF and furfural were determined by high performance liquid chromatography (HPLC) (L6, China) fitted with a Pgrandsil-TC-C18 column and the ultraviolet detectors for 5-HMF and furfural respectively, and then the internal standard substances (1-chloronaphthalene) was added into reaction mixture which was further diluted by methanol. The filtered solution was analyzed by HPLC. The dehydration reaction procedures of fructose and xylose were similar to that of glucose, and the glucose (450 mg) was replaced by fructose (450 mg) or xylose (375 mg), respectively.

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Author Contributions
The experiment and characterization work is done by H.J., X.Z., C.L. and Y.W. D.Y., Z.L. and X.Y. wrote the main manuscript text and prepared figures All authors reviewed the manuscript.

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