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Catalytic dehydration of sorbitol to isosorbide in the presence of metal tosylate salts and metallized sulfonic resins

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Abstract: Homogeneous catalytic dehydration of sorbitol to isosorbide has been performed with a series of metal tosylates as catalysts. Conversions up to 100 % and selectivities into isosorbide up to 67% were obtained with Bi(OTs)₃. The metals were exchanged with acidic sites of sulfonic resins and the resulting materials were evaluated as heterogeneous catalysts. On the contrary to their homogeneous counter parts, the heterogenized metal sites are non-active. The catalytic activity of the modified resins was systematically diminished in comparison to the native resins. The inhibition is greatly dependent on the nature of the metal and, on a larger extent, of the used resin for the cation exchange.

Keywords: isosorbide, sorbitol, dehydration, tosylate metal, sulfonic resins

1. Introduction

The use of bioresources instead of petro-sourced raw materials for the synthesis of chemicals is a major issue for future developments.¹⁻⁴ In this context, sugars are very important renewable molecules due to their large availability at industrial scales from very diversified vegetal sources. Sugars have since a long time found a great variety of applications.^{5,6} In many cases, these polyhydroxylated compounds are used without any chemical transformation, for example as energy source (glucose) or low-calorie sweetener (xylose). Their chemical transformation opens the way to a broader scope of applications. They have been for example used as starting materials for the synthesis of many industrially important chemicals such as furans (furfural and hydroxymethylfurfural), acids (glucaric acid), alcohols (ethanol) and alkyl polyglycosides.⁷

Difunctional molecules (diols, diacids) are part of a particularly attractive class of compounds for their use as monomers in polycondensation reactions. In this context, isosorbide is a very promising bio-derived platform molecule for the chemicals market for which applications should dramatically increase in the future years.⁸ Derived from glucose through a multistep hydrogenation/dehydration process, this diol is actually used for the production of high performance polymers, for example Poly Ethylene Isosorbide Terephthalate (PEIT), to increase properties of resistance and optical clarity and in polycarbonates as substitute of bisphenol A.⁹ This compound has also been chemically modified to synthesize alternative plasticizers to phthalates.¹⁰ In view of the applications of isosorbide at the industrial scale, a drastic increase of the production of this molecule is expected and this further strengthens the importance of developing more efficient synthetic pathways and related catalysts. The key step of the isosorbide synthesis is the double dehydration of sorbitol. As shown in Figure 1, dehydration of sorbitol leads after the first dehydration step to several different monoanhydrohexitols named sorbitans. Among them, only the 3,6-sorbitan and the 1,4-sorbitan are precursors of isosorbide after a second dehydration step. The others sorbitans ultimately lead, after further intra- or intermolecular dehydration steps, to colored oligomeric species named “humins”. The formation of humins drastically contributes to reduce the mass balance of the reaction. More active and selective catalysts are thus needed. The reaction has been first performed in the presence of sulfuric acid.¹¹ A variety of catalysts such as mineral⁹ and organic acids¹², metal salts¹³ or solid acid catalysts such as ions exchange resins^{14,15}, zeolites¹⁶⁻¹⁸ or metal phosphates¹⁹ have been developed. In the case of Bronsted acid, their pKa value is a key parameter for high catalytic activities as values below 0 are generally required.²⁰ Dehydration was also demonstrated under MW irradiation²¹ and in advanced reaction media such as sub- or supercritical solvents or in molten salts.²² Recently, Zhao proposed a one-step synthesis of isosorbide from cellulose in the presence of a combined catalytic system composed of strong acid and ruthenium supported on carbon²³. Dehydration could also be performed without any acid catalyst in high temperature liquid water.²⁴ Nevertheless, although this reaction gave rise to an important number of publications²⁵, sorbitol dehydration to isosorbide remains a challenge in terms of efficiency and selectivity.

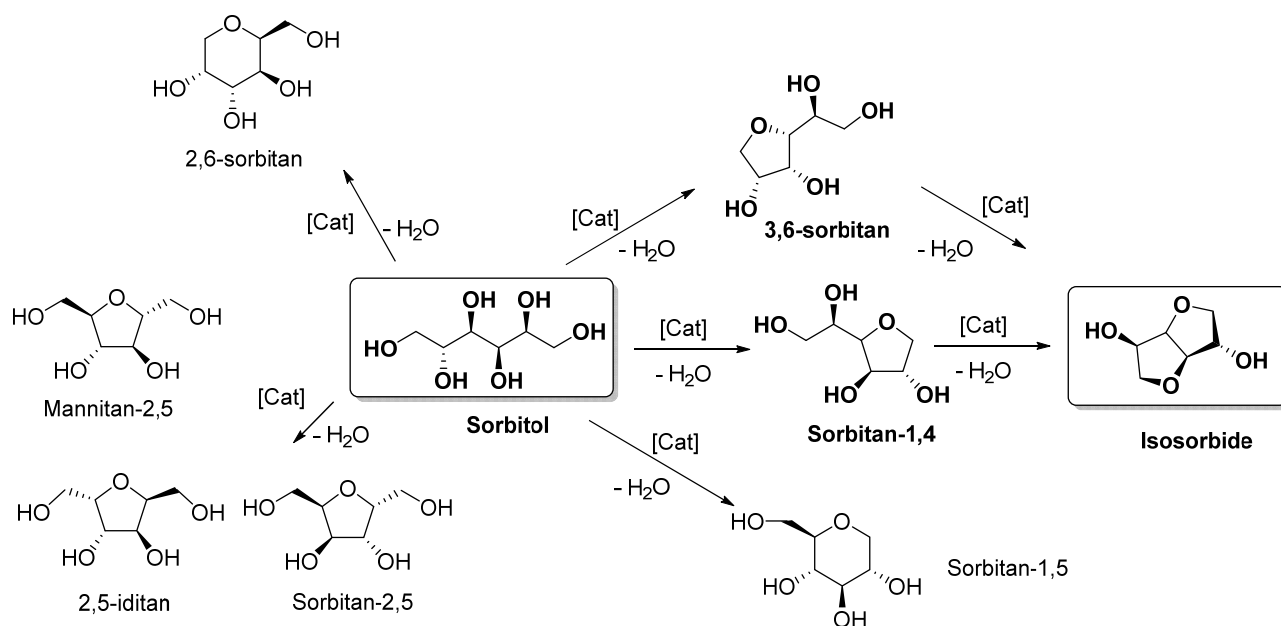


Figure 1: The different ways of dehydration of sorbitol.

Recently, water-tolerant Lewis acid catalysts based on triflate metals were found to be very efficient with, for example, an isosorbide yield up to 71% with only 0.05 mol% of $\text{Ga}(\text{OTf})_3$ at 160°C after 1 hour.²⁶ Metallic tosylates salts have a moderate cost in comparison to their triflate equivalents. Their straightforward synthesis and high stability prompted us to evaluate their efficiency as novel catalysts for the formation of isosorbide. Moreover, the metals were immobilized in a sulfonic resin through cation exchange and the synthesized materials were further studied as potent heterogeneous catalysts for the dehydration of sorbitol.

2. Experimental

2.1. Materials

Sorbitol, isosorbide, isomannide were given by Roquette Frères and used without further purification. Chemicals were purchased from Aldrich, Alfa Aesar, Acros or Strem.

2.2. Synthesis of the metallic tosylates precursors $\text{M}(\text{OTs})_n$

The metallic precursors were obtained according to described procedures.²⁷ The purity of the compounds was assessed by elemental analysis.

a) *From the chloride precursors:* the metallic precursor MCl_n (20 mmol) was mixed with 44 mmol PTSA (para-toluenesulfonic acid) (when $n=2$) or 66 mmol of PTSA ($n=3$) in 100 mL acetonitrile. After dissolution of the solids under vigorous stirring, the solvent was evaporated and the solid mixture was heated at 165°C for 4 hours under 1 mbar pressure. The solid was cooled and 100 mL of methanol were added. The resulting mixture was refluxed for 1 h and filtrated. The solvent was evaporated under low pressure. 100 mL of acetonitrile were added to the solid and the mixture was stirred and heated for 1 h at 50°C . The solid was filtrated and washed twice with 20 mL of hot acetonitrile then dried under vacuum at 150°C .

b) *From nitrate metallic precursor:* 40 mmol of metallic precursor $M(\text{NO}_3)_n$ were dissolved in 100 mL water under stirring. Then 50 mL of a solution of KOH (4 mol.L^{-1}) were added. The metallic hydroxides precipitated immediately and were isolated by filtration. The solid was washed with water (3 x 50 mL). The metallic tosylates were obtained according the same procedure used for the chloride precursors.

c) *From the hydroxide precursors:* the precursor $M(\text{OH})_n$ (20 mmol) was mixed with 44 mmol PTSA (when $n=2$) or 66 mmol of PTSA ($n=3$) in 100 mL methanol. The mixture was refluxed for 8 hours and filtrated on celite. Methanol was evaporated under vacuum and 100 mL of acetonitrile were added. The mixture was heated 1 h at 50°C , filtrated and washed twice with hot acetonitrile (20 mL). The resulting solid was finally dried overnight at 150°C under vacuum.

2.3. Preparation of the modified resins

The resin (5 mmol of H^+) was added to a 10 mL aqueous solution of metallic tosylate $M(\text{OTs})_n$ (example: 0.25 mmol of metallic tosylate for 5% metal in the resin).^{28,29} After 48 h stirring at ambient temperature, the resin was filtrated and washed with 10 mL of deionized water. The filtrate was titrated by a soda solution in order to determine the amount of PTSA released in the solution and thus to evaluate the percent of metal loaded in the resin. The calculated maximum amount of metal that can be loaded in the resin was in all cases in agreement with the amount of PTSA released in the water: $n(\text{metal}) = n_{\text{H}^+}/3$ in case of trivalent metals such as Cr^{3+} and $n(\text{metal}) = n_{\text{H}^+}/2$ in the case of divalent metals such as Mn^{2+} . In the case of iron, redox titration of the residual iron in the filtrate according to known volumetric procedures with SnCl_2 , HgCl_2 , $\text{K}_2\text{Cr}_2\text{O}_7$ could be performed to further check that all the Fe^{3+} have been exchanged with H^+ (quantitative cation exchange).^{30,31}

2.4. Catalytic tests

Dehydration reactions were performed either in a 250 mL glass reactor or in a 20 mL Schlenk tube from 10 g (0.055 mole) or 2.5 g (0.0137 mole) of sorbitol respectively. Sorbitol was first completely melted at 115°C then the mixture was stirred under vacuum at this temperature for 10 min in order to remove water. The reactor was filled with nitrogen and the catalyst was added. The pressure was adjusted to 40 mbar. The temperature of the solution was maintained at 115°C for one hour, heated to 130°C and stabilized for an additional hour, heated to 145°C and stirred for two additional hours. Aliquots of the reaction medium were sampled every hour and analyzed by GC.

2.5. Analysis and quantification of the products

Conversions and yields were determined by gas chromatography after derivatization of the hydroxyl groups of polyols with BSTFA (*N,O*-bis(trimethylsilyl)trifluoroacetamide). α -methylglucopyranoside was used as internal standard.

Calibration was first performed by weighing approximately precisely 50 mg of each polyol, isomannide, isosorbide, 1,4-sorbitan, sorbitol and α -methylglucopyranoside which were dissolved in 50 mL pyridine. 1 mL of this solution was mixed with 300 μ L BSTFA for one hour at 70°C. This mixture was injected in GC which allows determining the response factor of each polyol.

The reaction mixture could then be analyzed by GC after the same procedure: 25 mg of the crude mixture and 25 mg of α -methylglucopyranoside were dissolved in 10 mL pyridine. Then 1 mL of this solution and 300 μ L of BSTFA were mixed at 70°C for 1 h before injection in chromatography. The use of the response factors determined from the calibration allowed to quantify precisely each polyol. In all the tables, “others” includes humins and other unidentified side products of reaction. These amounts were determined from the mass balance of the reaction [others (%) = sorbitol conversion – (yield in isosorbide + yields in sorbitans)].

GC conditions: The GC analyses were performed on a GC Agilent 7890B equipped with a HT 5 column (30 m, 0.25 mm i.d., 0.25 μ m thickness). Conditions: injector and detector = 300°C, gas = hydrogen at 1.57 mL/min, temperature = 30 s at 140°C, ramp of 5°C/min up to 200°C, then ramp of 10°C/min up to 280°C and isotherm at 280°C during 10 min.

3. Results and discussion

We first synthesized a large variety of metallic tosylates with different metals as Cr(II), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Al(III), Bi(III), Ga(III) and Sn(II). The syntheses were readily implemented thanks to published procedures.²⁷ The metal salts could be obtained from the reaction of a metal hydroxide (Mn), metal nitrates (Cr and Fe) or metal chlorides (Al, Fe, Co, Ni, Cu, Zn, Bi, Ga and Sn) with a stoichiometric amount of *p*-toluenesulfonic acid. The yields in pure metal tosylates ranged from 60 to 80%.

The different salts were evaluated as homogeneous catalysts in dehydration reaction of sorbitol to produce isosorbide. Reactions were performed with 1 mol % of metal, at high temperatures ($T = 115\text{-}145\text{ }^{\circ}\text{C}$) and under vacuum (40 mbar) to eliminate water. Results are reported in Table 1. The results are compared to those obtained with sulfuric acid as catalyst. The reaction was stopped after 4 hours in order to obtain a satisfactory conversion and to limit the formation of other side compounds.

Table 1: Dehydration of sorbitol to isosorbide in the presence of tosylate salts.^a

Entry	Catalyst	Sorbitol Conv. (%)	Yield (%)			Others ^b (%)
			Isosorbide	1,4-Sorbitan	Sorbitans	
1	H ₂ SO ₄	100	68	0	6	26
2	PTSA	100	68	0	9	23
3	Co(OTs) ₂	97	11	51	12	23
4	Sn(OTs) ₂	100	24	39	9	27
5	Mn(OTs) ₂	13	0	0	0	13
6	Cu(OTs) ₂	53	1	30	7	15
7	Ni(OTs) ₂	5	0	0	0	5
8	Zn(OTs) ₂	100	7	51	12	30
9	Cr(OTs) ₃	100	64	0	7	29
10	Fe(OTs) ₃	100	66	0	10	24
11	Bi(OTs) ₃	100	67	2	10	21
12	Ga(OTs) ₃	100	50	19	10	21
13	Al(OTs) ₃	100	33	38	10	19

^a Reaction conditions : Sorbitol : 2.5 g (0.0137 mol); tosylate salt : 1% mol; $T = 115\text{-}145\text{ }^{\circ}\text{C}$ (115°C for 1 h, 130°C for 1 h, and 145°C for 2 h), $t = 4\text{ h}$.

^b Other side compounds formed during the reaction, including humins.

Metallic tosylates proved to be efficient in terms of activity and selectivity for the synthesis of isosorbide although they do not offer acidity as high as metal triflates.³² Indeed, the aromatic sulfonic acids are much weaker acids than triflic acid, *p*-toluenesulfonic acid, for example, is about 10^6 times weaker acid than triflic acid.³² The results are nevertheless very different according to the used metal with 5% to 100% sorbitol conversions and isosorbide selectivities from 0% to 67% (table 1). The best catalysts in terms of both activity and isosorbide selectivity are based on the trivalent metals rather than divalent ones. 11 % and 24 % yields in isosorbide are obtained with respectively $\text{Co}(\text{OTs})_2$ and $\text{Sn}(\text{OTs})_2$ (entries 3 and 4) and very few amounts of isosorbide are obtained with $\text{Mn}(\text{OTs})_2$, $\text{Cu}(\text{OTs})_2$, $\text{Ni}(\text{OTs})_2$, and $\text{Zn}(\text{OTs})_2$ (entries 5, 6, 7 and 8). $\text{Cr}(\text{OTs})_3$, $\text{Fe}(\text{OTs})_3$ and $\text{Bi}(\text{OTs})_3$ afford respectively 64 %, 66 % and 67 % yields in isosorbide (Entries 9, 10 and 11). $\text{Ga}(\text{OTs})_3$ and $\text{Al}(\text{OTs})_3$ showed a lower catalytic activity as respectively 33% and 50 % isosorbide yields were obtained along with these catalysts (Entries 12 and 13). In these two cases, the reaction did not reach completion within 4 hours as relatively high amounts of unreacted 1,4-sorbitan were obtained. The trivalent metals are likely more electrophilic than the divalent ones and hence more acidic. This higher acidity explains that trivalent metals are more active catalysts for the dehydration steps. Moreover, isosorbide yields compare well with those observed in the presence of sulfuric acid in the same catalytic conditions and the amounts of other side compounds attain 19-30%.

As the homogeneous metal tosylates showed interesting catalytic activity, we anticipated that a suitable chemical modification of acid sulfonic resins by metals could provide efficient hybrid systems with both Lewis and Brønsted acid sites. This choice was prompted by the fact that in a resin, Lewis acids would bear a similar structure with their homogeneous counterparts. In both cases, the counter-ions of the metals are arylsulfonate groups. We thus synthesized metal-modified resins by cation exchange between the protons of the sulfonic resins with the metals of the metallic tosylate salts. Among the large number of commercial sulfonic acids, we turned our attention toward highly acid and stable at high temperatures resins. Our choice was then orientated on different commercially available acidic resins and more particularly : 1) the Dowex® G26, Dowex® monosphere® (Uniform Particle Size) and Amberlyst® 70 that are polystyrene-co-divinylbenzene sulfonic acid resins. In the Amberlyst® 70, the presence of chlorine atoms confers a high temperature stability up to 190°C and has been described for the one-pot conversion of cellulose to isosorbide using metal catalysts and ion-exchange resin.³³ 2) the Nafion® NR50 is a tetrafluoroethylene sulfonated resin which is known as an efficient acid

catalyst for a wide scope of organic reactions³⁴ 3) the Aquivion® PW98, a perfluorinated polymer with sulfonic acid groups more recently launched on the market. This latter resin is described as a superacid solid capable to efficiently and selectively catalyze the oligomerization of glycerol³⁶, the glycosylation of glucose with fatty alcohols³⁷ and the conversion of cellulose into amphiphilic alkyl glycosides³⁸. Furthermore, the use of heterogeneous catalysts has several potential advantages, such as a fast and simple isolation of the reaction products as well as recovery and recycling of the catalyst. Main characteristic of these resins are summarized in Table 2.

Table 2. Characteristics of the sulfonated resins.^a

Resin	T _{max} (°C)	Structure	Size distribution (mesh)	Surface Area (m ² /g)	Size pores (diameter) (Å)	Total acid capacity (mmol H ⁺ /g)
Dowex® G26	150	Beads	22-25	n. d.	n. d.	1.63
Dowex® Monosphere® 650 C	150	Beads	21-25	n. d.	n. d.	1.63
Amberlyst® 70	170	Beads	25-40	36	220	2.55
Aquivion® PW98	160	Pellets	n. d.	n. d.	n. d.	0.980
Nafion® NR50	200	Beads	n. d.	n. d.	n. d.	0.8

^a Data from commercial source, n.d. = not determined

Very recently, the synthesis of sulfonic resins modified with metals such as Nafion-Fe, Aquivion-Fe and Aquivion-Ga³⁹ have been reported in literature. In our hands, the synthesis of the modified resins with metals was performed via cation exchange procedures (Figure 2, see experimental section). An aqueous solution containing the sulfonated resin and the adequate amount of the metallic tosylate salt were mixed for two days at ambient temperature then filtrated to obtain the modified resins. The amount of PTSA liberated in solution was determined by titration of the filtrate which allowed to calculate precisely the metal percent inserted into the resin. With this general method, Amberlyst 70 resin was modified with Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Al(III), Bi(III) and Ga(III) which were previously evaluated as tosylate salts under homogeneous conditions. All the metals could be easily loaded in the resin according to cation exchange reactions by mixing the Amberlyst with the metal

tosylate salts in aqueous solutions. Advantageously in the case of iron, the amount of non-exchanged metal remaining in the solution could be titrated in order to assess the quantity of iron in the resin (see experimental part). Titrations showed a quantitative immobilization of the metal in the material.

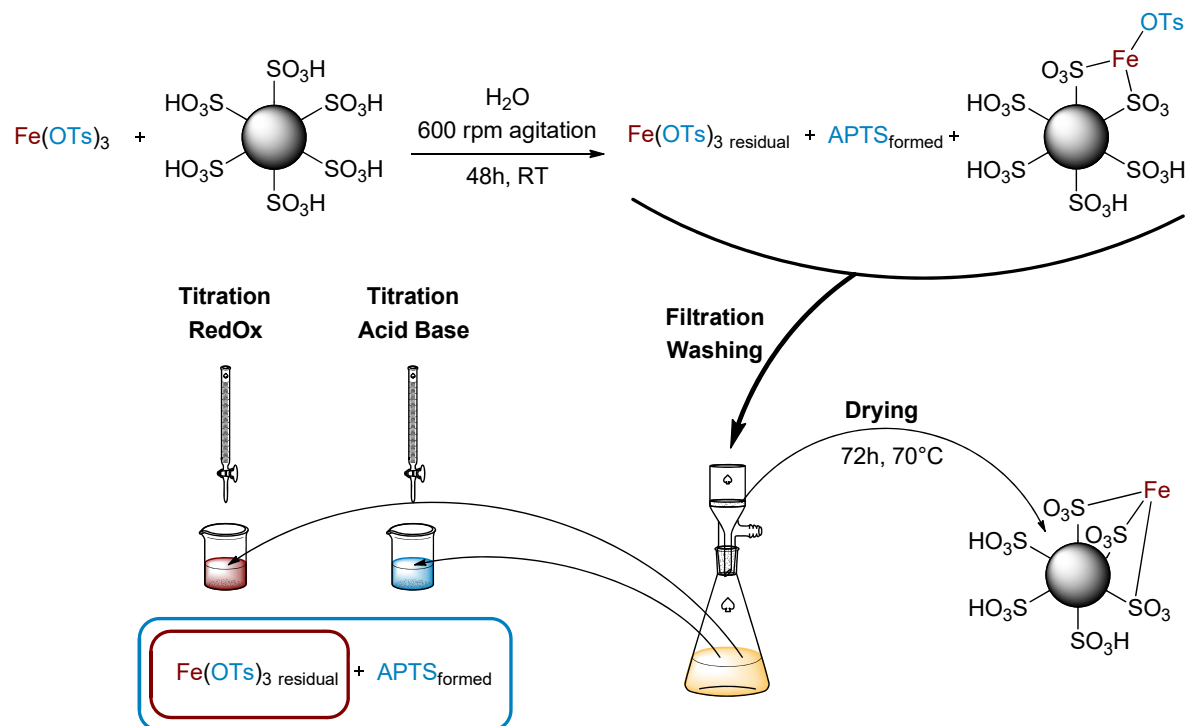


Figure 2. Synthesis of metallized sulfonic resins via ion exchange methods: example of iron

With the catalytic procedure reported above, we first explored the sorbitol dehydration reaction in the presence of the native resins as for most of them, nothing was found in literature. The reactions were performed with 1 mol % or 5 mol % of acidic site by adjusting the weight of resin. Table 3 reports the results obtained with different amounts of resins and comparison with sulfuric acid.

Table 3: Dehydration of sorbitol to isosorbide in the presence of native resins.^a

Entry	Catalyst	% mol H^+	Conv. (%)	Yield (%)			Others ^b (%)
				Isosorbide	1,4-Sorbitan	Sorbitans	
1	Nafion NR50	1	50	16	19	11	4
2	Monosphere	1	51	8	18	8	17
3	G26	1	52	9	18	8	17
4	Amberlyst 70	1	61	12	20	9	20
5	Aquivion	1	100	58	0	12	30
6	Nafion NR50	5	100	66	0	9	25

7	Monosphere	5	100	48	16	18	17
8	G26	5	100	51	16	19	15
9	Amberlyst 70	5	100	72	0	5	14
10	Aquivion	5 ^c	100	62	5	5	28

^a Reaction conditions : Sorbitol : 2.5 g (0.0137 mol); T = 115-145 °C (115°C for 1 h, 130°C for 1 h, and 145°C for 2 h), 40 mbar, t = 4 h.

^b Other side compounds formed during the reaction, including humins.

^c t = 2h; after 2 hours, the isosorbide yield decreased.

Reactions were first performed with 1 mol % of SO₃H group in respect to sorbitol. Nafion, monosphere, G26 and Amberlyst resins led to limited conversions of sorbitol ranging from 50% to 61% (Entries 1 - 4, Table 3). An increase of the resin loadings up to 5 mol % allowed obtaining full conversions of sorbitol (Entries 6-9, Table 3). The presence of 1,4-sorbitan with monosphere and G26 indicate a lower catalytic activity in comparison to Nafion and Amberlyst. With these two later resins, no intermediate sorbitan remains after 4 hours of reaction . 1% of the Aquivion resin proved to be sufficient to reach a full conversion within four hours albeit with a limited selectivity due to a residual amount of unreacted sorbitan and a high amount of side products (isosorbide yield = 58% yield, Entry 5).

Interesting features were observed thanks to GC monitoring in the case of the resins in comparison with the homogeneous system (sulfuric acid). Figure 3 presents curves that give the evolutions of the amounts of sorbitol, 1,4-sorbitan, isosorbide and side products with respect to the reaction time in the presence of sulfuric acid and Amberlyst 70 as catalysts. Although the maximum yields in isosorbide attained in both cases after 4 hours of reaction are very similar, the selectivity in sorbitans formed in the course of the reaction is markedly different.

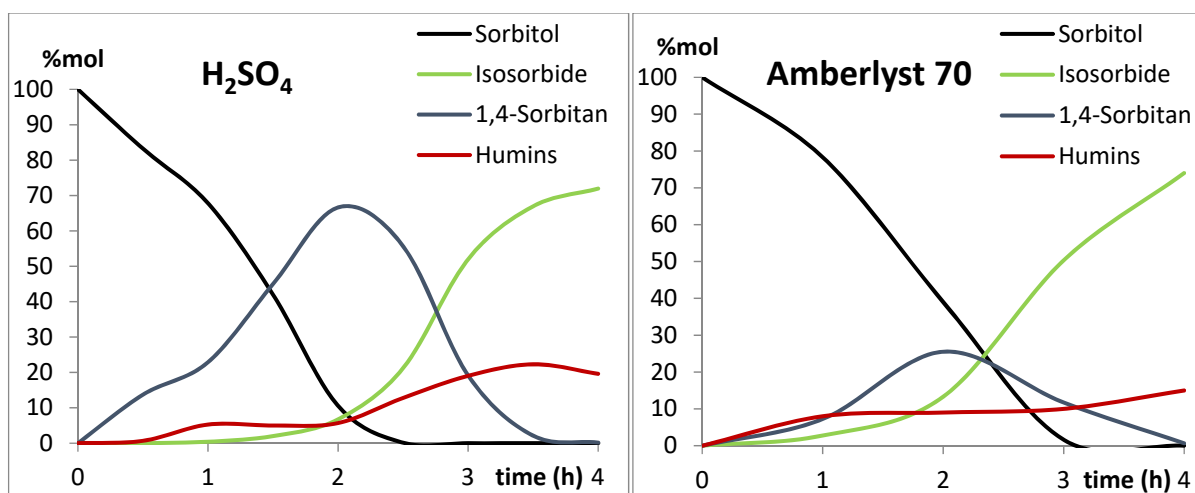


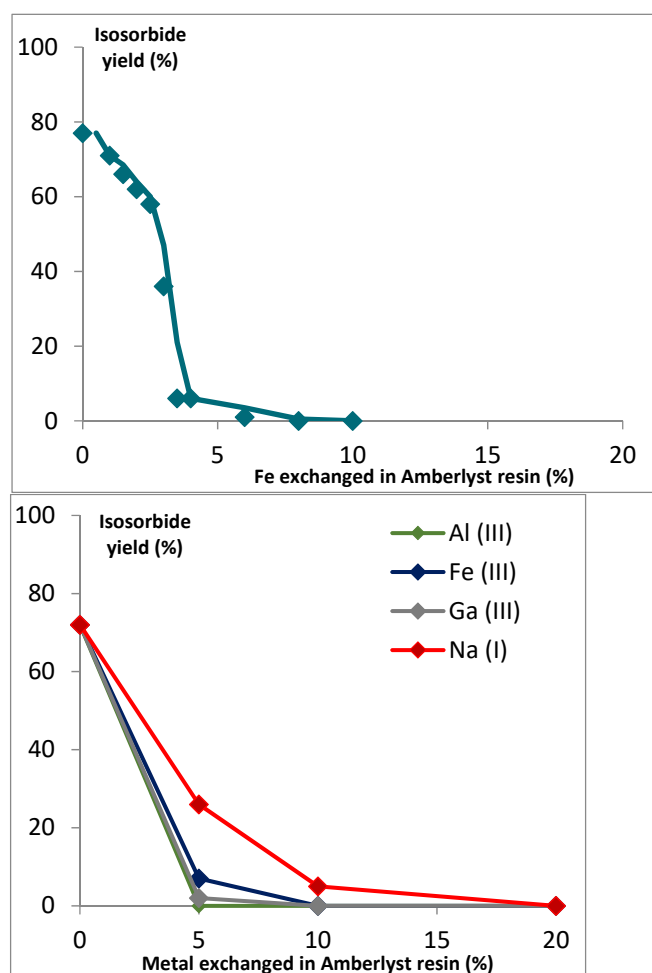
Figure 3: Comparison of the kinetic monitoring between H_2SO_4 (left side, 1% mol) and Amberlyst 70 (right side, 5% mol) during dehydration of sorbitol. Sorbitol 2.5 g (0.0137 mol); $T = 115\text{-}145\text{ }^\circ\text{C}$ (115°C for 1 h, 130°C for 1 h, and 145°C for 2 h), 40 mbar, $t = 4$ h. Maximum yields in isosorbide are attained after 4 hours of reaction in both cases.

Whereas the two dehydration steps were consecutive in the presence of sulfuric acid, in the case of Amberlyst 70, isosorbide is produced simultaneously with the 1,4-sorbitan. This difference is clearly evidenced by the amounts of the intermediate 1,4-sorbitan during the reaction. The amount of 1,4-sorbitan reaches 70 % in the case of sulfuric acid whereas the maximum yield is 30 % in the case of the resin. Moreover, in the heterogeneous system, side products are formed from the beginning of the reaction although the temperature does not exceed 115°C . At this temperature in homogeneous conditions, only the first sorbitol dehydration to sorbitans is observed. This effect can be due to the slow diffusion of sorbitans outside the strongly acidic pores of the resin. The local high concentration of sorbitans in this highly acid medium explains their rapid conversion into isosorbide and side products. Nevertheless, at the end of the reaction after 4 hours, the isosorbide yield remained very close to that obtained in the presence of sulfuric acid. Similar profiles were observed for all tested heterogeneous catalytic systems.

Similar catalytic conditions have been used with the resins modified with metals. A detailed catalytic study with Amberlyst 70 loaded with iron revealed a strong deactivation behavior at relatively low metal loadings as illustrated in Figure 4. Indeed, a dramatic drop of the catalytic activity appears from 3 % of iron loading. This shows that the catalytically active acid sites have been converted in inactive sites after the cation exchange. Clearly, these experiments show

that the active molecular catalyst is completely inefficient after being grafted in the resin as the chemical yield in isosorbide is roughly 0 % with 10 % loading of iron in the same reaction conditions. This difference of reactivity between the homogeneous and the heterogeneous systems can arise from the strong binding of the metal by the chelating tosylate groups within the resin. The brutal loss of activity observed suggests a surface deactivation of the material through the formation of an “egg shell like” metal loading. The most accessible acid sites for cationic exchange with metals are also the most accessible sites for substrates. This surface deactivation combined with the high viscosity of melted sorbitol lead to a rapid loss of the catalytic activity.

Figure 4: Influence of the % iron in Amberlyst 70 resin on the isosorbide yield (on left side) Influence of the % metal in Amberlyst 70 on the isosorbide yield (on right side).



Reaction conditions : Sorbitol : 10 g (0.055 mmol) ; T = 115-145 °C (115°C for 1 h, 130°C for 1 h, and 145°C for 2 h), t = 4 h. In the case of Al³⁺, Fe³⁺ and Ga³⁺, the percentage of H⁺ exchanged in the resin is 3 times the percentage of metal introduced.

A short comparative study regarding the nature of the metal (Al, Ga, or Na) in the modified Amberlyst resins underlines similar behaviors compared to iron (Figure 4, right side). Metals such as Al, Fe, Ga, lead to a very strong catalyst deactivation from 5% of metal loading and a complete deactivation with 10% loading. The results obtained with 5% loading allowed delineating slight differences between the metals. Considering the amount of metal exchanged in the resin, Na⁺ appears as the less deactivating metal in comparison to Fe³⁺, Al³⁺ or Ga³⁺. However, it should be taken into account that in the case of sodium, the number of neutralized acidic sites is three times smaller than with trivalent metals.

According to the same protocol, other resins listed Table 2 were loaded with different metals and evaluated in the catalytic synthesis of isosorbide from sorbitol. A representative example with gallium is shown Figure 5.

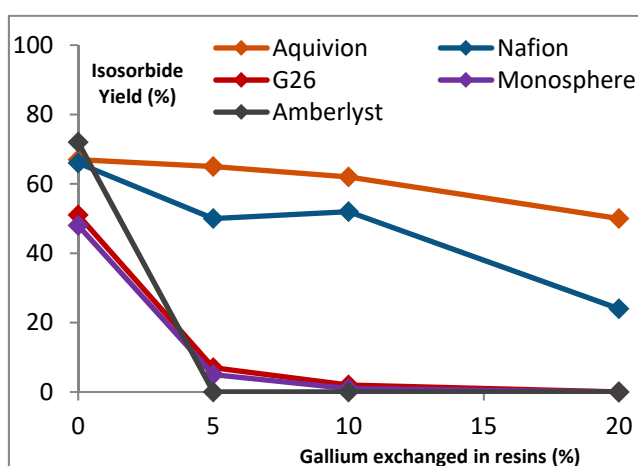


Figure 5: Influence of the % Ga in various resins on the isosorbide yield.

Reaction conditions : Sorbitol : 2.5 g ; resin : 5 mol % ; T = 115-145 °C (115°C for 1 h, 130°C for 1 h, and 145°C for 2 h), t = 4 h. The percentage of H⁺ exchanged in the resin is 3 times the percentage of Ga³⁺ introduced.

Unexpectedly, very different behaviors are observed depending on the nature of the resins used as support of gallium. On the one hand, metals exchanged in Monosphere and G26 resins show similar catalytic activities as those linked to Amberlyst 70: the catalytic activity of the three resins is very sensitive to metal exchange with a strong deactivation at low loadings. This trend is even stronger with Amberlyst resin. On the other hand, the Aquivion resin, that has already shown better catalytic activities toward isosorbide production in its native form (Table 3), led also to much better yields at higher metal loadings. The catalytic activity of the resin remains

almost unchanged even with 10% and 20 % of gallium. The Ga-Nafion resin has an intermediate behavior in terms of isosorbide yield. No drastic drop is observed but the yield in isosorbide gradually decreased with the amount of gallium that has been loaded in the resin. It should be noticed that the same trend has been observed with other trivalent metals thus indicating that this effect is not metal dependent. The higher acidity of the active sulfonic group in Aquivion and Nafion as well as a larger accessibility of the substrates to the acidic active sites probably explain that these two resins are less impacted by the exchanges with metals.

4. Conclusion

Metal tosylates are efficient catalysts for the conversion of sorbitol in isosorbide according to homogeneous conditions with up to 67 % yield of isosorbide. Heterogeneous based catalysts such as sulfonic resins also efficiently promote the reaction and show different selectivities in comparison to homogeneous acidic systems as they rapidly convert 1,4-sorbitan into isosorbide within the pores. Surprisingly, sulfonic resins loaded with metals through cation exchange show drastically reduced catalytic activity in comparison to the native resins. In the case of the Amberlyst, G26 and Monosphere resins used for this study, less than 5 % of metal is for example enough to completely deactivate the resin. This inhibiting effect is explained by the strong binding of the metal by the chelating tosylate groups within the resin and the surface deactivation of the resin.

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