Liquid-phase dehydration of sorbitol under microwave irradiation in the presence of acidic resin catalysts

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Abstract Liquid-phase dehydration of sorbitol has been investigated in wide reaction conditions especially under microwave irradiation in the presence of acidic resin catalysts. From the selectivity for sorbitan and isosorbide, it can be understood that the dehydration is a consecutive reaction (sorbitol to sorbitan, and finally to isosorbide) and that the sorbitan is an intermediate of the dehydration. By using microwave irradiation, the dehydration can be accelerated by around 20–34 times compared with the rate by conventional electric heating at the same temperature, or the reaction temperature can be decreased by around 40 °C for the comparable conversion in a similar reaction time. However, the microwaves do not have noticeable effects on the selectivity for isosorbide or sorbitan. The accelerated dehydration under microwaves is mainly due to decreased activation energy.

Keywords Sorbitol dehydration · Isosorbide · Solid acid · Microwave irradiation

Introduction

Recently, the utilization of renewable biomass has attracted much attention because of concerns for the environment and for saving energy [1]. Sorbitol is one of the useful biomass-derived chemicals that can be converted into polyols, and it can be obtained from cellulose via glucose. Isosorbide that can be obtained from

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dehydration of sorbitol is one of the useful chemicals in polymers and medicines [2–6].

Dehydration of sorbitol has been carried out in the presence of mineral acids like sulfuric acid and hydrochloric acid. However, the process using mineral acids has drawbacks with regard to the environment and to safety. Therefore, very recently, several solid catalysts like sulfated copper oxides [3], supported heteropoly acids [4], Nb₂O₅ modified with phosphoric acid [5] and metal phosphates [6], have been tried for the isosorbide production from sorbitol. Yamaguchi et al. [2] suggested dehydration with pure water (and in the absence of any catalyst) at high temperature because the dissociation of water molecules increases with increasing temperature.

Even though the dehydration is not a difficult reaction, the rapid reaction is beneficial for high throughput, energy saving and continuous operation. Especially, a rapid reaction may decrease the reaction temperature, which can be helpful for energy efficiency and for reducing investment costs. Microwaves (MWs) have been widely used to accelerate not only organic reactions [7] but also inorganic syntheses [8, 9]. To the best of our knowledge, however, there has been no attempt to use MWs in the dehydration of sorbitol. Moreover, the reason for accelerated syntheses or reactions under MWs has not been thoroughly understood.

In this work, the dehydration of sorbitol, in the presence of resin catalysts, has been studied under MW irradiation in order to accelerate the dehydration or to decrease the reaction temperature. The acceleration degree has been estimated quantitatively and the possibility of reducing the reaction temperature is suggested. The accelerated dehydration is mainly due to a decreased activation energy; however, there is little change in the selectivity for isosorbide and sorbitan with MW irradiation.

Experimental

The dehydration of sorbitol has been carried out at 130–170 °C with both conventional electric (CE) heating and microwave (MW) heating. Fifteen g of sorbitol (97%, Daejung Chemicals and Metals) was loaded into a 100-mL Teflon autoclave and allowed to melt at 120 °C in a conventional oven. Resin catalyst Amberlyst-15 (0.3 g, Aldrich, acid capacity 4.7 mequiv. H^+/g) was added to the liquid sorbitol of the Teflon autoclave which was sealed and placed in a preheated electric oven or in a MW oven (MARS-5, CEM, maximum power of 1,200 W). The autoclave in the MW oven was heated to the reaction temperature in 2 min and maintained for a predetermined time. The MW power was 400 W throughout all the synthesis steps including the heating-up stage. After the reaction for a fixed time, the autoclave was cooled to ~100 °C and the liquid product was recovered by filtration using a glass filter. The filtration was carried out inside a CE oven (at about 100 °C) to avoid the solidification of the product. Part of the dehydrated water was evaporated during filtration, and the products were further kept in an oven for 4 h to evaporate the remaining water.

The composition of the dried product was analyzed using HPLC (Younglin Instrument, Acme 9000) equipped with a refractive index (RI) detector and

Asahipak column (NH2P-50 4E, No. N712004). Acetonitrile/water (80/20) mixture was used as an eluent for the analysis with the flow rate of 1.0 mL/min. The temperature of RI detector was maintained at 35 °C throughout the analysis. The typical HPLC chromatogram which can separate sorbitol, sorbitan and isosorbide is shown in Fig. 1. The selectivities or yields of sorbitan or isosorbide were based on molar composition.

The kinetics of the dehydration was interpreted with the first-order kinetics based on the concentration of remaining sorbitol. The activation energy (E_a) and preexponential factor (A) of the dehydration were calculated using the kinetic constants at various temperatures with the Arrhenius equation.

Results and discussion

The dehydration of sorbitol has been conducted in wide reaction conditions and the typical results are displayed in Fig. 2. With increasing reaction time, the sorbitol conversion and isosorbide selectivity increase; however, the sorbitan selectivity



Fig. 1 Typical HPLC chromatogram of the obtained dehydrated products



Fig. 2 Effect of heating methods (a MW; b CE) and reaction time on the sorbitol conversion and selectivity for sorbitan and isosorbide

decreases. Remarkably, the rate of sorbitol dehydration is very high under MW irradiation to show complete conversion of sorbitol in 2 h. Under CE dehydration, however, the conversion cannot be reached up to 100 % even at 15 h of dehydration. The steady decrease and increase of sorbitan and isosorbide, respectively, with reaction time show the consecutive reaction (from sorbitol to isosorbide) of the sorbitol dehydration, and the sorbitan is an intermediate, in agreement with the reported results [2–4, 6].

To compare the relative kinetics of dehydration of sorbitol, the reactions were carried out at various times at 130–150 °C. The rates of reaction have been interpreted with the first-order kinetics based on the remaining concentration of sorbitol. As shown in Fig. 3, the kinetic constants with MW heating are very high compared with those of the dehydration with CE heating. The summarized kinetic constants are shown in Table 1 and it can be understood that the kinetic constants with MW heating are around 20–34 times of those with the CE heating at the same temperature.

So far, little comprehensive study has been done [7-10] to explain why reaction time is drastically decreased under MWs even though rapid syntheses of several materials have been observed. Instead, several hypotheses [8-11] have been proposed to explain the fast synthesis with MW, namely, (1) an increase in the heating rate of the reaction mixture, (2) more uniform heating of the reaction mixture, (3) change in association between species within the mixture, (4) superheating of the mixture, (5) creation of hot spots, and (6) enhancement of the dissolution of the precursor gel. According to Conner et al., rapid heating and creation of hot spots are important factors associated with an increase in synthesis rates under MWs [8, 11].

The accelerated reaction under MWs has been explained with various factors such as decreased activation energy or increased pre-exponential factor. For example, the accelerated process with MWs has been explained with low E_a in alumina sintering [12], polymerization of ε -caprolactone [13], a curing of a phenylethynyl terminated imide compound [14] and in an imidization reaction [15].

However, accelerated MW-syntheses of Cu₂O [16], molecular sieves like AlPO-11 and SAPO-11 [17] and metal–organic frameworks (MOFs) such as ironbenzenedicarboxylate [18] and copper-benzenetricarboxylate [19] are mainly due to a very large increase in pre-exponential factors (even with increased E_a). Very recently, Ahnfeldt et al. [20] have shown the accelerated synthesis of a MOF (CAU-1-(OH)₂) with MWs is due to an increase of pre-exponential factor. However, they have shown that the E_a does not change noticeably with heating methods.

To explain the accelerated dehydration under MWs, the reaction activation energy (E_a) and pre-exponential factor (A) of the Arrhenius equation are obtained from the Arrhenius plots (Fig. 4). The E_a values of MW and CE dehydration are 50.3 and 86.1 kJ/mol, respectively, showing the remarkable decrease of the E_a with MW heating. However, the A of MW heating (1.2×10^7 /h) is also decreased compared with the A of CE heating (1.4×10^{10} /h). Therefore, the high dehydration rate under MWs is mainly due to decreased E_a of the dehydration rather than the increased pre-exponential factor.



Table 1	First-order kinetic		
constants	of sorbitol dehydration		
with heating method and			
temperatu	re		

Heating method	Temperature (°C)	<i>k /</i> h	Ratio of k (k _{MW} /k _{CE})
MW	130	3.6	34.0
CE	130	1.1×10^{-1}	
MW	140	4.8	32.4
CE	140	1.5×10^{-1}	
MW	150	7.3	20.4
CE	150	3.6×10^{-1}	



Fig. 5 Effect of sorbitol conversion on the selectivity for **a** sorbitan and **b** isosorbide with MW and CE heating

The dependence of isosorbide or sorbitan selectivity on the sorbitol conversion has been analyzed to check whether there is any effect of MWs on the selectivity for the isosorbide or sorbitan. As shown in Fig. 5, irrespective of heating method, the isosorbide selectivity increases (and sorbitan selectivity decreases accordingly) with increasing sorbitol conversion in agreement with the fact of the consecutive reaction (sorbitol \rightarrow sorbitan \rightarrow isosorbide). However, there is negligible effect of MW or CE heating on the isosorbide or sorbitan selectivity, suggesting little effect of MWs on the mechanism or selectivity of the dehydration. In other words, accelerations may be obtained similarly both in the stage of sorbitol dehydration (to sorbitan) and sorbitan dehydration. Therefore, it may be suggested that MWs decrease the activation energies of the two consecutive dehydrations. However, further work is needed to confirm whether the reduction in the activation energy is true or superficial (by hot spots, transient temperature and pressure).

Even though the detailed reason of accelerated dehydration under MWs is not clear, it can be said that the MW-dehydration is a very efficient method to dehydrate sorbitol to isosorbide. Figure 6 compares the dehydration results at two different conditions (MW at 130 °C; CE at 170 °C) and it can be confirmed that the activity of sorbitol dehydration with MWs at a much lower temperature (130 °C) is higher



Fig. 6 Effect of heating methods, temperature (a MW at 130 $^{\circ}$ C; b CE at 170 $^{\circ}$ C) and reaction time on the sorbitol conversion and selectivity for sorbitan and isosorbide

than high temperature (170 °C) dehydration with CE heating. Therefore, the MW heating is very helpful to dehydrate facilely even at very low temperature.

Conclusions

From the liquid-phase dehydration of sorbitol in the presence of acidic resin catalysts, the following conclusions can be derived. The dehydration can be accelerated by 20–34 times (or the reaction temperature can be decreased by 40 °C for similar conversion in a similar reaction time) with MW irradiation at the same reaction temperature. The accelerated dehydration under MW irradiation is mainly due to decreased activation energy rather than increased pre-exponential factor. The MWs accelerate both the two stages of dehydration (sorbitol to sorbitan and sorbitan to isosorbide) and do not have noticeable effects on the selectivity for sorbitan and isosorbide.

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