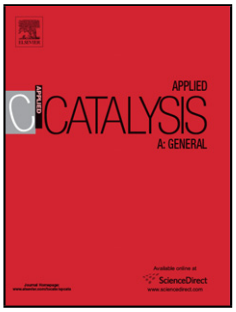

Title: Role of acid sites and selectivity correlation in solvent free liquid phase dehydration of sorbitol to isosorbide

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Role of acid sites and selectivity correlation in solvent free liquid phase dehydration of sorbitol to isosorbide

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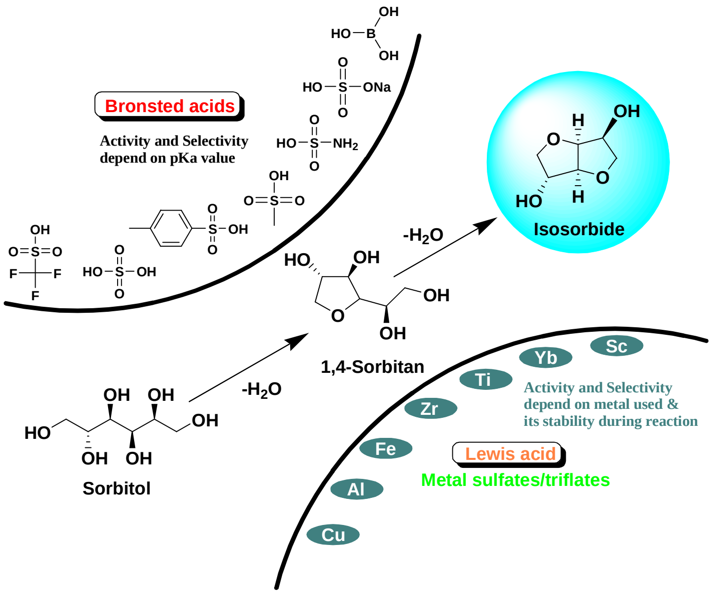
Graphic Abstract



Research highlights

- Influence of acid sites investigated in dehydration of sorbitol to isosorbide
- Brönsted acids are efficient to convert sorbitol to isosorbide than Lewis acids
- Strong Brönsted acids exhibit high TOF as well as yield of isosorbide
- The water formed during reaction induced Brönsted acidity on Lewis acid catalysts
- The Lewis-assisted Brönsted acid site enables high yield of isosorbide at 160 °C

Role of acid sites and selectivity correlation in solvent free liquid phase dehydration of sorbitol to isosorbide

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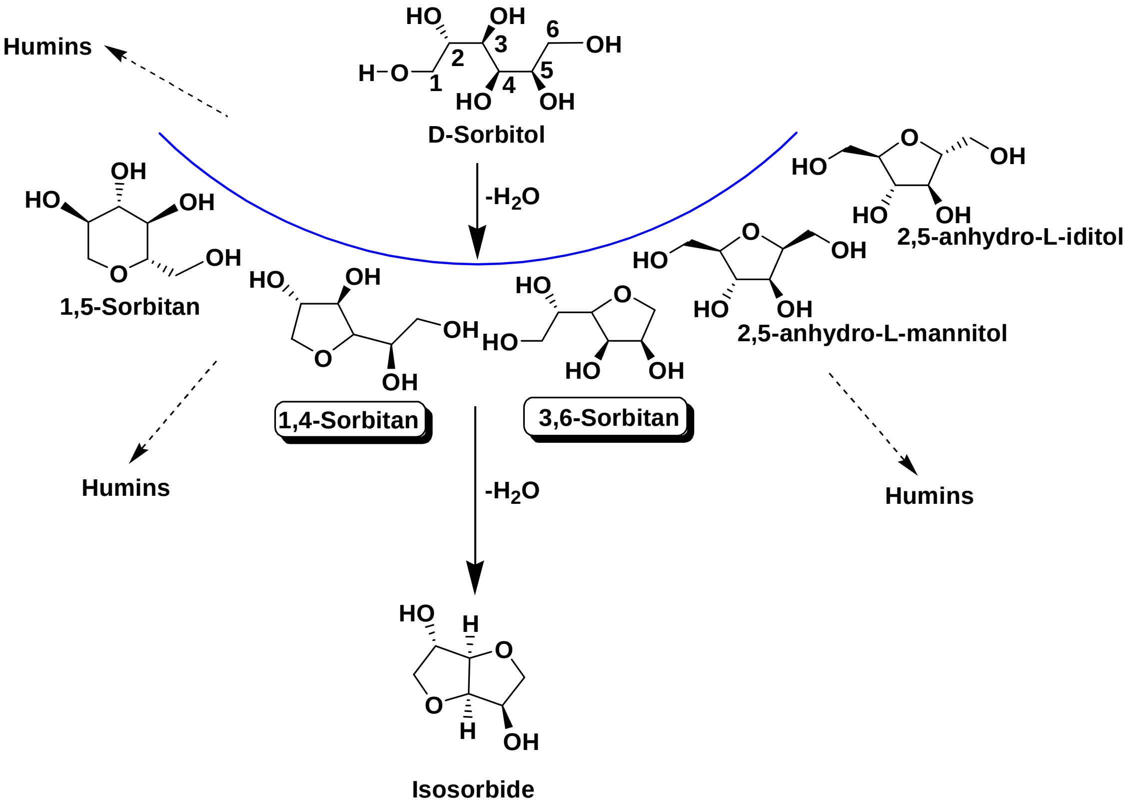
Abstract

A number of Brönsted acids (methanesulfonic acid, *p*-toluene sulfonic acid, triflic acid, sulfamic acid, citric acid, $NaHSO_4$, boric acid) and Lewis acids (metal sulfate/triflates) were employed in solvent free dehydration of sorbitol and their influence on anhydroalcohols selectivity has been investigated. The outcome indicated that all the acid catalysts produced first mono-dehydrated product sorbitan followed by second dehydration of 1,4-sorbitan to isosorbide. However, the formation and yield isosorbide were found to depend on the nature of acid sites and their acidic strength. The Brönsted acids are more efficient to convert sorbitol to isosorbide than Lewis acids. The Brönsted acids having lower pK_a value (i.e. strong acid) exhibited high catalytic activity as well as yield of isosorbide. In the case of Lewis acids, the catalytic activity and selectivity were radically depended on which metal used and their stability during the reaction. The water formed during reaction induced Brönsted acidity on Lewis acid metal site. The Lewis-assisted Brönsted acid site enabled high yield of isosorbide up to 70% at moderate temperature (160 °C).

Key words: Dehydration; sorbitol; selectivity; Brönsted acid; Lewis acid

1. Introduction

Over the last few decades, the catalytic conversion of sugar and sugar alcohols into fuels and value added chemicals have gained considerable interest due to their low cost and availability from renewable resources [1−9]. Sorbitol, a sugar alcohol can be produced either from hydrolysis-hydrogenation of cellulose/lignocellulosic biomass or by direct hydrogenation of glucose [10−15]. Recently, sorbitol has been listed as a platform bio-based molecule which can be used in the preparation of a variety of valuable non-petroleum derived commodity chemicals [10−20]. Dehydration of sorbitol produces anhydrosugar alcohols, including sorbitan (mono-anhydrosorbitol) and isosorbide (di-anhydrosorbitol). Both products sorbitan and isosorbide have achieved commercial importance and can be used to synthesize numerous intermediates applicable in the preparation of surfactants, pharmaceuticals, cosmetics and synthetic polymer industries [20−22]. Isosorbide, a compound containing bicyclic hetero atoms in its structure is obtained by sequential dehydration of sorbitol as shown in **Scheme 1**. In intramolecular dehydration of sorbitol, sorbitol is first dehydrated to give monocyclic products, such as 1,4-sorbitan (1,4-anhydro-d-sorbitol), 1,5-sorbitan and 2,5-sorbitan. 1,4-sorbitan is further dehydrated to produce bicyclic product, isosorbide (1,4:3,6-dianhydrosorbitol) whereas other sorbitans cannot produce isosorbide. Isosorbide can also be formed via 3,6-sorbitan although it has been considered that first cyclization occurred between C_1 and C_4 position. Moreover, the formation of ‘humins’ (colored polymeric side products) is major impurity in the case of sorbitol dehydration. The high molecular weight condensation/degradation undesired colored by products (‘humins’) are start to generate from the beginning of the reaction indicating major formation of side products from sorbitol and sorbitan [22].



Scheme 1 Acid catalyzed dehydration of sorbitol to isosorbide via sorbitan

The dehydration of sorbitol was first studied under homogeneous condition using traditional strong mineral acids such as H_2SO_4, H_3PO_4, HCl and high yield of isosorbide was achieved with H_2SO_4 [23]. Later on, various processes have been developed for the production of isosorbide by sorbitol dehydration using range of acid catalysts to enhance conversion of sorbitol and yield of isosorbide under homogeneous as well as heterogeneous condition [24−32]. Many researchers employed the solid acid heterogeneous catalysts to avoid the drawbacks of mineral acids *i.e.* required tedious product separation, mineral acid handling risk, equipment corrosion and less stability of product [33−42]. The various solid acids such as zeolites, Amberlyst-15 resin, Metal (IV) phosphates, phosphated Nb_2O_5, sulfated copper oxides, sulfated zirconia/titania, and supported heteropolyacid have been applied for the synthesis of isosorbide under different reaction conditions [33−42]. Gu et al studied aqueous phase dehydration of sorbitol to isosorbide using metal (IV) phosphates of tin, zirconium and titanium and achieved 97% conversion of sorbitol and isosorbide yield in the range of 45−47% at the reaction temperature of 300 °C [35]. Khan et al investigated dehydration of sorbitol under solvent free condition and reported 61% isosorbide selectivity with 100% conversion of sorbitol at 210 °C using sulfated zirconia catalyst [38]. A number of advantages have been realized by using solid acid catalysts compared to the homogeneous mineral acid catalysts as they are safe in handling, easy to separate from products and can be reuse. However, most of the solid acid catalysts showed a low catalytic activity and required comparatively high temperature (200−300 °C) and longer reaction time to achieve satisfactory yield of isosorbide [33−42]. On the other hand, Li et al studied the dehydration of sorbitol using molten salt hydrate as reaction medium ($ZnCl_2$, 70 wt% in water) and achieved high selectivity to isosorbide at 200 °C [43,44]. Yamaguchi et al showed sorbitol dehydration without using any acid catalyst in high temperature liquid water [45]. The maximum yield of isosorbide reached up to 57% but requires high temperature (317 °C) and pressure. Based on the reported literature and our previous studies on dehydration of sorbitol [38−40], we observed that (i) the acid catalyst is key requirement for efficient conversion of sorbitol at moderate reaction temperature, (ii) the selectivity of anhydroalcohols is affected by type of selected acid catalyst and its properties. However, there is no systematic study available in the literature outlining the influence of acid catalyst properties such as Brönsted acid (proton donors) and Lewis acid (electron pair acceptor) on conversion of sorbitol and the anhydrosugar alcohols selectivity. Since the activity of acid catalysts depends on the catalyst acid strength and nature of acid sites. More importantly, such systematic data would be useful in the designing of rational catalyst system for the efficient dehydration of sorbitol. With this view, we intended to explore the dehydration of sorbitol using a series of acid catalysts having different acidic strength and nature of acid sites (Brönsted and Lewis sites). Organic acids having Brönsted acid sites and metal sulfate/triflates as Lewis acids were selected to examine the role of Brönsted acid and Lewis acid in the dehydration of sorbitol. The influence of Brönsted acid and Lewis acid are emphasized by linking the catalyst activity and anhydroalcohols selectivity. Under optimum reaction condition, the complete conversion of sorbitol with high yield of isosorbide up to 70% was achieved at moderate reaction temperature (160 °C). In addition, the dehydration of sorbitol was investigated under solvent free condition instead of aqueous phase and without using complicated pressure reactor setup. The water formed during reaction was continuously removed by vacuum. In fact, the water present in the reaction medium directly affects the rate of dehydration and requires longer time to complete the reaction. Moreover, the additional distillation step is required to separate water from the product.

2. Results and discussion

2.1. Brönsted acid catalyzed dehydration of sorbitol

The dehydration reaction of sorbitol was performed in a liquid phase batch type dehydration reactor under solvent free condition. The main dehydrated products observed were 1,4−sorbitan and isosorbide along with small amount of 1,5−sorbitan. Non-indentified soluble and insoluble polymeric compounds (‘humins’) are reported here as ‘unknown. The catalytic dehydration of sorbitol was investigated under homogeneous condition using distinct acid catalysts. Two types of acid catalyst were selected in the present study: (i) Organic acid catalysts with ‘Brönsted acid sites’ and (ii) transition/non transition metal salt acting as ‘Lewis acid’. Compared to strong mineral acids, selected acid catalysts are less corrosive and ease in handling. Firstly, we studied the effect of Brönsted acid catalysts on activity and selectivity of sorbitol dehydration by picking number of acid catalysts having different $\mathrm{p}K_\mathrm{a}$ value such as Triflic acid (TFA, $\mathrm{p}K_\mathrm{a} = -12$), p-toluenesulfonic acid (PTSA, $\mathrm{p}K_\mathrm{a} = -2.8$) methanesulfonic acid (MSA, $\mathrm{p}K_\mathrm{a} = -1.9$), Sulfamic acid (SFA, $\mathrm{p}K_\mathrm{a} = 1.0$), sodium hydrogen sulfate, $NaHSO_4$ (SHS$_,$ $\mathrm{p}K_\mathrm{a} = 1.99$), citric acid (CTA, $\mathrm{p}K_\mathrm{a} = 3.13$)**,** boric acid (BA, $\mathrm{p}K_\mathrm{a} =$

9.24)**.** For comparison, few experiments were also performed with H_2SO_4 (SA, pK_a = −3). The results of dehydration of sorbitol using different acid catalysts are summarized in **Table 1**.

Table 1 Dehydration of sorbitol using Brönsted acid catalysts[a]

Catalyst (H$^+$ mmol)	**pK_a (pH)[b]**	**Temp. (°C)**	**Time (min)**	**Conv. (%)**	**Selectivity (%)**		
					IS	**ST**	**UN**
H_2SO_4 (SA) (0.52)	-3 (3.29)	160	30	100	48	39	13
			60	100	68	16	16
TFA (0.52)	-12 (3.21)	160	30	100	39	46	15
			60	100	63	18	19
PTSA (0.52)	-2.8 (3.27)	160	30	100	45	43	12
			60	100	66	19	15
MSA (0.52)	-1.9 (3.25)	160	30	100	46	43	11
			60	100	66	20	14
SFA (1.04)	1.0 (2.8)	180	30	95	14	71	15
			60	100	41	43	16
SHS (1.04)	1.99 (2.9)	180	30	92	10	81	07
			60	98	14	79	07
CTA (1.56)	3.13 (3.5)	180	60	48	04	89	07
			120	64	06	86	08
BA (1.56)	9.24 (6.7)	180	60	41	03	90	07
			120	55	04	89	07

[a] Reaction condition: Sorbitol = 54.9 mmol, Stirring speed = 800 rpm

IS: Isosorbide, ST: Sorbitan (1,4-sorbitan + 1,5-sorbtian), UN: Unknown, non-detected products ('Humins')

[b] pH of reaction mixture after reaction (2% aqueous solution)

The results pointed out that the catalyst activity and yield of isosorbide were changed depending on pK_a value of acid catalyst used. The formation of side products was also influenced by the type of acid catalyst and its acidic strength. It was noticed that acid catalysts having pK_a value < 1 were found to produce high yield of isosorbide at 160 °C however their catalyst performance were almost similar in term of activity and selectivity. In another case of acid catalysts having pK_a value > 1, the catalyst activity and formation of isosorbide were found to decrease gradually with an increase in pK_a value of acid catalyst. In addition, such acid catalysts required higher catalyst concentration, temperature (180 °C) and longer reaction time to attain complete conversion of sorbitol **(Table 1).** For example, organic acids MSA, PTSA, and TFA having pK_a < 1 exhibited high selectivity to isosorbide (63−66%) in 60 min at 160 °C comparable to H_2SO_4. On other side, SFA (pK_a = 1.0), SHS (pK_a = 1.99), CTA (pK_a = 3.13) and BA (pK_a = 9.24) displayed isosorbide selectivity 41%, 14%, 4% and 3% respectively in 60 min at 180 °C and also required higher catalyst concentration **(Table 1)**. Initially, we compared results of all Brönsted acid catalyst based on selective formation of isosorbide at higher conversion level of sorbitol. Because the dehydration of sorbitol to isosorbide is sequential reaction and the quantitative formation of isosorbide was observed after 70% conversion of sorbitol. For better evaluation of studied acid catalysts as well as their proper comparison, the catalyst activities in term of turn over frequency for sorbitol (represented as TOF_{SB} where SB = sorbitol) were determined. The initial TOFs for sorbitol (TOF_{SB}) for all Brönsted acid catalyst were calculated at sorbitol conversion in the range of 10−20% and presented in **Fig. 1**.

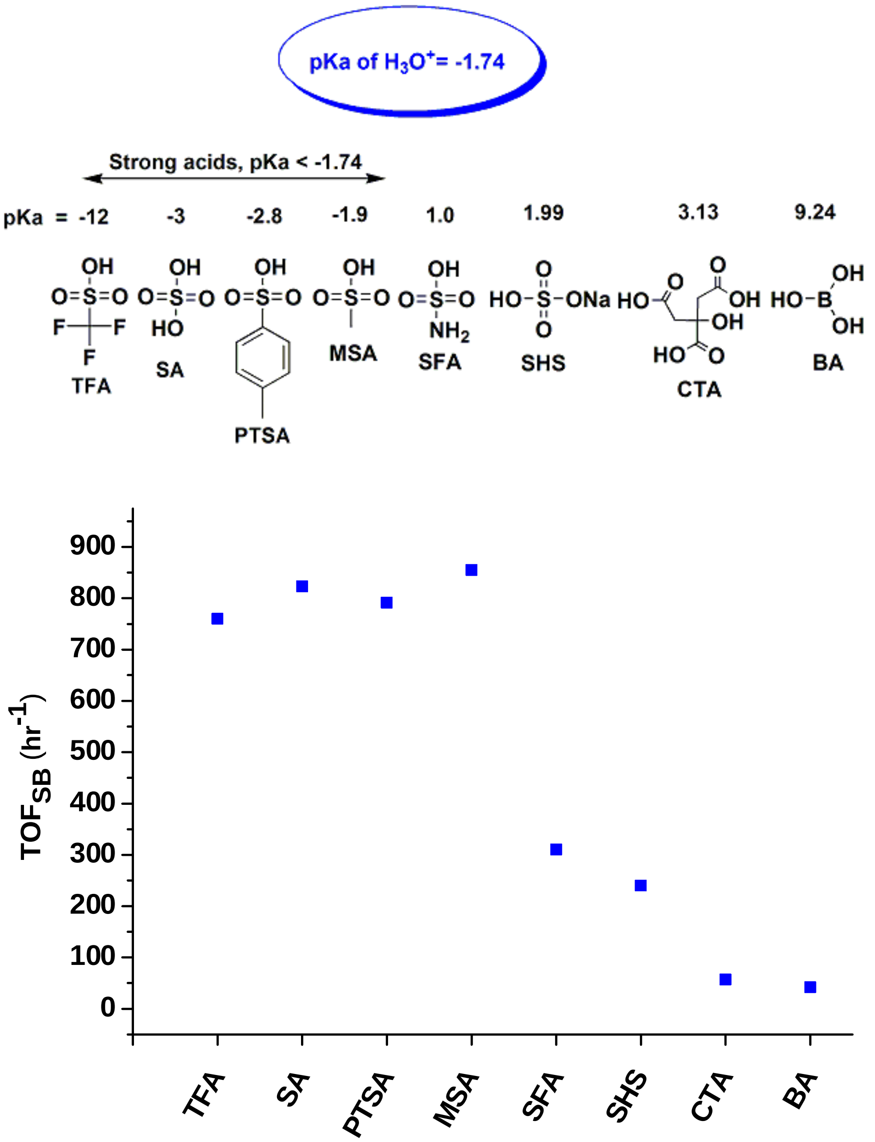


Fig. 1 The catalytic activity (in term of TOF) of distinct Brönsted acids in dehydration of sorbitol; Reaction conditions are the same as mentioned in Table 1.

The conversion of sorbitol and yield of isosorbide were also determined with different Brönsted acid catalysts and the results are presented at different time of interval **(Fig. 2).** The organic Brönsted acids MSA, PTSA and TFA exhibited almost the same TOFs (760−855 hr^{-1}) and yield of isosorbide (63−66%) as TOF (823 hr^{-1}) and yield of H_2SO_4 (68%). The SFA (310 hr^{-1}), SHS (240 hr^{-1}), CTA (57 hr^{-1}) and boric acid (42 hr^{-1}) gave lower TOFs and isosorbide yield than H_2SO_4. The H_2SO_4 and organic acids (MSA, PTSA and TFA having $–SO_3H$) are considered as strong acids. The strong acids have a larger *Ka* (acid dissociation constant) i.e. ionizes or dissociates completely in a solution. These acids are stronger in aqueous solution than hydronium ion (H_3O^+) i.e. strong acids have $pK_a < -1.74$ (pK_a of H_3O^+) [46]. The above achieved results with different Brönsted acids suggested that strong acidity is necessary to achieve high activity and yield of isosorbide at moderate temperature. However, the behaviors of all strong acids (having $pK_a < -1.74$) are same exhibiting almost comparable TOFs and yield of isosorbide **(Fig. 1**). On other hand, the catalytic activity and yield of isosorbide were observed to decrease gradually with an increase in pK_a value of catalyst (in the case of $pK_a > 1$) as the acid strength of catalyst is decreased depending on pK_a of acid **(Fig. 1 and Fig. 2).**

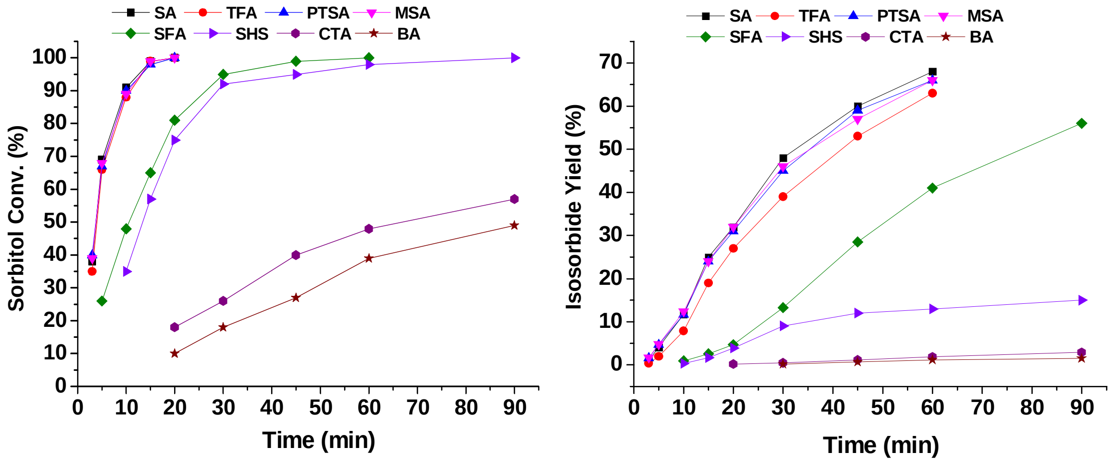


Fig. 2 Influence of distinct Brönsted acids on sorbitol conversion and isosorbide yield in dehydration of sorbitol; Reaction conditions are the same as mentioned in Table 1.

G. Fleche and M. Huchette studied aqueous phase dehydration of sorbitol using different mineral acids such as H_2SO_4 ($pK_a = -3$), HCl ($pK_a = -6.3$) and H_3PO_4 ($pK_a = 2.1$) [23]. Under similar reaction conditions (Temp. 135 °C, reaction time = 20 h), they observed high conversion (100%) and yield of isosorbide (70−75%) with H_2SO_4 and HCl as both acids are strong acids ($pK_a < -1.74$). Whereas H_3PO_4 having $pK_a = 2.1$ showed only 12% yield of isosorbide with 87% sorbitol conversion. These results are consistent with our achieved results further indicating the requirement of strong acidity for efficient conversion of sorbitol to isosorbide at moderate reaction temperature.

The effects of reaction time, temperature and H^+ concentration were then examined to understand if further improvements are possible with organic acid using MSA as a catalyst. The reaction profile for conversion of sorbitol (at 160 °C) and formation of sorbitan as well as isosorbide is presented with respect to time in **Fig. 3**. In 3 min, 39% conversion of sorbitol was observed that was increased to 68% in 5 min. The conversion of sorbitol was reached 89% in 10 min then the reaction became sluggish. 99% of conversion of sorbitol was attained in 15 min. The catalytic dehydration of sorbitol yielded sequentially sorbitan and isosorbide. At the outset sorbitan selectivity was high and selectivity to isosorbide was low. As the reaction proceeded, selectivity to sorbitan was decreased leading to increase isosorbide selectivity up to 66% in 60 min **(Fig. 3).** On further increase of reaction time, the yield of isosorbide was not changed significantly.

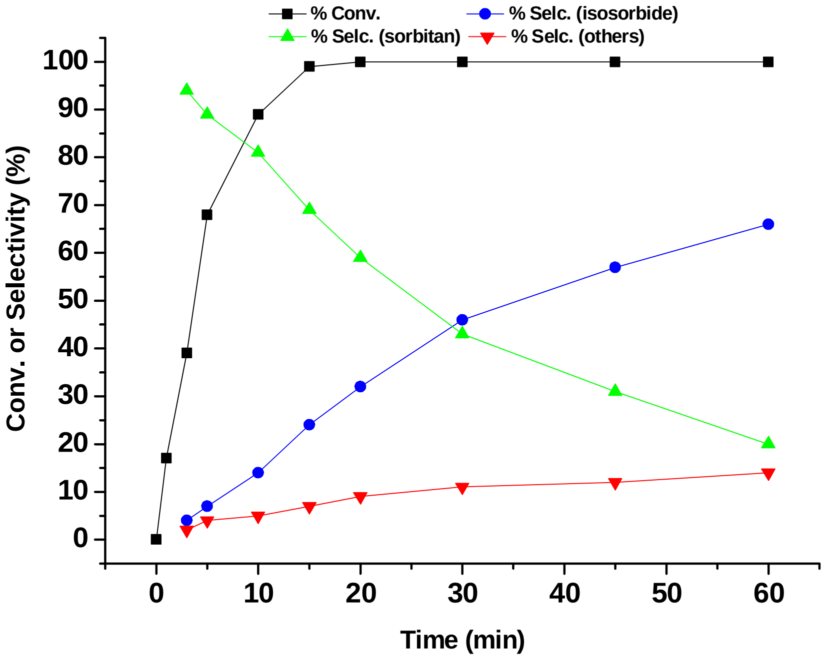


Fig. 3 Reaction profile of sorbitol dehydration using MSA as catalyst; Reaction condition: sorbitol = 54.9 mmol, catalyst (MSA) = 0.52 mmol, reaction temperature = 160 °C.

The effect of temperature was studied by varying reaction temperature in the range of 140 to 170 °C at constant amount of sorbitol (54.9 mmol) and MSA catalyst (0.52 mmol). From the **Fig. 4**, it can be seen that the temperature had significant effect on catalytic activity and isosorbide selectivity. With an increase in temperature the reaction proceeded faster and led to increase isosorbide selectivity via sorbitan. At lower reaction temperature (140 °C), initial TOF of sorbitol was 401 hr^{-1}. With an increase in temperature from 140 to 170 °C, the initial TOF of sorbitol was increased considerably from 401 to 1266 hr^{-1} indicating catalyst activity increased by factor of ~3. Similarly, selectivity of isosorbide was found only 18% in 30 min at 140 °C which was considerably increased up to 62% at 170 °C. However, the formations of side products were also increased with an increase of reaction temperature **(Fig. 4).**

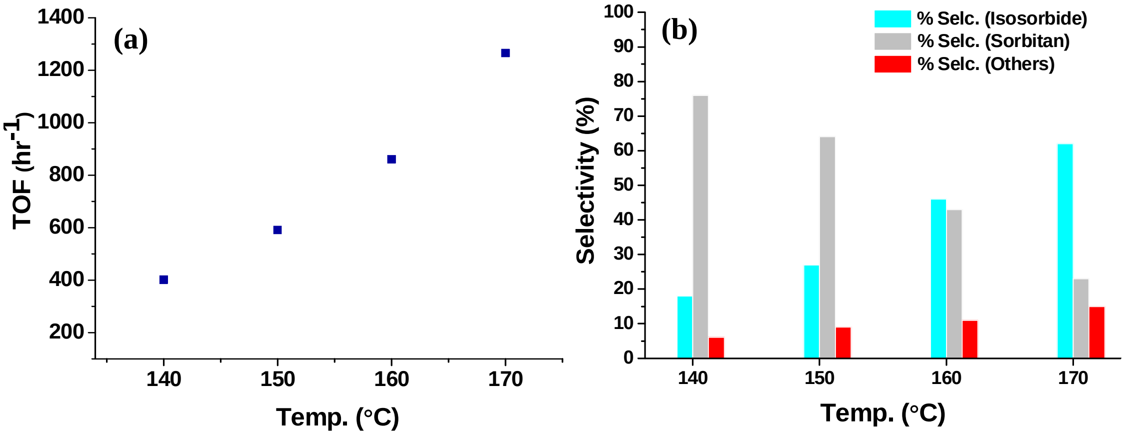


Fig. 4 Effect of temperature on TOF (a) and product selectivity (b) in MSA catalyzed dehydration of sorbitol; Reaction condition: sorbitol = 54.9 mmol, catalyst (MSA) = 0.52 mmol, reaction time = 30 min.

The effect of H^+ concentration was also studied by varying MSA concentration 0.26, 0.52, 0.78 and 1.04 mmol **(Fig. 5).** The conversion of sorbitol was increased with an increase of H^+ concentration and complete conversion of sorbitol was attained relatively in shorter reaction time. Similarly, the isosorbide yield was increased with an increase H^+ concentration and high yield was obtained comparatively in shorter reaction time. These results indicate that the sorbitol conversion and yield of isosorbide are influenced by number of bronsted acid sites and augmented up to certain limit with an increase of relative number of Brönsted sites. It is also noticed that higher H^+ concentration and longer reaction time led to the formation of side products.

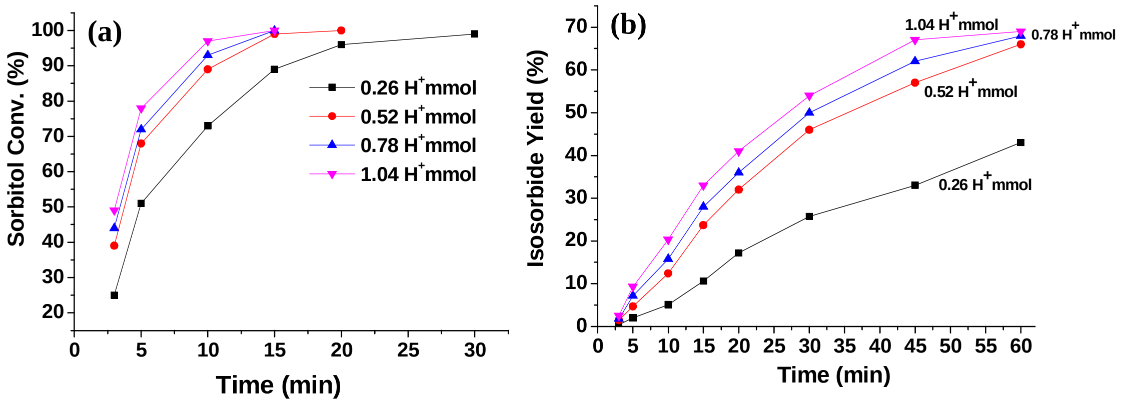


Fig. 5 Effect of H^+ concentration on sorbitol conversion (a) and isosorbide yield (b) in MSA catalyzed dehydration of sorbitol; Reaction condition: sorbitol = 54.9 mmol, reaction temperature = 160 °C.

2.2. Lewis acid catalyzed dehydration of sorbitol

Next, we studied the effect of Lewis acid catalysts on dehydration of sorbitol. Transition/non transition metal salt (MS, where M = metal cation, S= anion) of different metal M = Ti, Fe, Co, Ni, Cu, Zn, Zr, and Al with specific anion S= Cl^{-1} and SO_4^{-2} were selected to elucidate the role of Lewis acid site. The metal salts of Fe, Cu, Al, Zr, and Ti in sulfate form were found to give appreciable yields of isosorbide compared to their chloride and the conversion of sorbitol and yield of isosorbide were varied depending on which metal used **(Table 2).** For example, $CuSO_4$ gave very low initial TOF (18 hr^{-1}) with only 35% conversion of sorbitol at 170 °C and also formation of isosorbide was not observed. At 180 °C, the initial TOF was increased up to 249 hr^{-1} and exhibited complete conversion of sorbitol with 61% isosorbide selectivity in 2 h (Table 2). The strong Lewis acids, $Ti(SO_4)_2$ and $Zr(SO_4)_2$ displayed high initial TOFs and isosorbide selectivity (65−68%) at 160 °C in 60 min resemblance to strong Brönsted acids. The other metal sulfates gave lower initial TOF and isosorbide selectivity (<60%). Additionally, they required relatively higher reaction temperature to enhance yield of isosorbide.

Table 2 Dehydration of sorbitol using Lewis acid catalysts [a]

Catalyst	pH[b]	X_i[c]	Temp. (°C)	TOF_{SB}[d] (hr^{-1})	Time (min)	Conv. (%)	Selectivity (%)		
							IS	ST	UN
$CuCl_2$	5.79	---	180	126	120	100	12	82	06
$CuSO_4$	5.51	9.5	170	18	120	35	0	96	04
			180	249	60	99	44	47	09
					120	100	61	23	16
$Fe_2(SO_4)_3$	3.04	12.6	170	86	60	56	04	88	08
					120	77	09	80	11
$Al_2(SO_4)_3$	3.97	10.5	170	240	60	99	31	57	12
					120	100	56	29	15
$Zr(SO_4)_2$	2.94	12.6	160	798	30	100	48	38	14
					60	100	65	18	17
$Ti(SO_4)_2$	3.01	13.5	160	886	30	100	50	38	12
					60	100	68	16	16
$Yb(OTf)_3$	5.6	---	160	22	60	21	02	96	02
			180	133	60	96	21	70	09
					120	100	55	33	12
$Sc(OTf)_3$	3.8	---	160	675	30	100	49	38	13
					60	100	67	18	15

[a] Reaction condition: Sorbitol = 54.9 mmol, catalyst = 0.52 mmol, stirring speed = 800 rpm

[b] pH of reaction mixture after reaction (2% aqueous solution)

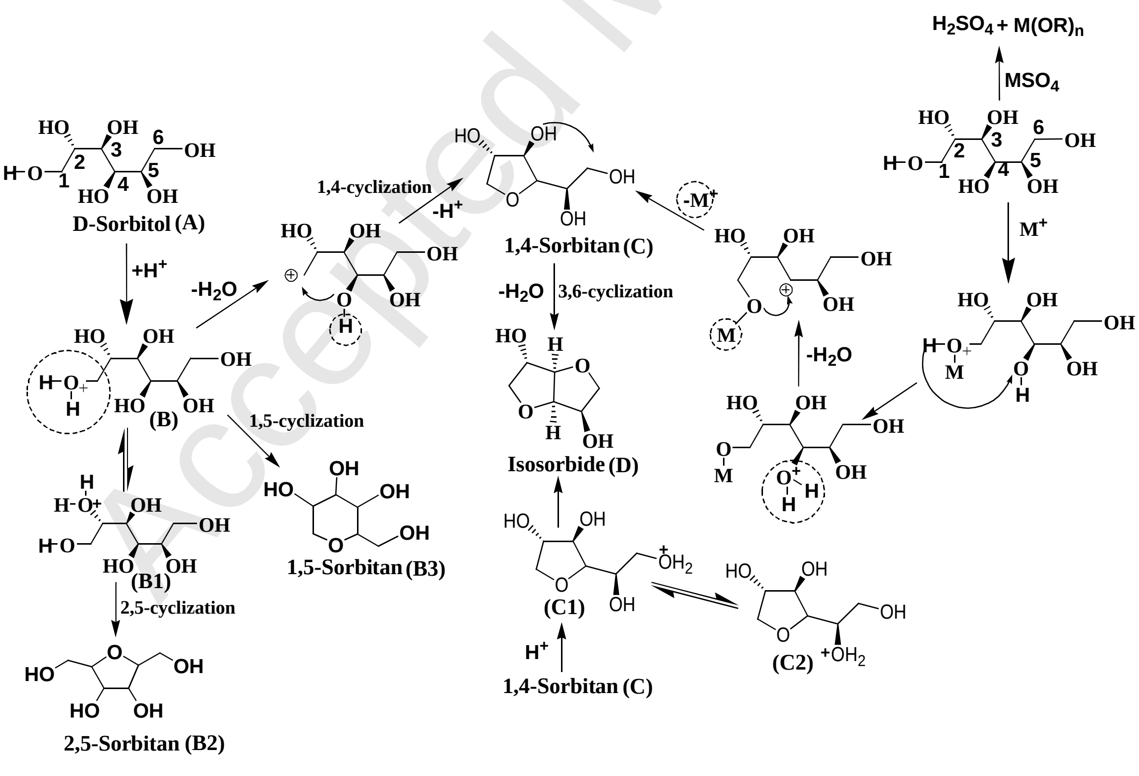
[c] $X_i = (1+ 2Z) X_o$; where X_o = electronegativity of the neutral atom, Z = charge of the ion [47]

[d] TOF_{SB} = initial turnover frequency for sorbitol calculated at 10−20% sorbitol conversion

Previously, we and Xia et al studied dehydration of sorbitol to isosorbide using sulfated metal oxides of different metals such as Ni, Cu, Al, Zr and Ti under heterogeneous condition [37−39]. It was observed that catalyst activity and isosorbide selectivity were varied with metal used and high catalyst isosorbide selectivity was achieved with sulfated TiO_2 (70%). The above achieved results with homogeneous Lewis acid catalysts are in accordance with previous results and realized high yield at relatively low reaction temperature (160 °C against 200−220 °C) was due to homogenous condition. The reason for high activity of $Ti(SO_4)_2$ and $Zr(SO_4)_2$ may be due to their higher electronegativity (Table 2, for $Ti(SO_4)_2$, X_i= 13.5 and for $Zr(SO_4)_2$, X_i= 12.6). The electronegativity is an important parameter for metal sulfates to determine their catalytic activity and selectivity in acid-catalyzed reactions [47–49]. However, $Fe_2(SO_4)_3$ having high electronegativity (X_i = 12.6) produced less isosorbide because of less solubility of $Fe_2(SO_4)_3$ in molten sorbitol as reaction was performed in solvent free condition. The acidic properties of metal sulfates also depend upon their degree of rehydration [50]. In presence of water, Lewis acids induce Brönsted acidity by co-ordination of water molecules to the metal centre, thereby polarizing the O–H bond and rendering them substantially more Brönsted acidic (water derived induce Brönsted acidity) than the parent compound [51]. On the other side, It has also been reported that metal chloride react with the hydroxyl groups of sugar to form metal alkoxides, $M(OR)_n$ and HCl [52]. Similarly, it can be assume the formation of H_2SO_4 or the generation of bronsted acid sites on metal sulfates due to the formation of water during reaction. The degree of metal sulfates rehydration and coordination of sugar to metal are vary from one to another during dehydration; hence the activity/selectivity of metal sulfates varied from one metal to another metal. In view of above, metal sulfates could not act as ‘true Lewis acid’ due to the generation of water during reaction and their activities are water dependent. The metal sulfates $Ti(SO_4)_2$ and $Zr(SO_4)_2$ displayed high activity but their the reaction mixture (2% aqueous solution) are quite acidic i.e. pH around ~3 which is similar to the pH of organic acids catalyzed reaction mixture **(Table 2).** Also, the dehydration of sorbitol catalyzed by such metal sulfates $Ti(SO_4)_2$ and $Zr(SO_4)_2$ exhibited similar isosorbide yield to Brönsted acid under identical reaction condition with major intermediate product 1,4-sorbitan (see supporting information). It is suggested that observed higher activity with such metal sulfates may not raised solely by Lewis acids sites but generation of Brönsted acid sites on the surface of metal sulfates or formation of H_2SO_4. Later, we selected metal triflates such as $Yb(OTf)_3$, and $Sc(OTf)_3$ as Lewis acid catalysts to study dehydration of sorbitol. Such metal triflates are considered as stable water-soluble Lewis acids. At 160 °C, The catalytic activity of $Yb(OTf)_3$ was considerably less than $Sc(OTf)_3$ exhibiting only 21% conversion with 2% isosorbide selectivity. $Sc(OTf)_3$ showed initial TOF (675 hr^{-1}) somewhat lower than $Ti(SO_4)_2$ and $Zr(SO_4)_2$ but produced isosorbide with high selectivity (67%) in 60 min at 160 °C. Initially, catalyst activity and formation of isosorbide to some extent were low due to the slow mixing of this triflate. Once it dissolved completely in molten sorbitol ensuing high yield of isosorbide comparable to $Ti(SO_4)_2$, $Zr(SO_4)_2$ and strong organic acid. However, pH of $Sc(OTf)_3$ reaction mixture is relatively less around 3.8 than the $Yb(OTf)_3$ (pH = 5.6). The generation of triflic acid from metal triflate has also been observed in some cases termed as 'Hidden Brönsted Acidity' [53]. Wang et al studied dehydration of fructose to 5-hydroxymethylfurfural (5-HMF) in DMSO using various metal triflates. The high catalytic activity and yield of 5-HMF were achieved with $Sc(OTf)_3$ and $Yb(OTf)_3$ due to their smaller ionic radius [54]. In the case of sorbitol dehydration by such metal triflates displayed incongruous catalyst performance. The high catalytic activity only achieved with $Sc(OTf)_3$ with less pH of reaction mixture. This indicates the generation of hidden Brönsted acid site in the case of $Sc(OTf)_3$ which considerably enhance its catalytic activity. From the results of Brönsted and Lewis acid catalysts, it can be seen that Brönsted acid site and Lewis-assisted Brönsted acidity (water-derived Brönsted acidity) played significant role for efficient dehydration of sorbitol to isosorbide. The above results are in connection with results of xylose (pentose sugar) dehydration to furfural reported by Weingarten et al [55]. They investigated dehydration of xylose using homogeneous Brönsted and Lewis acid catalysts. They observed that the catalyst selectivity is a function of the Brönsted to Lewis acid site ratio for both the heterogeneous and homogeneous catalyst. The Brönsted acid catalyst or catalyst with higher Brönsted to Lewis acid ratio produced high yield of furfural while Lewis acid sites decrease furfural selectivity by catalyzing a side reaction between xylose and furfural [55]. In the case of xylose dehydration, Lewis acid site first isomerizes the xylose to xylulose or lyxose. The further conversion of these products strongly depends on nature of acid sites whereas isomerization does not take place in case of sorbitol (a sugar alcohol). Therefore, influence of Lewis acid site in sorbitol dehydration is less than Brönsted acid site. Moreover, G. Fleche and M. Huchette reported that the performance of Lewis acid catalysts (such as $AlCl_3$ and $SnCl_4$) in aqueous phase dehydration of sorbitol is lower than Brönsted acid catalyst and are less efficient for production of isosorbide [23].

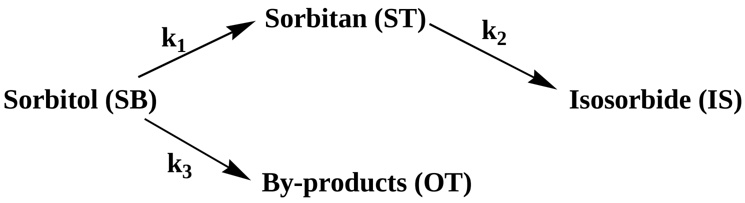
Based on the literature and characterization data [34,42,43], possible mechanism is outline for sorbitol dehydration using Brönsted and Lewis acid catalyst **(Scheme 2).** The mechanism for dehydration of sorbitol by Brönsted acid (H^+) can explained by preferential protonation of the hydroxyl group at C_1 or C_6 position in the sorbitol **(Scheme 2)** and then cyclic dehydration of these carbons with C_4 or C_3 produces 1,4-sorbitan or 3,6-sorbitan [34]. However, most of authors suggest first cyclization occur between C_1 and C_4 positions (1,4-cyclization, B→C) which produces 1,4-sorbitan [34,40,42−45]. The further protonation of C_6 hydroxyl group of 1,4-sorbitan and cyclic dehydration with C_3 (3,6 cyclization, C1→D) forms a bicyclic product, isosorbide (1,4:3,6-dianhydrosorbitol). The first cyclic dehydration can also be take placed between C_2 and C_5 or C_1 and C_5 which leads to the formation of 2,5-

sorbitan (through intramolecular hydrogen bonding, B→B2) and 1,5-sorbitan (B→B3). There is also possibility of protonation at C_5 in the case of 1,4-sorbitan through intramolecular hydrogen bonding (C1→C2) [45]. Therefore, the second cyclic dehydration proceeds slowly then first dehydration step. In addition, the formation of colored side products ('humins') can be observed from the beginning of the reaction (**Scheme 1).** This indicates that the side products may be generate by the dehydration of two sorbitol molecule or by the condensation of sorbitol with one of the sorbitans and their degradation [23,34]. On the other hand, In the case of metal sulfate, the reaction is either proceed with direct protonation of the C_1 or C_6 hydroxyl groups of sorbitol by metal cation or metal sulfate first react with the hydroxyl groups of sorbitol to form metal alkoxides, M(OR)n [52] and H_2SO_4 ensuing isosorbide similar to Brönsted acid.



Scheme 2 Proposed reaction mechanism for Brönsted and Lewis acid catalyzed dehydration of sorbitol

From the achieved results of metal sulfates, it has been observed that the catalyst TS exhibited catalyst activity similar to MSA. The catalytic behavior of both catalysts (TS and MSA) was also compared by considering kinetic aspect in order to get more insight about formation products with their activation barriers using both catalysts. Based on reaction mechanism of sorbitol dehydration and experimental data, the simplified reaction scheme is proposed with rate constants (k_1, k_2 and k_3) and corresponding rate equations (1 to 4) are derived from the reaction **scheme 3**. The sorbitol undergoes to produce sorbitan or other by products (parallel reactions) and sorbitan further dehydrates to produce isosorbide (consecutive reaction). The constant k_1 represents the dehydration of sorbitol (SB) to sorbitan (ST), the constant k_2 represents dehydration of sorbitan (ST) to isosorbide (IS) and the constant k_3 correspond to the formation of other dehydration and degradation by products (OT) from Sorbitol or sorbitan. In order to determine order of reaction, the tests for zero, first and second order were carried out. The plot of $-\log[SB]/[SB]_0$ against time is observed to be linear indicating that the dehydration of sorbitol using both catalysts follows the first order with respect to sorbitol **(Fig. S4 and S5).**



Sorbitan (ST) = 1,4-Sorbitan + 1,5-Sorbitan
or
3,6-Sorbitan

$$\frac{d[SB]}{dt} = -k_1[SB] - k_3[SB] \qquad (1)$$

$$\frac{d[ST]}{dt} = k_1[SB] - k_2[ST] \qquad (2)$$

$$\frac{d[IS]}{dt} = k_2[ST] \qquad (3)$$

$$\frac{d[OT]}{dt} = k_3[SB] \qquad (4)$$

Scheme 3 Simplified reaction scheme for sorbitol dehydration with rate constant and corresponding rate equations.

Oltmanns et al [42], Li et al [44] and Yamaguchi et al [45] also proposed kinetic model for dehydration of sorbitol assuming first order reaction for all the steps. The experiment data of both catalysts MSA and TS at different temperatures (140,150,160 and 170 °C) were fitted to the above kinetic model for the estimation of the three rate constants. The POLYMATH 6.1 software was used for the numerical integration of above differential equations and for parameter estimations. The good concord between experiment data and modeled data can be seen in all cases (Figure S6). In the present model, the measure data of sorbitan is combined concentration of 1,4- and 1,5-sorbitan as peak of both intermediate products are not well separated by HPLC. For both catalysts of MSA and TS, the rate constants (k_1, k_2 and k_3) of the three reaction steps at various reaction temperatures have been determined and presented in **Table 3**. The activation energies and pre-exponential factors corresponding to each rate constants were calculated for both catalysts by Arrhenius plot **(Fig. 6)** and presented also in **Table 3.** The observed activation energy values of the steps k_1 and k_2 for both catalysts MSA and TS are comparatively less than other reported silicotungsticacid [42] and $ZnCl_2$ molten salt catalyst [44] systems indicating efficiency of both catalyst systems under solvent free conditions. Although, both catalysts exhibited the activation energy values comparable to H_2SO_4 catalyst for the formation of sorbitan and isosorbide (E_{a1} = 47.9 and E_{a2} = 51 kJ/mol) [56]. It is noted that activation energy barrier of step 2 for isosorbide formation from sorbitan is higher than step 1 for sorbitan formation. This indicated that the second cyclic dehydration proceeds slowly then first dehydration step and coincides with above proposed mechanism. In individual comparison of TS with MSA catalyst, the achieved activation energy values using TS catalyst for each step are found to be comparable with MSA catalyst. This confirm that the behavior of TS catalyst is similar to Brönsted acid MSA and generation of bronsted acid site on the surface of metal sulfates as pure lewis acid catalyst is less efficient for sorbitol dehydration to isosorbide.

Table 3 Estimated rate constants and corresponding activation energies for the dehydration of sorbitol using MSA and TS catalysts

Catalyst	Rate Constant (10^{-2} min^{-1})	Temp. (K)				Ea (kj/mol)	A
		413	423	433	443		
MSA	k_1	12.4	16.85	26.1	30.8	48.2	1.57E+05
	k_2	1.10	1.45	2.58	3.20	57.5	1.99E+05
	k_3	1.10	2.08	4.20	7.20	96.4	1.69E+10
TS	k_1	12.0	15.5	26.15	32.0	52.7	5.42E+05
	k_2	1.0	1.57	2.86	3.18	62.1	7.44+E05
	k_3	1.0	1.92	4.3	7.1	101.7	7.27E+10

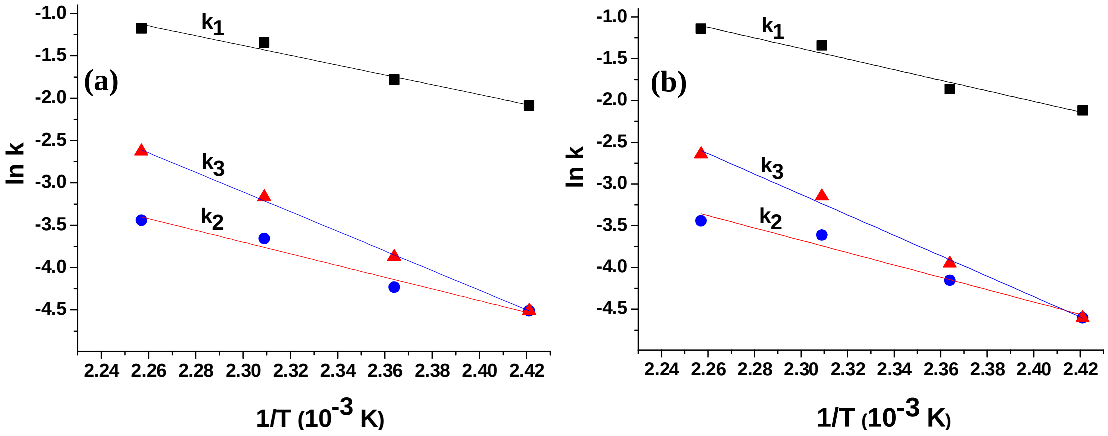


Fig. 6 Arrhenius plots of three reaction steps for both catalysts MSA (a) and TS (b).

In order to confirm further role of acid sites and their influence on isosorbide selectivity, the few experiments were also performed by combining two catalyst systems. It has been reported that the combination of Brönsted and Lewis acid catalyst or the catalyst having Brönsted as well as Lewis acid sites can greatly influence the catalyst activity and selectivity [38−40, 55,57]. Subsequently, we combined Brönsted and Lewis acid catalyst in equal ratio of 1:1 without varying final concentration of catalyst (0.52 mmol) and studied their influence on activity/selectivity. Two sets of experiments were performed one with combining MSA and $Ti(SO_4)_2$ (TS) and another with MSA and $Sc(OTf)_3$ (SCT). **Figure 7** shows yield of isosorbide at different time of interval for individual and combined catalysts. In the case of combined catalyst (MSA+TS), the initial reaction rate and isosorbide yield were same as individual catalyst system and exhibited a maximum isosorbide yield (70%) at final stage. On another hand, the initial reaction rate and isosorbide yield were slightly improved at initial stage in the case of MSA+SCT than individual one. The addition of MST to SCT increased amount of Brönsted acid site which led to enhance catalyst performance. However, this combined catalyst showed almost comparable isosorbide yield (68%) after 1 h. The above results confirm the key role of Brönsted acid site and catalyst with Lewis-assisted Brönsted acid site (water-derived Brönsted acidity) performs similar to Brönsted acid catalyst. Moreover, the catalyst with higher amount of Brönsted acid sites led to enhance catalyst activity and isosorbide selectivity. In this view, present findings would be useful in designing of efficient heterogeneous catalyst system for dehydration of sorbitol.

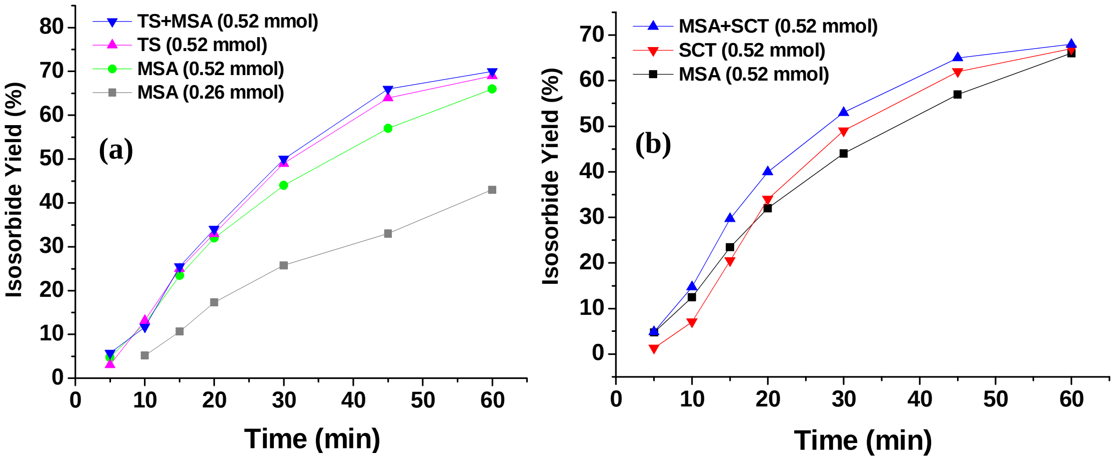


Fig. 7 Dehydration of sorbitol using combination of Brönsted and Lewis acid catalyst, (a) MSA and TS, (b) MSA and SCT; Reaction condition: Sorbitol = 54.9 mmol, temperature = 160 °C.

3. Conclusions

Dehydration of sorbitol to isosorbide has been investigated under solvent free condition using a range of acid catalysts such as organic acids, metal sulfates and metal triflates. The strength and nature of acid sites played an important role in improving the sorbitol conversion and isosorbide selectivity. Based on the experiment results of distinct Brönsted acids, it is stated that the strong acidity ($pK_a < -1.74$) is necessary to achieve high activity and yield of isosorbide at moderate temperature. All strong organic acids such as MSA, PTSA, TFA having $pK_a < -1.74$ exhibit almost similar catalyst activity and isosorbide selectivity. The catalysts with modest or weak acidity produce high amount of sorbitan (a mono-dehydrated product). Beyond acidic strength of catalyst, the catalyst activity and anhydroalcohols selectivity are also affected by the nature of Brönsted and Lewis acid sites. The Brönsted acid catalyst or catalyst with high amount of Brönsted acidity is effective for dehydration of sorbitol to isosorbide than Lewis acid. The catalyst activity of Lewis acid catalyst is depended on which metal used and the generation of Brönsted acid site on the metal centre. The Lewis-assisted Brönsted acid site (water-derived Brönsted acidity) exhibits similar performance as Brönsted acid catalyst and enables high yield of isosorbide (70%) at moderate temperature (160 °C).

4. Experimental

4.1. Materials

D-Sorbitol, 1,4-sorbitan, 1,5-sorbitan, isosorbide, p-toluenesulfonic acid (PTSA), methane sulfonic acid (MSA), trifloromethane sulfonic acid (TFA), sulfamic acid (SFA), Citric acid (CTA), $NaHSO_4$ (SHS), Boric acid (BA), $CuCl_2 \cdot 2H_2O$, $CuSO_4 \cdot 5H_2O$, $Fe_2(SO_4)_3 \cdot xH_2O$, $NiSO_4$, $Al_2(SO_4)_3 \cdot xH_2O$, $Yb(OTf)_3$, $Sc(OTf)_3$, acetonitrile (99.5%) were purchased from Sigma-Aldrich company, Inc, (USA). H_2SO_4 (95%), $Ti(SO_4)_2$ and $Zr(SO_4)_2$ were purchased from Junsei chemical Co. Ltd, Japan. All the chemicals used in this study were used without further purification. De-ionized water was used as solvent for making all solutions.

4.2. General procedure for the dehydration of sorbitol

The dehydration of sorbitol was performed in simple reactor setup under solvent free and reduce pressure condition. This process involved the following steps: (i) Melting of sorbitol at 110 °C through conventional heating with heating rate of 5 °C/min in air. (ii) Addition of catalyst in order to start dehydration reaction at desire reaction temperature. (iii) Neutralization of acidic catalyst and then filtration of reaction mixture to separate solid impurities from the product. The dehydration of sorbitol was performed under vacuum (100 mm Hg) and was maintained constantly throughout reaction to remove water from the reaction mixture. The dehydration of sorbitol was carried out in liquid phase using a round bottomed 100 mL three-neck flask equipped with temperature indicator and a water-cooled condenser attached to a vacuum pump. Sorbitol (54.9 mmol) was first charged into the dehydration reactor. The temperature was heated to 110 °C. After melting of sorbitol, the reactor was heated to desire reaction temperature. An appropriate amount of acid catalyst (the number of acid site was kept constant at 0.52 mmole in most of cases) was then added to the liquid sorbitol to start the dehydration reaction. The reaction mixture was stirred at 800 rpm and vacuum was applied (100 mm Hg). The vacuum was maintained continuously to remove water from the reaction mixture. Samples were withdrawn at selected times, diluted by DI water and filtered with a 0.2 μm syringe filter prior to analysis. The composition of the dehydrated products was analyzed using HPLC (Younglin Instrument, Acme 9000) equipped with a refractive index (RI) detector and Asahipak column (NH2P-50 4E, No. N712004). An acetonitrile/water (80/20) mixture was used as an eluent for the analysis with a flow rate of 1.0 mL/min. The temperature of the RI detector was maintained at 35 °C throughout the analysis. The products and sorbitol were well separated by HPLC and indentified by their pure samples (see supporting information). The main dehydration products detected were isosorbide and sorbitan (mostly 1,4-sorbitan with small amount of 1,5-sorbitan). The sorbitol and isosorbide were quantified using their own response factors whereas response factor of 1,4-sorbitan was used to quantify both sorbitans. Based on molar compositions, the conversion of sorbitol (SB) and selectivity of isosorbide (IS) and sorbitan (ST) were calculated according to the reported method [34,35] by using following equations. The non-indentified soluble and insoluble compounds were reported as unknown or others (humins). The yield of humins or unknowns was deduced from the difference between initial mole of sorbitol and sum of the moles of isosorbide and sorbitan analyzed by HPLC (i.e. it gives mole of remaining unknown compounds from initial mole of feed Sorbitol). In order to calculate carbon balance, the total mass of carbon in the liquid phase is obtained by TOC analysis

(Table S1). The initial TOF for sorbitol (TOF_{SB}) were calculated at sorbitol conversion in the range of 10–20%.

$$\text{TOF}_{SB} = \frac{\text{moles of sorbitol converted}}{\text{moles of H}^{+}\text{ x hr}} \quad \text{(in the case of Bronsted acid)}$$

$$\text{TOF}_{SB} = \frac{\text{moles of sorbitol converted}}{\text{moles of acid x hr}} \quad \text{(in the case of Lewis acid)}$$

$$\text{Conversion}_{SB}\,(\%) = \left(1 - \frac{\text{mole of sorbitol at particular time}}{\text{Initial mole of sorbitol}}\right) \text{ x } 100$$

$$\text{Yield}_{ST}\,(\%) = \left(\frac{\text{mole of sorbitan in product}}{\text{Initial mole of sorbitol}}\right) \text{ x } 100$$

$$\text{Selectivity}_{ST}\,(\%) = \left(\frac{\text{Yield of sorbitan}}{\text{Sorbitol conversion}}\right) \text{ x } 100$$

$$\text{Yield}_{IS}\,(\%) = \left(\frac{\text{mole of isosorbide in product}}{\text{Initial mole of sorbitol}}\right) \text{ x } 100$$

$$\text{Selectivity}_{IS}\,(\%) = \left(\frac{\text{Yield of isosorbide}}{\text{Sorbitol conversion}}\right) \text{ x } 100$$

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