

## Phosphoric Acid Modified Nb<sub>2</sub>O<sub>5</sub>: A Selective and Reusable Catalyst for Dehydration of Sorbitol to Isosorbide

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Niobium oxide (Nb<sub>2</sub>O<sub>5</sub>) and phosphated Nb<sub>2</sub>O<sub>5</sub> were synthesized and used as catalysts for sorbitol dehydration to isosorbide. The characterization results of N<sub>2</sub> adsorption, XRD and NH<sub>3</sub>-TPD revealed that the phosphoric acid modification could well prevent the crystallization of Nb<sub>2</sub>O<sub>5</sub>. And the amorphous phosphated Nb<sub>2</sub>O<sub>5</sub> catalysts kept the relatively large surface area and stable acidity at high calcination temperature. The catalytic results showed that the selectivity to isosorbide could be dramatically enhanced over phosphated Nb<sub>2</sub>O<sub>5</sub>. The excellent catalytic performance with 100.0% sorbitol conversion and 62.5% isosorbide selectivity were obtained over the 0.8P/NBO-400 catalyst. Comparing with Nb<sub>2</sub>O<sub>5</sub> catalysts, phosphated Nb<sub>2</sub>O<sub>5</sub> catalysts regenerated through a simple calcination process showed no significant activity loss after recycling three runs.

**Key Words:** Niobium oxide, Phosphoric acid, Sorbitol, Isosorbide, Dehydration

### Introduction

Isosorbide is a versatile and key intermediate in therapeutics, food additives, surfactants industry and more recently in polyesters<sup>1-3</sup> and polyether.<sup>4</sup> Isosorbide is the only “sugar diol” that is technically produced in large quantities.<sup>5</sup> Hence, it is the only relatively inexpensive diol which is based on renewable resources and is not based on oil or coal chemistry. Currently, isosorbide is produced by heating of D-sorbitol under vacuum and in the presence of an acidic catalyst to result in a stepwise cyclization with elimination of water. Examples of acid catalysts used commercially include mineral acids such as H<sub>2</sub>SO<sub>4</sub>,<sup>6</sup> HCl and H<sub>3</sub>PO<sub>4</sub>.<sup>7</sup> Despite a strong catalytic effect, the use of homogeneous catalyst suffers from drawbacks,<sup>8</sup> such as difficulties in product separation and recovery, equipment corrosion, and having to deal with acid-containing waste. The development of a heterogeneous process, which is both convenient and economically viable, would be of great importance.

The high water solubility of sorbitol, due to the high extents of hydroxyl groups, makes aqueous-phase processing an attractive and necessary step. Among many solid acid catalysts, Nb<sub>2</sub>O<sub>5</sub> has been used as the water tolerant catalysts for various water involving reactions, such as esterification, dehydration, Friedel-Crafts alkylation and polymerization.<sup>9-13</sup> However, Nb<sub>2</sub>O<sub>5</sub> was sensitive to the pretreatment temperature.<sup>9</sup> At the pretreatment temperature above 500 °C, the crystallization of Nb<sub>2</sub>O<sub>5</sub> resulted in the decrease in surface acidity and catalytic activity.<sup>14</sup> This limitation on the temperature restricted the reaction conditions and the possibility for the regeneration of used catalysts *via* simple high temperature calcination. However, the phosphoric acid modification was effective to prevent the crystallization of Nb<sub>2</sub>O<sub>5</sub> and retain the strong acidity.<sup>15</sup> It well meets the heterogeneous catalysis requirement in the aqueous-phase processing, which need stable and active acidity in hydrothermal environ-

ments. Most importantly, the phosphoric acid modification made it possible to regenerate the spent Nb<sub>2</sub>O<sub>5</sub> catalyst by simple air calcination.

This work elucidates the influence of calcination temperature and phosphoric acid modification on the surface structure of Nb<sub>2</sub>O<sub>5</sub> catalysts *via* detailed characterizations. A correlation of texture properties and the catalytic performance of Nb<sub>2</sub>O<sub>5</sub> catalysts in sorbitol dehydration has been provided. The understanding of the effect of the phosphoric acid modification in this system will provide new insights into the catalyst requirements for the dehydration of sorbitol and the key factors in simple catalyst regeneration.

### Experimental

**Catalyst preparation.** Hydrated niobium oxide (Nb<sub>2</sub>O<sub>5</sub>·nH<sub>2</sub>O) supplied by Guangzhou Youyuan Nonferrous Metals Co. Ltd. was dried in the air at 120 °C for 6 h before use. The phosphoric acid modified catalysts were prepared by a method similar to that described by Okazaki S.<sup>15</sup> Briefly, Nb<sub>2</sub>O<sub>5</sub>·nH<sub>2</sub>O (11 g) was immersed in 30 mL phosphoric acid solution with a given concentration (0.25, 0.5, 1, 2, 2.5, 3, 4 mol L<sup>-1</sup>). The suspension of Nb<sub>2</sub>O<sub>5</sub>·nH<sub>2</sub>O was stirred for 48 h and dried in the air at 120 °C. Nb<sub>2</sub>O<sub>5</sub>·nH<sub>2</sub>O and phosphated Nb<sub>2</sub>O<sub>5</sub> were calcined at 300 - 600 °C in the air for 5 h with a heating rate of 2 °C min<sup>-1</sup>. The prepared catalysts were denoted as NBO-x and nP/NBO-x, where n and x represented the P/Nb (molar ratio: 0.1, 0.2, 0.4, 0.8, 1.0, 1.2, 1.6) and calcination temperature, respectively. The catalyst powders were pressed, crushed, and sieved to 30 - 50 mesh before use. The used catalysts were regenerated by calcination at 500 °C in the air for 3 h and tested again for sorbitol dehydration.

**Characterization.** BET surface area, pore volume and average pore diameter were measured by N<sub>2</sub> adsorption at -196 °C with

a Micromeritics ASAP 2020 surface area and porosity analyzer. The samples were pretreated at 200 °C in vacuum for 4 h before analysis.

XRD patterns of the samples were recorded in the 2θ region of 10° - 80° using a Philips X'Pro X-ray diffractometer with Cu Kα irradiation. The X-ray source was operated at 40 kV and 40 mA.

NH<sub>3</sub> temperature programmed desorption (NH<sub>3</sub>-TPD) was carried out with the BEL-CAT-B-82 equipment, which was connected with a thermal conductivity detector. Typically, the sample of 150 mg loaded in the quartz tube was first pretreated with high purity He of 50 mL min<sup>-1</sup> at 150 °C for 45 min. The adsorption of NH<sub>3</sub> was performed at 100 °C in an NH<sub>3</sub>-He (10 vol % NH<sub>3</sub>) mixture for 0.5 h, and then the physically adsorbed NH<sub>3</sub> was purged by high purity He. TPD of ammonia was performed in the He flow by raising the temperature to 700 °C at a rate of 5 °C min<sup>-1</sup> and the NH<sub>3</sub> liberated was detected by on line thermal conductivity detector.

**Catalytic reaction.** The aqueous-phase dehydration of sorbitol was conducted under atmosphere pressure in a vertical fixed-bed quartz reactor (8.3 mm i.d.) using 0.5 g catalyst. The reaction temperature for the Nb<sub>2</sub>O<sub>5</sub> and phosphated Nb<sub>2</sub>O<sub>5</sub> catalysts were 250 °C and 225 °C, respectively. Before the reaction, the catalyst was pretreated at the reaction temperature for 30 min in flowing carrier gas N<sub>2</sub> (30 mL min<sup>-1</sup>). The reaction feed, an aqueous solution containing 10 wt % sorbitol, was introduced into the reaction system using a constant-flow pump. The reaction products were analyzed by HPLC (Dionex Ultimate 3000) equipped with an Aminex HPX-87 H column and differential refractive index detector.

Conversion of sorbitol and selectivity for products were obtained from the following calculations:

$$\text{Sorbitol conversion (\%)} = \frac{\text{Moles of sorbitol reacted}}{\text{Moles of sorbitol in the feed}} \times 100$$

$$\text{Product selectivity (\%)} = \frac{\text{Moles of carbon in a product defined}}{\text{Moles of carbon in sorbitol reacted}} \times 100$$

## Results and Discussion

**Characterization.** Texture properties of Nb<sub>2</sub>O<sub>5</sub> and phosphated Nb<sub>2</sub>O<sub>5</sub> at various calcination temperatures are listed in Table 1. The surface area of Nb<sub>2</sub>O<sub>5</sub> obviously decreased with the increase in calcination temperature. The surface area of Nb<sub>2</sub>O<sub>5</sub> dropped sharply when the calcination temperature was above 400 °C, owing to the crystallization at 550 - 570 °C.<sup>9</sup> After phosphoric acid modification with P/Nb molar ratio at 0.4 and 0.8, the surface area of the samples calcined at 400 °C slightly decreased (from 100.8 to 93.9 m<sup>2</sup> g<sup>-1</sup>) with the increase in P/Nb molar ratio. The surface area of the 1.6P/NBO-400 drastically decreased to 2.9 m<sup>2</sup> g<sup>-1</sup>, which might be due to the phosphoric acid modified Nb<sub>2</sub>O<sub>5</sub> converting to niobium phosphate.<sup>16</sup> This speculation will be elucidated combining with XRD results. The phosphated Nb<sub>2</sub>O<sub>5</sub> calcined at 600 °C (0.4P/NBO-600) main-

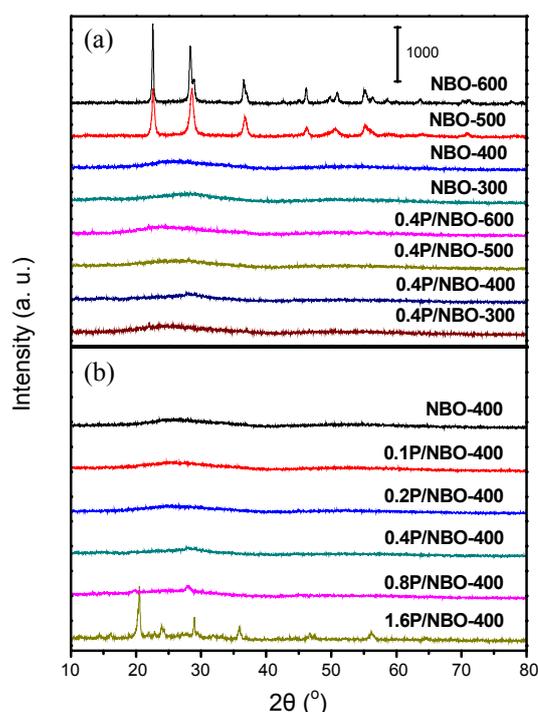
**Table 1.** Texture properties of Nb<sub>2</sub>O<sub>5</sub> and phosphated Nb<sub>2</sub>O<sub>5</sub>

Catalyst	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Average pore diameter <sup>a</sup> (nm)
NBO-300	148.9	0.28	69.5
NBO-400	130.1	0.25	57.2
NBO-500	59.9	0.25	156.7
NBO-600	25.2	0.18	280.5
0.4P/NBO-400	100.8	0.25	83.0
0.4P/NBO-600	74.3	0.23	113.6
0.8P/NBO-400	93.9	0.28	90.9
1.6P/NBO-400	2.9	0.018	439.4

<sup>a</sup>BJH desorption method

tained relatively large surface area (74.3 m<sup>2</sup> g<sup>-1</sup>), compared with the Nb<sub>2</sub>O<sub>5</sub> (NBO-600) (25.2 m<sup>2</sup> g<sup>-1</sup>) calcined at the same temperature. Hence, the phosphoric acid modification significantly suppressed the descending trend at high calcination temperature, suggesting that the phosphoric acid modification with a proper P/Nb molar ratio could effectively preserve the high surface area of catalyst.

The structural changes of Nb<sub>2</sub>O<sub>5</sub> and phosphated Nb<sub>2</sub>O<sub>5</sub> at various calcination temperatures were investigated by XRD method. As shown in Figure 1(a), Nb<sub>2</sub>O<sub>5</sub> calcined at 300 °C and 400 °C were amorphous materials. Intense diffraction peaks appeared in the patterns of Nb<sub>2</sub>O<sub>5</sub> calcined at 500 °C, which accorded well with the T-T phase Nb<sub>2</sub>O<sub>5</sub>. The diffraction peaks at 2θ = 28.4°, 36.7°, 50.5°, 55.3° split into two peaks with the calcination temperature up to 600 °C, indicating a transformation of the pseudo-hexagonal T-T phase to the orthorhombic T phase.<sup>17</sup> It should be emphasized that phosphated Nb<sub>2</sub>O<sub>5</sub> catal-



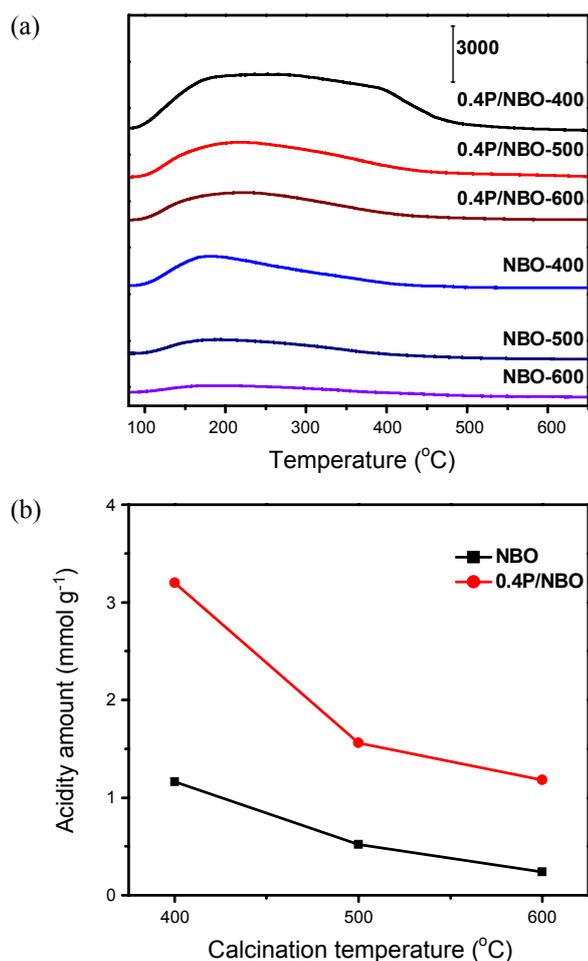
**Figure 1.** XRD patterns of Nb<sub>2</sub>O<sub>5</sub> and phosphated Nb<sub>2</sub>O<sub>5</sub> with different calcination temperatures (a) and P/Nb molar ratio (b).

ysts with P/Nb molar ratio at 0.4 were all amorphous despite the varying calcination temperatures. The XRD patterns of Nb<sub>2</sub>O<sub>5</sub> modified with different P/Nb molar ratios (calcined at 400 °C) are depicted in Figure 1(b). All the samples showed amorphous phase without sharp peaks, except the catalyst 1.6P/NBO-400. Diffraction peaks appeared in the 1.6P/NBO-400 sample might be ascribed to the formation of niobium phosphate. The XRD pattern of 1.6P/NBO-400 was close to that given in PDF card 2004 no. 51-1738 (Nb<sub>1.91</sub>P<sub>2.82</sub>O<sub>12</sub>) and no. 40-0124 (NbPO<sub>5</sub>), demonstrating that the mixture of the two crystalline presented in 1.6P/NBO-400 sample. And the formation of the new crystalline might cause the sharp decrease of the sample's surface area. This was well consistent with the results of surface area in Table 1. The results of XRD patterns suggested that Nb<sub>2</sub>O<sub>5</sub> was sensitive to the calcination temperature.<sup>9,14</sup> The phosphoric acid modification (except for the P/Nb molar ratio at 1.6) would result in the formation of amorphous niobium phosphate on the surface of Nb<sub>2</sub>O<sub>5</sub>, which did not show the corresponding diffraction peaks on XRD patterns.<sup>12</sup> This amorphous niobium phosphate well prevented the Nb<sub>2</sub>O<sub>5</sub> crystallization and reduced the sensitivity of Nb<sub>2</sub>O<sub>5</sub> to calcination temperature. Therefore, phosphated Nb<sub>2</sub>O<sub>5</sub> with a proper P/Nb molar ratio could retain the amorphous phase and relatively high surface area even at the

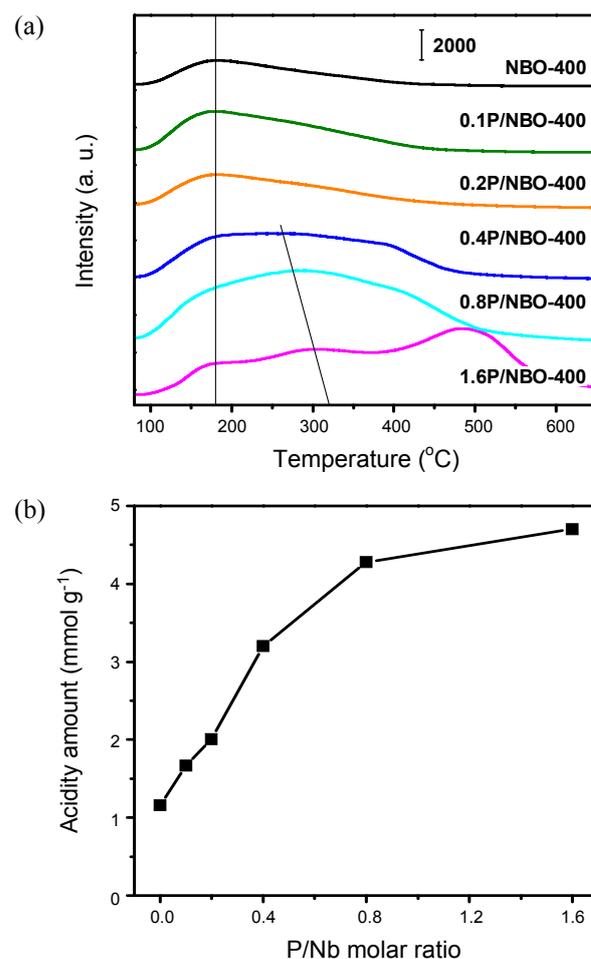
high calcination temperatures.

The acid properties of Nb<sub>2</sub>O<sub>5</sub> and phosphated Nb<sub>2</sub>O<sub>5</sub> were examined by NH<sub>3</sub>-TPD. Figure 2 and Figure 3 reveal the dependence of the acidity on the calcination temperature and P/Nb molar ratio, respectively. Figure 2(a) shows the profiles of NBO-x and 0.4P/NBO-x calcined at 400 - 600 °C. All the NH<sub>3</sub>-TPD profiles displayed one or two wide peak from 100 to approximately 450 °C. Thus, it seemed that there was a broad distribution of acidity in NBO-x and 0.4P/NBO-x. The quantitative results of acidity in Figure 2(b) indicated that the acid amount of NBO-x and 0.4P/NBO-x gradually decreased with the increase of calcination temperature. It should be noted that the 0.4P/NBO-x samples possessed the larger acid amount than the NBO-x, especially at the high calcination temperature.

As can be seen in Figure 3(a) and Figure 3(b), the acid amount of phosphated Nb<sub>2</sub>O<sub>5</sub> increased with the increase in P/Nb molar ratio. It could be found that a new desorption peak appeared at 260, 280, 300 °C on 0.4P/NBO-400, 0.8P/NBO-400 and 1.6P/NBO-400, respectively, indicating a moderate strong acid site formed on the phosphated Nb<sub>2</sub>O<sub>5</sub> surface. That might be due to the formation of the POH groups as Brønsted acids on the surface which were stronger than the NbOH sites.<sup>11</sup> Besides, a peak corresponding to strong acid appeared at around 500 °C in the



**Figure 2.** NH<sub>3</sub>-TPD profiles of Nb<sub>2</sub>O<sub>5</sub> and phosphated Nb<sub>2</sub>O<sub>5</sub> calcined at various temperatures (a); Acid amount as a function of calcination temperature (b).

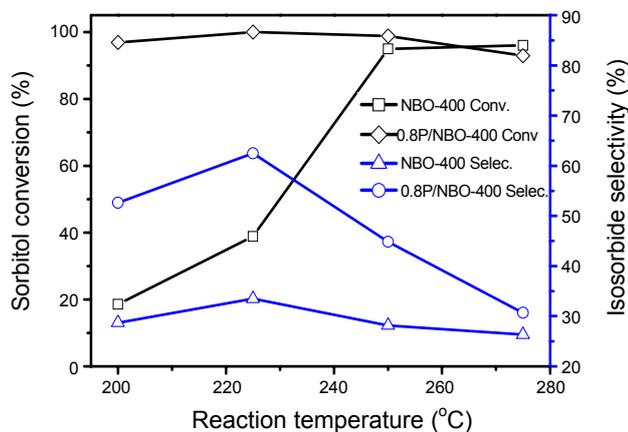


**Figure 3.** NH<sub>3</sub>-TPD profiles of phosphated Nb<sub>2</sub>O<sub>5</sub> at various P/Nb molar ratios (a); Acid amount as a function of P/Nb molar ratio (b).

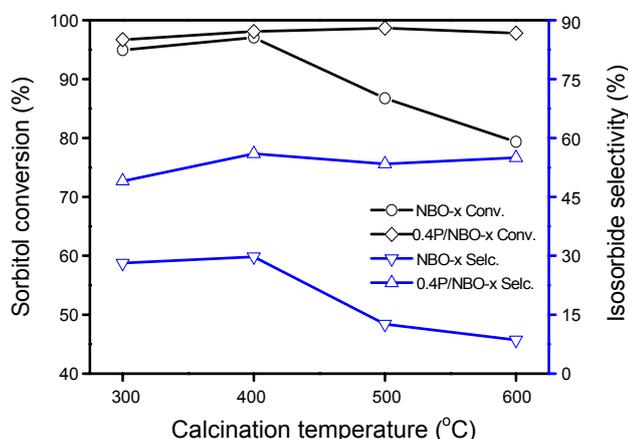
profile of 1.6P/NBO-400. Therefore, the  $\text{NH}_3$ -TPD profiles displayed a wide range of acid strength distribution and a large acid amount. The phosphoric acid modification was the key factor to the formation of moderate strong acid site and maintenance for acid amount even at the high calcination temperature.

It could be summarized from the characterization results that the phosphoric acid modification was determinant to prevent the crystallization on the  $\text{Nb}_2\text{O}_5$  surface and keep it as the amorphous phase. The amorphous surface presented relatively large surface area, which seemed to be crucial to the maintenance of the acid amount of  $\text{Nb}_2\text{O}_5$ , especially at high calcination temperature.<sup>9,14</sup> Moreover, the phosphoric acid modification (the P/Nb molar ratio at 0.4 and above) gave the formation of the stronger acid site than unmodified  $\text{Nb}_2\text{O}_5$ .

**Catalytic reaction.** Effect of reaction temperature on catalytic performance over the  $\text{Nb}_2\text{O}_5$  (NBO-400) and phosphated  $\text{Nb}_2\text{O}_5$  (0.8P/NBO-400) catalysts is depicted in Figure 4. As could be seen, the optimum reaction temperature for the selective dehydration of sorbitol to isosorbide over NBO-400 and 0.8P/NBO-400 was 250 °C and 225 °C, respectively. By comparison with NBO-400, the acid strength and acid amount of 0.8P/NBO-400 catalyst were greatly enhanced, thus the better catalytic performance of 0.8P/NBO-400 catalyst could be realized at a lower temperature (225 °C).



**Figure 4.** Effect of reaction temperature on catalytic performance of  $\text{Nb}_2\text{O}_5$  and phosphated  $\text{Nb}_2\text{O}_5$ .



**Figure 5.** Effect of calcination temperature on catalytic performance of  $\text{Nb}_2\text{O}_5$  and phosphated  $\text{Nb}_2\text{O}_5$ .

The catalytic performance of  $\text{Nb}_2\text{O}_5$  and phosphated  $\text{Nb}_2\text{O}_5$  calcined at different temperatures has been shown in Figure 5. The sorbitol conversion over NBO- $x$  catalysts was high at low calcination temperature (300 and 400 °C), but it dropped from 97.1 to 79.3% with the calcination temperature above 500 °C. The similar trend was observed on the isosorbide selectivity (from 29.8 to 8.6%). Comparing to the  $\text{Nb}_2\text{O}_5$  catalysts, the phosphated  $\text{Nb}_2\text{O}_5$  (0.4P/NBO- $x$ ) exhibited remarkably improved catalytic performance for sorbitol dehydration, over which 56.0% isosorbide selectivity could be gained at a 98.1% sorbitol conversion. It demonstrated that the phosphoric acid modification had an important influence on catalytic performance. Furthermore, sorbitol conversion and isosorbide selectivity kept steadily at a high level with increase of the calcination temperature, suggesting that the catalytic performance of phosphated  $\text{Nb}_2\text{O}_5$  was not sensitive to the calcination temperature. Combining with the results of  $\text{NH}_3$ -TPD and surface area, the better catalytic performance over 0.4P/NBO- $x$ , especially at the high calcination temperature, could be ascribed to the higher acid amount, stronger acid site and larger surface area.

Table 2 reveals the effect of P/Nb molar ratio on the catalytic performance of phosphated  $\text{Nb}_2\text{O}_5$ . All the tested catalysts had high catalytic activity that the conversion of sorbitol was 97.1% at least. The selectivity for isosorbide continuously increased from 29.8 to 62.5% while P/Nb molar ratio from 0 to 0.8, whereas the selectivity for 1,4-sorbitan decreased from 8.4 to 0.5%. It has been reported that 1,4-sorbitan was the intermediate during the dehydration of sorbitol to isosorbide. The selectivity to 1,4-sorbitan decreased with the increase of the isosorbide selectivity.<sup>18,19</sup> The catalytic performance of 1.6P/NBO-400 dropped slightly, owing to the low surface area, excessively strong acidity and fast deactivation in the reaction. The catalysts, including 0.8P/NBO-400, 1.0P/NBO-400 and 1.2P/NBO-400, exhibited the similar catalytic performance, which could be considered as the optimum catalysts in this system. The selectivity to isosorbide over phosphated  $\text{Nb}_2\text{O}_5$  improved with increasing P/Nb molar ratio, in well agreement with the increase in the acid amount and acid strength from the  $\text{NH}_3$ -TPD results. This result indicated that the moderate strong acid site on the catalysts (from 0.4P/NBO-400 to 1.2P/NBO-400) more effectively catal-

**Table 2.** Effects of P/Nb molar ratio on catalytic performance of phosphated  $\text{Nb}_2\text{O}_5$

Catalyst	Conversion (%)	Selectivity (%)		
		Isosorbide	1,4-Sorbitan	others <sup>a</sup>
NBO-400	97.1	29.8	8.4	61.9
0.1P/NBO-400	98.5	35.1	7.0	57.9
0.2P/NBO-400	98.4	43.9	5.4	50.7
0.4P/NBO-400	98.1	56.0	4.6	39.5
0.8P/NBO-400	100.0	62.5	0.5	37.1
1.0P/NBO-400	99.8	62.1	0.1	37.8
1.2P/NBO-400	99.7	62.5	0.1	37.4
1.6P/NBO-400	98.4	47.4	3.5	49.0

<sup>a</sup>Selectivity for others = 100-total selectivity for all identified products; other products mainly include coke and unknowns. Reaction condition: Sorbitol feedstock, 10 wt %;  $F = 2.4 \text{ mL h}^{-1}$ ;  $\text{N}_2$  flow rate,  $30 \text{ mL min}^{-1}$ ; catalyst, 0.5 g; TOS, 5 h; Temperature, 250 and 225 °C for  $\text{Nb}_2\text{O}_5$  (NBO-400) and phosphated  $\text{Nb}_2\text{O}_5$  (nP/NBO-400), respectively.

**Table 3.** Catalytic performances of sorbitol dehydration over regenerated catalysts

Catalyst	Conversion (%)	Selectivity (%)		
		Isosorbide	1,4-Sorbitan	others <sup>d</sup>
0.8P/NBO-400 <sup>a</sup>	100.0	62.5	0.5	37.1
0.8P/NBO-400 <sup>b</sup>	99.9	61.4	1.3	37.4
0.8P/NBO-400 <sup>c</sup>	98.9	59.0	2.9	38.2
NBO-400 <sup>a</sup>	97.1	29.8	8.4	61.9
NBO-400 <sup>b</sup>	84.3	19.5	26.2	45.7

<sup>a</sup>First run; <sup>b</sup>Second run; <sup>c</sup>Third run; <sup>d</sup>Selectivity for others = 100-total selectivity for all identified products; other products mainly include coke and unknowns. Reaction condition: Sorbitol feedstock, 10 wt %; F = 2.4 mL h<sup>-1</sup>; N<sub>2</sub> flow rate, 30 mL min<sup>-1</sup>; Catalyst, 0.5 g; TOS, 5 h; Temperature, 250 and 225 °C for Nb<sub>2</sub>O<sub>5</sub> (NBO-400) and phosphated Nb<sub>2</sub>O<sub>5</sub> (0.8P/NBO-400), respectively.

alyzed the selective dehydration of sorbitol for isosorbide production.<sup>20</sup> And the amorphous surface seemed to be crucial to the maintenance of the acid amount of Nb<sub>2</sub>O<sub>5</sub> and high catalytic performance. Therefore, 0.8P/NBO-400 catalyst exhibited the best catalytic performance, which might be due to the large moderate strong acid amount and the relatively large surface area.

Based on the catalytic results above, the phosphated Nb<sub>2</sub>O<sub>5</sub> was the efficient acidic catalyst to this dehydration reaction. The acidic sites of Nb<sub>2</sub>O<sub>5</sub> and phosphated Nb<sub>2</sub>O<sub>5</sub> involved a Nb=O group, or a hydroxyl group associated with a Nb=O group.<sup>21,22</sup> Thus the high activity of phosphated Nb<sub>2</sub>O<sub>5</sub> could be due to the interaction of reactive molecules with Nb=O and adjacent hydroxyl groups (POH and NbOH groups). The mechanism started with the protonation of the primary hydroxyl groups at C1 in sorbitol molecules, followed by an intramolecular nucleophilic substitution produced by the oxygen of another hydroxyl group at C4.<sup>23</sup> This S<sub>N</sub>2 reaction could be easier on a primary carbon. 1,4-sorbitan could undergo a second but slower cyclo-dehydration which led to isosorbide.

The catalytic performances of regenerated catalysts were tested and the results were shown in Table 3. Sorbitol conversion and isosorbide selectivity of regenerated 0.8P/NBO-400 decreased slightly, while the catalytic performance of regenerated NBO-400 dropped drastically. As shown in Table 3, 98.9% sorbitol conversion and 59.0% isosorbide selectivity of 0.8P/NBO-400 were obtained after recycling three times. This implied that the deactivation of 0.8P/NBO-400 did not occur with regeneration of the catalyst. It also indicated that the regeneration had a negative effect on the Nb<sub>2</sub>O<sub>5</sub> catalyst, which might be caused by the crystallization on the surface of Nb<sub>2</sub>O<sub>5</sub>. As no obvious difference were shown in the structure and catalytic performance over the catalysts calcined at 400 and 500 °C, it could be deduced that regeneration conditions had minor influence on 0.8P/NBO-400. In short, the phosphoric acid modification prevented the crystal phase change of Nb<sub>2</sub>O<sub>5</sub> under the regeneration condition and made it possible to reuse the spent catalyst by the simple calcination.

### Conclusion

Our work demonstrated that Nb<sub>2</sub>O<sub>5</sub> and phosphated Nb<sub>2</sub>O<sub>5</sub>

were effective for the aqueous dehydration of sorbitol. The catalytic performance of selective dehydration towards isosorbide over Nb<sub>2</sub>O<sub>5</sub> was improved significantly by the phosphoric acid modification. The phosphoric acid modification well prevented the crystallization of Nb<sub>2</sub>O<sub>5</sub> and kept the relatively large surface area, especially at the high calcination temperature. Therefore, the spent phosphated Nb<sub>2</sub>O<sub>5</sub> catalyst could be regenerated *via* simple calcination. Moreover, the selectivity to isosorbide improved obviously due to the increment in surface acid strength and moderate strong acid amount of catalyst after proper phosphoric acid modification. The amorphous 0.8P/NBO-400 catalyst possessed the large moderate strong acid amount and relatively large surface area, and exhibited the highest efficiency for the formation of isosorbide. And the regenerated catalyst (0.8P/NBO-400) showed nearly no loss in catalytic performance.

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