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## PAPER

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# Sequential dehydration of sorbitol to isosorbide over acidified niobium oxides†

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Isosorbide is a bio-based functional diol, which is prepared by sequential dehydration of sorbitol and widely used in plasticizers, monomers, solvents or pharmaceuticals. In this study, a variety of acidified  $Nb_2O_5$  catalysts were prepared and used for the sequential dehydration of sorbitol to isosorbide. Acidification can effectively regulate the surface acidity of catalysts, which was measured by pyridine infrared spectroscopy and  $NH_3$ -TPD analysis. The catalytic performance was related to the surface acidity, including the reaction temperature and the amount of catalysts. After optimization of reaction conditions, the yield of isosorbide reached 84.1% with complete sorbitol conversion during reaction at 150 °C for 3 h over 2 M sulfuric acid modified  $Nb_2O_5$ . Finally, the reaction mechanism regarding the role of Lewis acid sites was discussed. This study is of great significance for further development of an efficient catalytic system for the dehydration of carbohydrates to isosorbide.

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## Introduction

The depletion of fossil resources and environmental pollution have stimulated the need for new alternative resources.<sup>1</sup> Sorbitol is one of the platform chemicals derived from biomass that can be used for the production of various chemicals.<sup>2</sup> For example, the dehydration of sorbitol could lead to the formation of isosorbide, which is widely used in plasticizers, monomers, solvents or pharmaceuticals.<sup>3,4</sup> Isosorbide is prepared by sequential dehydration reactions of sorbitol with 1,4-sorbitan as the intermediate (Scheme 1).<sup>5</sup> Isosorbide is produced commercially by sulfuric acidcatalyzed dehydration of sorbitol under decompression conditions. Other homogeneous catalysts, such as hydrochloric acid and organic acids, are also efficient for the conversion of sorbitol.<sup>5,6</sup>

However, mineral or organic acids have many inevitable shortcomings, such as equipment corrosion, difficult continuous production, tedious product separation, catalyst reuse procedure, *etc.*<sup>7</sup> Solid acid is environmentally friendly and easy to separate from a reaction system, and can be reused. Since 1940s, researchers have been engaged in the



H-beta zeolite with a Si/Al ratio of 75 could give promising vields of isosorbide in the range of 76-80% at 127 °C under heterogeneous reaction system.<sup>14,15</sup> Metal phosphates usually need high temperatures (>200 °C) to obtain isosorbide yields over 50%.<sup>16</sup> However, both their structure and surface acidity are vulnerable to high reaction temperatures, especially in the presence of water. The group VB pentoxides are very attractive catalysts in water-involved reactions due to their strongly acidic and highly water-resistant properties.<sup>17</sup> Zhang et al. prepared a series of phosphoric acid modified hydroxides  $(Ta_2O_5 \cdot nH_2O)$  and used them for the dehydration of sorbitol to isosorbide.<sup>18</sup> The introduction of phosphate could transform hydrated titan oxide into a new crystalline phase. By comparing the activities using different P/Ta molar ratios (0.4, 0.8, 1, and 1.2), it was concluded that 0.8 was the optimum P/Ta molar ratio with a high amount of total acid sites essential for the dehydration reactions. Using P/Ta (0.8) as the catalyst and reacting at 225 °C for 6 h, the yield of



Scheme 1 Sequential dehydration of sorbitol to isosorbide.

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isosorbide reached 48.3% with almost complete conversion of sorbitol.

Niobium and tantalum are vanadium paragroup elements with the highest and the most stable valence state of +5. Due to their similar radius, they have similar properties. The acid strength of Nb<sub>2</sub>O<sub>5</sub> loaded with  $H_3PO_4$  can be significantly improved,<sup>19</sup> and its acidity can still be effectively maintained in an aqueous environment.<sup>20,21</sup> Through the comparison of different P/NbO ratios, it was found that when it was 2, sorbitol could be completely converted and gave the highest yield of isosorbide (62.49%). However, the synergetic effect of Brønsted acid and Lewis acid sites on solid acids was not clarified.

In this study, readily prepared  $Nb_2O_5$  was further modified *via* acidification by various kinds of liquid acids and used for the sequential dehydration of sorbitol to isosorbide. The type and proportion of acid sites on the surface of the catalyst were measured by pyridine infrared spectroscopy, and the surface acidity and total acid content of the catalyst were measured by  $NH_3$ -TPD. The effects of the acid type, acid concentration, acidification temperature, reaction temperature and amount of the catalyst on the yield of isosorbide were discussed. Furthermore, a possible reaction mechanism emphasizing the important role of Lewis acid sites was proposed.

### Results and discussion

#### Acidity and catalytic performance of acidified Nb<sub>2</sub>O<sub>5</sub> catalysts

The results of NH<sub>3</sub>-TPD showed that there were both strong and medium acid centers on the surface of the catalyst acidified by phosphoric acid. Only the strong acid center appeared on the surface of the catalyst acidified by sulfuric acid, but no acidity was detected on the surface of the catalyst acidified by nitric acid, which was consistent with the results of pyridine infrared spectroscopy. It could be possibly explained that the hydrogen ion on the surface of the catalyst combined with the residual nitrate to form HNO<sub>3</sub> that desorbed during the process of heating or vacuum treatment. This hypothesis was credible considering that the vacuum degree during the reaction was less than 5 kPa, which was consistent with the characterization process. The samples acidified with sulfuric acid had the highest amount of total acid sites (0.5781 mmol g<sup>-1</sup>), followed by those acidified with phosphoric acid (0.4608 mmol  $g^{-1}$ ) and nitric acid (0.3413 mmol  $g^{-1}$ ).

The surface acidity of the catalysts was modified by acid treatment. Pyridine FTIR and  $NH_3$ -TPD were used to determine the surface acidity of the catalysts (Fig. 1). Meanwhile, the catalytic activity was related to the surface acidity. Phosphoric acid, nitric acid and sulfuric acid were used during the acidification procedure. Because the optimal reaction temperature was observed to be 150 °C according to the following section for reaction condition optimization, the pyridine desorption temperature was selected at the same temperature. The pyridine FTIR spectra showed that the catalyst



Fig. 1 (a) NH<sub>3</sub> profiles and (b) FTIR spectra of different acid modified Nb<sub>2</sub>O<sub>5</sub> catalysts in the fingerprint domain after pyridine sorption and evacuation at 150 °C.

only exhibited Brønsted acidity (1540 cm<sup>-1</sup>) after phosphoric acid acidification. However, the catalyst after sulfuric acid acidification showed obvious Lewis acidity (1450 cm<sup>-1</sup>). Nitric acid acidification cannot enhance the surface acidity of the catalyst, and similar spectra of pyridine desorption to those of the untreated Nb<sub>2</sub>O<sub>5</sub> sample were obtained. The relative Brønsted and Lewis acid site ratio could be obtained by integrating the areas under the bands at 1540 cm<sup>-1</sup> and 1450 cm<sup>-1</sup>, while taking the extinction coefficients into account. Using the values of  $\varepsilon_{\text{Brønsted}} = 1.88$  and  $\varepsilon_{\text{Lewis}} = 1.42$ ,<sup>22</sup> the B/L ratio obtained by sulfuric acid acidification was 3.0.

The catalysts obtained by acidifying Nb<sub>2</sub>O<sub>5</sub> with 2 M sulfuric acid, nitric acid and phosphoric acid at 60 °C for 3 h were labeled as SO4<sup>2-</sup>/Nb2O5, NO3<sup>-</sup>/Nb2O5 and PO4<sup>3-</sup>/Nb2O5, respectively. Their catalytic performance for sorbitol dehydration was evaluated, and the results are shown in Table 1. After 8 h, the conversion of sorbitol was 60.4%, the yield of 1,4-sorbitan was 50.6%, and the yield of isosorbide was only 7.7% over NO3-/Nb2O5. It is worth mentioning that Table 1 gives not only the final yield of the intermediate product but also the highest yield of the intermediate product during the reaction. It was showed that NO<sub>3</sub>/Nb<sub>2</sub>O<sub>5</sub> could not efficiently catalyze the subsequent dehydration of sorbitol to 1,4-sorbitan. Therefore, there was a plateau for the yield of the intermediate. The samples acidified with phosphoric acid and sulfuric acid could completely convert sorbitol. The yield of the intermediate over PO<sub>4</sub><sup>3-</sup>/Nb<sub>2</sub>O<sub>5</sub> was 82.5%, while that over  $SO_4^{2-}/Nb_2O_5$  was 73.7%, which was significantly higher than that over NO<sub>3</sub>/Nb<sub>2</sub>O<sub>5</sub>, suggesting

Table 1 Acidity and catalytic performance of the acidified Nb<sub>2</sub>O<sub>5</sub> samples

Entry	Catalysts	Total acid sites (mmol g <sup>-1</sup> )	B/L ratio	Conv. (%)	1,4-Sorbitan Highest yield (%)	1,4-Sorbitan Final yield (%)	Isosorbide Yield (%)
1	Nb <sub>2</sub> O <sub>5</sub>		_	65.0	51.0	35.2	6.5
2	$NO_3^{-}/Nb_2O_5$	0.3413	_	60.4	50.6	50.6	7.7
3	$2.0 \text{ M}-\text{SO}_4^{2-}/\text{Nb}_2\text{O}_5$	0.5781	3.04	100	73.7	14.5	84.1
4	$PO_4^{3-}/Nb_2O_5$	0.4608	_	100	82.5	64.4	33.7
5	$0.5 \text{ M-SO}_4^{2-}/\text{Nb}_2\text{O}_5^a$	0.1492	7.14	95.2	92.2	69.7	27.8
6	$1.0 \text{ M-SO}_4^{2^-}/\text{Nb}_2\text{O}_5$	0.3723	5.28	96.8	80.1	40.9	58.1
7	$1.5 \text{ M-SO}_4^{2-}/\text{Nb}_2\text{O}_5$	0.4586	4.20	97.9	85.6	33.2	60.9
8	2.5 M-SO <sub>4</sub> <sup>2-</sup> /Nb <sub>2</sub> O <sub>5</sub>	0.4800	4.37	97.9	87.0	18.8	69.0
9	20 °C-SO <sub>4</sub> <sup>2-</sup> /Nb <sub>2</sub> O <sub>5</sub>	0.2961	3.80	100	60.4	40.5	54.8
10	40 °C-SO <sub>4</sub> <sup>2-</sup> /Nb <sub>2</sub> O <sub>5</sub> <sup>b</sup>	0.4409	3.37	100	58.1	30.2	61.0
11	80 °C-SO <sub>4</sub> <sup>2-</sup> /Nb <sub>2</sub> O <sub>5</sub>	0.3146	6.02	100	68.9	20.3	66.2

<sup>*a*</sup> *n* M-SO<sub>4</sub><sup>2-</sup>/Nb<sub>2</sub>O<sub>5</sub>, where *n* refers to the acid concentration. <sup>*b*</sup> *X* °C-SO<sub>4</sub><sup>2-</sup>/Nb<sub>2</sub>O<sub>5</sub>, where *X* refers to the acid treatment temperature. The acidification temperatures were 60 °C, except for the last three samples.

that the PO<sub>4</sub><sup>3-</sup>/Nb<sub>2</sub>O<sub>5</sub> and SO<sub>4</sub><sup>2-</sup>/Nb<sub>2</sub>O<sub>5</sub> samples could greatly improve the dehydration efficiency of sorbitol. Moreover, with the extension of reaction time, the yield of the intermediate decreased gradually, indicating that further dehydration reactions occurred. Obviously, in the  $PO_4^{3-}/$ Nb<sub>2</sub>O<sub>5</sub> catalyzed reaction system, the final yield of the intermediate product was still as high as 64.4%, and the yield of isosorbide was only 33.7%. Fortunately, the final yield of the intermediate product decreased to 14.5%, and the yield of isosorbide reached 84.1%. The crystal structure varied slightly comparing the XRD patterns of the different acid modified Nb<sub>2</sub>O<sub>5</sub> samples (Fig. S1<sup>†</sup>). After sulfation treatment, the specific surface area increased significantly from 1.8 to 8.6  $m^2 g^{-1}$ , which was also beneficial for the heterogeneously catalysed dehydration of sorbitol. Compared with that of the carbonaceous solid acid catalyst reported by Zhang et al., the preparation method of the current catalyst was simpler, and the yield of isosorbide was higher (84.1% vs. 72.1%).<sup>23</sup> Clearly, the synthesized sulphated niobia was more efficient for the dehydration of sorbitol to isosorbide compared with the sulphated zirconia.<sup>24</sup> Therefore, the following study would focus on the optimization of acidification conditions and reaction conditions of sulfuric acid modified Nb2O5 samples.

Acidification conditions, such as acid concentration, temperature and reaction time, were optimized. Firstly, Nb<sub>2</sub>O<sub>5</sub> was acidified with 0.5–2.5 M sulfuric acid at 60 °C for 3 h. The results of pyridine IR and NH<sub>3</sub>-TPD showed that the surface acid properties of Nb<sub>2</sub>O<sub>5</sub> could be effectively controlled by changing the concentration of sulfuric acid (Fig. 2). Moreover, the relative content of Lewis acid sites increased firstly and then decreased with the increase of the sulfuric acid concentration, resulting in the change of the B/L ratio (Table 1, entries 3, and 5–8). The acidification process could certainly make more Brønsted acid sites on the surface of the Nb<sub>2</sub>O<sub>5</sub> samples; however, both the pyridine FTIR analysis and reaction were conducted under reduced pressure at high temperatures, thus leading to the generation of Lewis acid sites. According to the reaction results shown in Fig. 3, the highest sorbitol conversion and isosorbide yield could be obtained over the 2.0  $M-SO_4^{2-}/Nb_2O_5$  sample, which has the highest Lewis acid sites, while the yield of the intermediate product was the lowest. The highest yield of isosorbide was reached after 6 h. However, the highest yield of isosorbide was reached after 5 h over 2.5  $M-SO_4^{2-}/Nb_2O_5$  and decreased gradually with the extension of the reaction time, indicating the existence of side reactions of isosorbide. In addition, the final yield of the intermediate product was still above 10%, even if the best catalyst was used, indicating that



Fig. 2 (a) NH<sub>3</sub> profiles and (b) FTIR spectra of the sulfuric acid acidified Nb<sub>2</sub>O<sub>5</sub> catalysts in the fingerprint domain after pyridine sorption and evacuation at 150 °C.



Fig. 3 Conversion of sorbitol to isosorbide over the sulfuric acid acidified  $Nb_2O_5$  samples. (a) Conversion of sorbitol, (b) yield of 1,4-sorbitan, and (c) yield of isosorbide (reaction conditions: 5 g sorbitol, 1 g catalyst, 130 °C, 6 kPa).

the dehydration of sorbitol to isosorbide was reversible. That is, the dehydration process was accompanied by hydration reactions, and the reactants could not be completely converted to isosorbide. The  $NH_3$ -TPD results showed that with the increase of sulfuric acid concentrations, the surface acid strength and the amount of total acid sites increased firstly and then decreased. When the sulfuric acid concentration was 2 M, the acid strength and the amount of total acid sites of the catalyst were the highest, giving the best catalytic performance. Therefore, it was preliminarily proposed that the higher the acid strength and the amount of total acid sites and Lewis acid sites on the surface of the catalyst, the more favorable the dehydration of sorbitol to isosorbide. View Article Online Catalysis Science & Technology

In the investigated temperature range, the lowest B/L ratio (3.04) and the highest amount of total acid sites were obtained at 60 °C. It can be seen from Fig. 4a that Nb<sub>2</sub>O<sub>5</sub> acidified at 60 °C had the highest surface acid strength. The acidification temperature could effectively modify the surface B/L ratio of the catalyst (Fig. 4b). Obviously, the conversion rate of sorbitol accelerated gradually with the increase of acidification temperature. The catalyst acidified at 60 °C could completely convert sorbitol in the shortest time, and then its catalytic activity decreased with the increase of acidification temperature (Fig. 5). The yield of the intermediate (1,4-sorbitan) still followed the trend of increasing first and then decreasing. The yield of isosorbide increased from 20 °C to 60 °C. When the acidification temperature was 60 °C, the yield of isosorbide reached 84.1% after 6 h, and remained unchanged afterwards. When the acidification temperature was increased to 80 °C, the highest yield of isosorbide decreased dramatically, indicating that the optimum acidification temperature was 60 °C. However, comparing the catalytic performance of the catalysts with different amounts of total acid sites as shown in Table 1, we found that there was no positive correlation between sorbitol conversion and total acid sites of the catalysts, for example, entry 7 vs. entry 9. In this study, the yield of isosorbide is supposed to be dominated by the Lewis acid sites. The higher



Fig. 4 (a)  $NH_3$  profiles and (b) FTIR spectra of the sulfuric acid acidified  $Nb_2O_5$  catalysts at different temperatures in the fingerprint domain after pyridine sorption and evacuation at 150 °C.





Fig. 5 Conversion of sorbitol to isosorbide over the sulfuric acid acidified  $Nb_2O_5$  samples at different temperatures. (a) Conversion of sorbitol, (b) yield of 1,4-sorbitan, and (c) yield of isosorbide (reaction conditions: 5 g sorbitol, 1 g catalyst, 130 °C, 6 kPa).

Fig. 6 Conversion of sorbitol to isosorbide over the sulfuric acid acidified Nb<sub>2</sub>O<sub>5</sub> samples with different acidification times. (a) Conversion of sorbitol, (b) yield of 1,4-sorbitan, and (c) yield of isosorbide (reaction conditions: 5 g sorbitol, 1 g catalyst, 130 °C, 6 kPa).

the amount of Lewis acid sites was, the more favorable the dehydration reaction of intermediate to isosorbide was.

The conversion rate of sorbitol increased slightly with the increase of acidification time from 1 h to 3 h and decreased afterwards with the prolongation of acidification time (Fig. 6a). When the acidification time was 3 h, the conversion rate of 1,4-sorbitan and the formation rate of isosorbide were both the fastest (Fig. 6b and c).

#### **Optimization of reaction conditions**

The effect of catalyst amounts and reaction temperature were further explored. Fig. 7 shows the effect of different amounts of catalyst on the yield of isosorbide. Increasing the amount of catalyst could facilitate the reaction; however, an excessive catalyst amount led to fast dehydration of sorbitol, resulting into decreased yield of isosorbide due to the formation of humins. Therefore, the optimal amount of the catalyst was determined to be 20 wt%. With the increase of reaction temperatures from 130 °C to 150 °C (Fig. 8), the yield of isosorbide reached the highest in 3 h. It is worth mentioning that the yield of isosorbide decreased obviously when the reaction temperature was above 150 °C. The dark brown reaction solution indicated further dehydration or polymerization of the products.

To verify the reusability of the catalyst, five consecutive reactions were conducted with  $2.0 \text{ M-SO}_4^{2-}/\text{Nb}_2\text{O}_5$  (Fig. 9).

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Fig. 7 Effect of the catalyst dosage on the conversion of sorbitol to isosorbide: (a) conversion of sorbitol, (b) yield of 1,4-sorbitan, and (c) yield of isosorbide (reaction conditions: 5 g sorbitol, 130 °C, 6 kPa).

**Fig. 8** Effect of reaction temperature on the conversion of sorbitol to isosorbide: (a) conversion of sorbitol, (b) yield of 1,4-sorbitan, and (c) yield of isosorbide (reaction conditions: 5 g sorbitol, 1 g catalyst, 6 kPa).

Between runs, the catalyst was regenerated by washing with deionized water, filtration, and further acidification. Complete conversion of sorbitol was observed without a significant loss of the isosorbide yield. The yield of 1,4-sorbitan increased only slightly to 18.7%. There is no significant change in the surface acidity (Fig. S2†), and the crystalline structure was maintained even after the fifth run (Fig. S3†). Therefore, the catalyst was recyclable.

## Proposed mechanism

Theoretically, sorbitol ( $C_6H_{14}O_6$ ) is firstly dehydrated into 1,4-sorbitan ( $C_6H_{12}O_5$ ) by removing one molecule of water, and then 1,4-sorbitan is further dehydrated into isosorbide

by removing one more molecule of water (Scheme 1). The kinetic study showed that the dehydration of sorbitol under atmospheric pressure catalyzed by acids was a pseudo first order reaction. The primary hydroxyl group at the  $C_1$  or  $C_6$  position was prone to be protonated firstly, and then replaced by  $S_N2$  through the  $C_4$ -OH or  $C_3$ -OH group to obtain a *trans* linked tetrahydrofuran ring.<sup>25</sup> Generally, the interaction of the catalyst with sorbitol is stronger than that with 1,4-sorbitan, which makes it easier for a Brønsted acid catalyst to form adducts with sorbitol than with 1,4-sorbitan. This is also the key factor that limits the dehydration rate of 1,4-sorbitan, which makes the dehydration of 1,4-sorbitan the rate-determining step.<sup>26</sup> Indeed, in this study, the final yields of the intermediate in many cases were higher than



Fig. 9 Results of the reusability study (reaction conditions: 5 g sorbitol, 1 g 2.0  $M\text{-SO}_4^{2-}/Nb_2O_5,\,130$  °C, 6 kPa, 3 h).

50% (Table 1, entry 4 and 5). The high yield of isosorbide obtained over  $SO_4^{2-}/Nb_2O_5$  resulted from the profound dehydration of 1,4-sorbitan.

It is reported that both Brønsted and Lewis acid sites can function during the first dehydration step of sorbitol, while Brønsted acid sites can catalyze the further dehydration of 1,4-sorbitan to isosorbide more effectively than Lewis acid sites. However, in this study, the yield of isosorbide was significantly increased in the presence of Lewis acid sites. The synergic catalytic effect of Lewis acid sites and Brønsted acid sites was previously reported with a 70% yield of isosorbide at 160 °C.27 On the one hand, Lewis acid can synergistically polarize with the water formed during reaction to form a O-H bond, turning into Brønsted acid sites on the Lewis acid centers to promote the dehydration of 1,4-sorbitan. On the other hand, considering the high vacuum of the reaction system, the induced water during reaction might be taken out simultaneously. Therefore, the Lewis acid sites was supposed to catalyze the dehydration reaction through coordination with the hydroxyl groups of the reactants (Scheme 2, step 1). In the current study, the catalytic activity of the Nb2O5 samples with a certain amount of Lewis acid sites was better than that of pure Brønsted acid catalysts. Therefore, a higher yield of isosorbide might be expected by adjusting the B/L ratio in the catalytic system.



Scheme 2 Proposed reaction mechanism for the dehydration of 1,4-sorbitan to isosorbide.

In addition, due to the hydrogen bond between the  $C_5$ and  $C_6$  hydroxyl groups of 1,4-sorbitan, Brønsted acid preferentially protonated the  $C_5$  hydroxyl group and hindered its dehydration reaction. Therefore, it is suggested that the Lewis acid center may coordinate with the  $C_5$  hydroxyl group, which is beneficial to the protonation of the  $C_6$  hydroxyl group by Brønsted acid sites, leading to the dehydration of 1,4-sorbitan (Scheme 2, step 2). To prove this, dehydration of sorbitol using concentrated sulfuric acid and AlCl<sub>3</sub> were conducted. The yields of isosorbide in the concentrated sulfuric acid catalytic system reached the highest value quickly, and decreased significantly with the extension of reaction time (Fig. 10). The main product of AlCl<sub>3</sub> catalyzed



Fig. 10 Conversion of sorbitol to isosorbide over  $H_2SO_4$  and/or  $AlCl_3$  catalysts. (a) Conversion of sorbitol, (b) yield of 1,4-sorbitan, and (c) yield of isosorbide (reaction conditions: 5 g sorbitol, 0.5 g  $H_2SO_4$ , 0.2 g  $AlCl_3$ , 130 °C, 6 kPa).

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dehydration of sorbitol was 1,4-sorbitan, and the yield of isosorbide was only about 10%. The yield of isosorbide didn't decrease with the extension of time. It was noted that the highest yield of isosorbide co-catalyzed by concentrated sulfuric acid and  $AlCl_3$  was 5% higher than that catalyzed by concentrated sulfuric acid; the decrease of isosorbide yields was obviously slowed down. This indicated that the synergy between the Brønsted and Lewis acid sites is helpful to improve the yield of isosorbide and inhibit side reactions. However, the specific role of Lewis acid needs to be clarified by further research.

## Conclusions

Isosorbide was efficiently obtained from sorbitol over novel acidified Nb<sub>2</sub>O<sub>5</sub> catalysts. Pyridine-FTIR and NH<sub>3</sub>-TPD analysis were used to investigate the surface acidity of the Nb<sub>2</sub>O<sub>5</sub> catalysts. The catalytic performance was closely related to the surface acidity and reaction conditions. The optimum yield of isosorbide reached 84.1% with complete sorbitol conversion during reaction at 150 °C for 3 h. Moreover, the significant role of Lewis acid sites was discussed. This study is of great significance for further development of efficient solid acid catalyzed dehydration of carbohydrates to isosorbide.

## Experimental

All Nb<sub>2</sub>O<sub>5</sub> supports were prepared by precipitation of potassium niobate according to a previously reported method.<sup>28</sup> Specifically, the precipitator was acetic acid in this study. The obtained emulsion is filtered, washed and dried to obtain Nb<sub>2</sub>O<sub>5</sub> supports. Afterwards, an acid solution was used to acidify the Nb<sub>2</sub>O<sub>5</sub> supports in a round-bottom flask using different acid concentrations, reflux temperatures and reaction times. A white powder catalyst was then obtained by filtration, washed with deionized water, and vacuum dried overnight.

The Lewis and Bronsted acid sites were investigated by FTIR using pyridine as the probe molecule.<sup>29</sup> Self-supported wafers less than 20 mg in size were activated in a customized IR cell under vacuum at 150 °C for 1 h before the adsorption procedure. The adsorption of pyridine was performed at room temperature for 45 min before time-controlled evacuation. The backgrounds of all the samples were collected at evacuation temperatures to obtain high SNR spectra. The FTIR spectra were recorded on a Bruker Vertex 70 spectrometer with an MCT detector.

The total acid sites were determined by  $NH_3$ -TPD (OmniStar, MS200) with a thermal conductivity detector. A sample of approximately 100 mg (60 mesh) was initially degassed at 300 °C for 2 h under a constant  $N_2$  flow of 40 mL min<sup>-1</sup>. The sample was cooled, and  $NH_3$  was adsorbed at 90 °C for 30 min to reach saturation. Afterwards, the ammonia supply line was shut off, and  $N_2$  was purged at 30 mL min<sup>-1</sup> for 1 h to remove physically adsorbed  $NH_3$ . The

sample was then heated linearly at a rate of 5  $^{\circ}$ C min<sup>-1</sup> from 90  $^{\circ}$ C to 800  $^{\circ}$ C.

The dehydration of sorbitol was conducted in a roundbottom flask under vigorous stirring in an oil bath. The catalysts were added after melting sorbitol at 130 °C in air. The reaction was performed under vacuum (5 kPa) and was maintained constantly to remove water from the reaction mixture. Samples were withdrawn at selected times, diluted by water and filtered with a 0.2 µm syringe filter prior to analysis. The concentrations of the reactants and product samples were analyzed by HPLC (Agilent 1200, USA) using a Biorad Aminex HPX-87H column at 35 °C with a 0.005 M H<sub>2</sub>SO<sub>4</sub> eluent at a flow rate of 0.5 mL min<sup>-1</sup>. A refractive index detector was employed. The conversion of sorbitol and the yield of sorbitan and isosorbide were determined based on the amount of carbon.<sup>27</sup>

## Conflicts of interest

There are no conflicts to declare.

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