Catalytic Performance of Acid Catalysts for Sorbitol Dehydration to Isosorbide

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This research studied dehydration of sorbitol in aqueous solution to isosorbide over heterogeneous catalysts (Amberlyst-15, Purolite CT269, and H-beta) and a homogeneous catalyst (sulfuric acid). The dehydration of sorbitol was carried out in a high-pressure reactor under a nitrogen gas atmosphere at a fixed initial pressure of 2 MPa. It was found that the Purolite CT269 catalyst gave the highest sorbitol conversion of 100% and an isosorbide selectivity of 42% after 6 h at 453 K. The results showed that an increase in the reaction temperature gave rise to sorbitol conversion. However, the solid-compound was formed during the reaction at high temperature by polymerization of the product. The high acidity could catalyze the dehydration process; however, strong acid such as sulfuric acid gave low selectivity to isosorbide. Thus, the acidity of the catalyst plays a vital role in catalytic performance for the sorbitol dehydration to isosorbide.

Key Words
Amberlyst-15, Purolite CT269, H-beta, sulfuric acid catalyst, Isosorbide

1. Introduction

Recently, there has been great interest in biomass for use as a feedstock instead of fossil fuels and chemicals because it is renewable and environmentally friendly. Isosorbide is one of the biomass products from agriculture. Grand View Research reported that the isosorbide market trends had increased from $73.8 million in 2012 to $324.6 million in 2020 since it can be used in a wide range of applications such as medicine and synthetic polymer industries. Isosorbide has also been promoted as the alternative to bisphenol A in the synthesis process of polyethylene isosorbide terephthalate (PEIT) to reduce the danger of cancer. Especially, it is also expected to be used as a building block for a new polymer. Due to the increasing demand of isosorbide, the production process of isosorbide has received greater attention.

Isosorbide can be produced from a three-stage process, comprising 1) enzymatic depolymerization of starch feedstock into glucose, 2) hydrogenation of glucose to sorbitol, and 3) double dehydration of sorbitol into isosorbide using an acid catalyst. In double dehydration of sorbitol, sorbitol is first dehydrated to intermediates such as 1,4-sorbitan, 1,5-sorbitan, 2,5-sorbitan, and 3,6-sorbitan. However, only 1,4-sorbitan and 3,6-sorbitan can be converted to isosorbide by the second dehydration (Fig. 1).

Generally, the dehydration of sorbitol to isosorbide is studied under two reaction systems: solvent-free sorbitol and an aqueous sorbitol solution. Flèche et al. reported dehydration of sorbitol in solvent-free conditions with homogeneous strong acid catalysts. It was found that H₂SO₄ catalyst gave high sorbitol conversion of 99% and isosorbide yield of 77% after 20 h at 408 K. However, the disadvantages of using homogeneous strong acid catalysts are corrosion in reactors, difficult separation, and environmental pollution. These problems could be solved by the use of heterogeneous
catalysts such as acid resin \(^7\), metal oxides \(^8\), zeolites \(^9\), and metal phosphates \(^10\). Otomo \textit{et al.} studied the use of zeolite catalysts in aqueous sorbitol solution to obtain isosorbide. Eighty percent yield of isosorbide was achieved using H-beta (75) catalyst at 473 K for 12 h \(^11\). More recently, the acid resin has been popularly studied due to its hydrophobic property that facilitates the water molecule removal from the surface of the catalyst. Ginés-Molina \textit{et al.} (2007) studied commercial sulfonic acid resins (Purolite and Amberlyst types) in solvent-free and showed that the best 75% isosorbide yield could be achieved using Purolite CT269 catalyst at 413 K for 12 h \(^7\). However, dehydration of sorbitol in an aqueous solution system can be more beneficial than the solvent-free system in terms of the processing continuity of isosorbide production and cost reduction.

Therefore, the catalytic performance of different acid catalysts for sorbitol dehydration in an aqueous solution to produce isosorbide was investigated and compared in this study. Homogeneous, zeolite, and resin types of the catalyst were used. Sulfuric acid was utilized as the homogenous catalyst. Zeolite catalysts included H-beta (104) and H-beta (440). Resin catalysts were Purolite CT269 and Amberlyst-15. The catalytic performance was investigated for various reaction temperatures and reaction times.

2. Methodology

2.1 Materials

All chemicals were analytical grade: Isosorbide (98%) and 1,5-sorbitan were purchased from Sigma-Aldrich, 1,4-sorbitan was purchased from Sigma, D-sorbitol (70%) was purchased from Lab valley limited partnership (Thailand), sulfuric acid (98%) was purchased from RCI Labscan Ltd. Different commercial ion-exchange resins were also purchased: Purolite CT269 from Purolite\textsuperscript{®}, and Amberlyst-15 from Sigma-Aldrich. Two different H-beta catalyst: H-beta (104) (Si/Al=104, HSZ-960HOA) and H-beta (440) (Si/Al=440, HSZ-980HOA) from TOSOH.

2.2 Catalyst characterization

The textural properties of the catalyst were analyzed by Nitrogen Adsorption–Desorption at a liquid nitrogen temperature of 77 K (NOVA200e, Quantachrome, USA). The sample was outgassed at 393 K for 12 h under vacuum. The surface area was determined by Brunauer–Emmett–Teller (BET) equation, and the pore volume was calculated from the Barrett-Joyner-Halenda (BJH) equation.
The acid sites of catalysts were determined by titration as follows. First, the catalyst ~1 gram was dried at room temperature for 24 h. After accurately weighing a sample of the air-dried catalyst, the catalyst was stirred in 300 mL 0.5 M NaCl solution for 24 h. The mixture was filtered to separate the catalyst. After that, the filtrate was titrated with standard NaOH solution using phenolphthalein as an indicator.

### 2.3 Catalytic measurements

Dehydration of sorbitol was tested in a 250 mL stainless steel autoclave equipped with a pressure gauge. Typically, a catalyst (5 g) was added in 100 mL of 70 wt% aqueous sorbitol solution. The reactor was purged with N₂ and then pressurized to an initial pressure of 2 MPa with N₂. The temperature of the solution was heated up to a setpoint, time was recorded, and stirrer speed was adjusted at 550 rpm. After a specified time period, the autoclave was cooled down to room temperature. The catalyst in solid form was extracted by a centrifuge, and the liquid solution was then analyzed using high-performance liquid chromatography (HPLC: Shimadzu, LC-20AD) equipped with a refractive index detector (Shimadzu, RID-20 A) and Phenomenex Rezex RCM-monosaccharide column (8%; Ca²⁺, 300 × 7.80 mm). The temperature of the HPLC column was set at 358 K, and the mobile water phase was used with a flow rate of 0.5 mL/min. The sorbitol conversion, selectivity, and yield of the product were calculated to follow total mole balance equations (1), (2), and (3):

\[
\text{Sorbitol conversion (\%)} = \frac{\text{moles of reacted sorbitol}}{\text{moles of initial sorbitol}} \times 100 \quad (1)
\]

\[
\text{Selectivity (\%)} = \frac{\text{moles of defined product}}{\text{moles of reacted sorbitol}} \times 100 \quad (2)
\]

\[
\text{Yield (\%)} = \frac{\text{moles of defined product}}{\text{moles of initial sorbitol}} \times 100 \quad (3)
\]

For the identification of products from sorbitol dehydration, we detected the products by HPLC. Then, the data were compared with commercial standards. Previous research showed that the reaction pathway of sorbitol dehydration is shown in Fig. 1 ; Sorbitol can be converted into a variety of different sorbitan isomers, depending on C-O bond cleavage. It is important to note that only 1,4-sorbitan and 3,6-sorbitan can be converted to isosorbide in the second dehydration. Li et al. (2010) reported that the pathway of isosorbide could be quickly converted from isosorbide to 1,2,6-hexanetriol under dehydration and hydrogenation. In this work, we identified three main peaks that were 1,4-sorbitan, isosorbide, and sorbitol, but 1,5-sorbitan was not detected. As for other possible by-products such as 2,5-sorbitan, 3,6-sorbitan and 1,2,6-hexanetriol were treated as unknown.

### 3. Results and discussion

We first examined to compare the selected catalysts under the given condition: temperature of 423 K for 6 h using catalyst 5 g. As shown in Fig. 2, the resin group showed excellent catalytic performance of acid catalysts.
for sorbitol dehydration to isosorbide. The purolite CT269 gave the highest 74% of sorbitol conversion and 9% of isosorbide selectivity. H-beta catalysts were found to give low conversion of sorbitol. Considering the total acid site of the catalyst shown in Fig. 3, it is seen that isosorbide yield increases with the number of acid sites. In the case of low acidity, H-beta catalysts in the second dehydration of 1,4-sorbitan yielded a low quantity of isosorbide. This may be due to an insufficient acid site. Therefore, acid sites influenced the selectivity of isosorbide. Dabbawala et al. also reported similar results. In contrast, strong acid catalysts like sulfuric acid appeared to yield other by-products or unknowns. Production of the unknowns might be due to strong acidity, which promoted dehydration or hydrogenation of isosorbide to 1,2,6-hexanetriol.

As shown in Table 1, H-beta had more surface area than acid resins, indicating that the influence of acidity was greater than the surface area. Moreover, Zhang et al. (2018) reported the catalyst had a large pore size that was advantageous to the diffusion of substrates and products. Also, mesoporous pore sizes of purolite CT269 and amberlyst-15 might promote easier diffusion of sorbitol to active sites on the catalyst surface than the microporous pore of H-beta.

Based on the merit of purolite CT269 as previously discussed, it was selected as the catalyst for the dehydration of sorbitol to form isosorbide under aqueous sorbitol solution to study the optimum condition by varying temperature and reaction time. Fig. 4A shows the effects of time on sorbitol conversion and isosorbide selectivity. It shows that the conversion of sorbitol was complete for the reaction time selected. The selectivity of isosorbide gradually increased with increasing reaction time and became steady at 40-43% after 6 h, while the selectivity of 1,4-sorbitan decreased with increasing reaction time. It can be seen that the selectivity of the unknown and 1,4-sorbitan also remained constant after the reaction time of 6 h. This implies that 1,4-sorbitan could be a limiting reactant for the reaction. This result is consistent with the previous work of Yuan et al. (2019), which reported that 1,4-sorbitan could only be converted to isosorbide to a certain limit no matter how long the reaction time was. Since the reaction temperature is one key parameter, this study selected the range of 438-483 K for investigation. The increase in temperature resulted in an increase of sorbitol conversion from 74% to 100% and isosorbide selectivity from 9% to 42% at 453 K. As the temperature further increased from 453 K, isosorbide selectivity decreased to only 32% at 483 K. Additionally, the production of yet-to-be-identified products (unknowns) tended to rise with temperature increase. However, at 483 K, the solid compounds were formed during the reaction by polymerizing the products. After filtration, the remained solid compounds mixed with the catalyst used were found. Thus, the optimum condition for dehydration of sorbitol in aqueous solution to form isosorbide over purolite CT269 was given by 5 wt% catalyst loading, 453 K, 6 h to prevent the formation of the solid-compounds.

The reusability of purolite CT269 catalyst for isosorbide production was performed at 453 K for 6 h. After each run, the catalyst was reused according to the method of Gines-Molina. The result shown in Fig. 6 revealed that sorbitol conversion remained 100% after four runs, but isosorbide selectivity decreased from 42% to 25%. The decrease of isosorbide might be the loss of active sites due to the covering of dehydrated hydrocarbons on the active site, as reported by Brandi et al. (19).

### Table 1: Structure and acid properties of acid catalysts

| Sample        | Surface area (m²/g) | Pore volume (cm³/g) | Average pore size (nm) | Acid site [a] (meq/g) |
|---------------|---------------------|---------------------|------------------------|-----------------------|
| Amberlyst 15  | 36.48               | 0.32                | 21.98                  | 1.42                  |
| Purolite CT269| 34.22               | 0.32                | 29.74                  | 1.57                  |
| H-beta (104)  | 613                 | 0.29                | 0.71                   | 0.24                  |
| H-beta (440)  | 489.53              | 0.13                | 0.71                   | 0.16                  |

[a] Measured by acid-base titration

4. Conclusion

The catalytic dehydration of sorbitol in aqueous solution to form isosorbide over acid catalysts indicated that the acid site greatly influenced the catalytic activity. Purolite CT269 catalyst gave the highest sorbitol conversion of 100% and an isosorbide selectivity of 42% after 6 h at
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Fig. 4 Catalytic dehydration of sorbitol over Puroline CT269 with A) different reaction time (453 K) B) different temperature (6 h); (○) conversion of sorbitol, (■) selectivity of 1,4-sorbitan, (◆) selectivity of isosorbide, (▲) selectivity of unknown. Conditions: 5 wt% catalyst loading.

Fig. 5 Solid compounds after dehydration of sorbitol over Puroline CT269. Reaction conditions: catalyst/sorbitol = 5 wt%, 2 MPa, 483 K, 6 h.

Fig. 6 Reusability of Puroline CT269 for sorbitol dehydration to isosorbide. Reaction conditions: catalyst/sorbitol = 5 wt%, 2 MPa, 453 K, 6 h.

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