Heterogeneously novel xWO₃/SO₄²⁻/SnO₂ catalysts to improve the direct etherification of glycerol with D-Glucose in absence of organic solvents

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Abstract We have synthesized different diastereomers of α- and β-D-glucopyranosyl glycerol without organic solvent, using 15wt% SO_4^{2-}/SnO_2 with different ratios of tungsten oxide and the prepared catalysts were calcined at 400 °C. The present catalytic process is a new route of a synthesis of free salt and metal for the nucleophilic addition of polyol to a monosaccharide. In this article, the catalytic performance of solid acids $WO_3/SO_4^{2-}/SnO_2$ was investigated for the etherification of glycerol with D-glucose in solvent-free conditions. Under optimized conditions, up to 95.82 % yield of glycerol ethers (α- and β-D-glucopyranosyl glycerol) was obtained. The activity results revealed the promoted catalysts $WO_3/SO_4^{2-}/SnO_2$ show an excellent catalytic selectivity in the etherification of glycerol in comparison of other known catalysts. α- and β-D-glucopyranosyl glycerol synthesized are precursors of amphiphilic surfactants. The reaction progress was monitored with a gas chromatography-mass spectrometry GC-MS, after silylation reaction of the products to ease the separation and identification.

Key words: α- and β-D-glucopyranosyl glycerol, catalysts, isomerization, etherification, oligomerization, amphiphilic and silylation.

INTRODUCTION

Glucose is the most available hexose as it can be obtained from the most abundant and renewable biomass on earth. The catalytic conversion of glucose can proceed via three chemical routes. Firstly, glucose isomerization can produce fructose. Secondly, the dehydration process of glucose to obtain 1,6-anhydroglucose and finally, a retro-aldol condensation to obtain hydroxymethyl furfural. Titanium oxide TiO_2 catalysts appear to be an appropriate catalyst for an industrial process whereby glucose is converted due to both its acidic and basic properties [1].

Glycerol is a stable and multifunctional compound used as a building block in fine chemical synthesis. The use of catalysts, especially heterogeneous catalysts, remain the green approach for tailoring carboxylation and acetylation routes to achieve the desired products, namely, glycerol carbonate and glycerol acetyl esters [2]. However, up to now, all the studies were mainly dedicated to the transformation of glycerol to low value added chemicals such as surfactants [3], fuel additives [4], etc ...

Tanabe classified acid and base solid catalysts, he found that SnO_2 posses both acidic and basic properties [5]. It was noticed that the formation of combined mixed oxides is accompanied with increasing of their acidic and basic properties, catalytic activity and mechanical stability. Loading of some metal oxides with sulfate ion produced very active catalysts (super acid) for various acidic catalytic reactions like polymerization, acylation and esterification. These super acid solids posses both Lewis and Brønsted acid sites and are environmentally friendly and noncorrosive for reactors; compared to the corrosive known liquid acids like HF and H_2SO_4 [6-8].

Heteropolyacids possess both acid and redox properties, thus promote a variety of acid-catalyzed reactions, as well as catalytic oxidation reactions in both homogeneous and heterogeneous systems; for example, the synthesis of ethyl acetate from ethylene and acetic acid, the oxidation of ethylene to acetic acid, were accelerated using supported Heteropolyacids catalysts [9].

Pariente and co-workers [10],.reported the catalytic etherification of glycerol with ethanol over various solid acid catalysts in 2009. A maximum 40% yield of monoethoxy glyceryl ethers was obtained at 433 K by using sulfonated polystyrene resins and zeolites with a Si/Al ratio of ca. 25. Although this work was a significant step towards new catalytic routes for the selective etherification of glycerol with aliphatic alcohols, it was hampered by the formation of very large amounts of diethyl ether.

Here, in this paper, we wish to describe a new heterogeneous catalytic route allowing the direct etherification of glycerol with D-glucopyranose and affording the corresponding amphiphilic glycerol glycoside diastereomers. These catalysts possess very active Lewis and Brønsted sites for the metal and salt free etherification. We have improved the yield of the etherification reaction which is the precursor of amphiphilic bio-based surfactants. Indeed glycerol glycoside resulting from these

transformations is highly valuable chemical to cosmetic and dermatological preparations containing aquaporin stimulators and their use to improve the moisturizing of the skin.

EXPERIMENTAL

Preparation of novel WO₃/SnO₂ catalysts:

(i) Preparation of SnO₂ gel: pure tin oxide hydrogel was prepared by a dropwise addition of ammonia solution (10% wt) to 0.5 M solution of $SnCl_4.5H_2O$ with continuous vigorous stirring for 4 hours. The pH of the hydrogel was adjusted to an 8.0 and the gel was left overnight then washed by decantation with 1% ammonium acetate solution until all Cl^- ions eliminated. Then, the product was washed with bi-distilled water. The resulting SnO₂ gel was dried at 120 °C for 4 h.

(ii) Preparation of 15%SO_4^{2-}/ SnO₂ carrier: S.Sn was prepared by vigorous mixing of appropriate amount of 1 M H_2SO_4 with SnO₂ gel for 4 h, the ratio of loaded sulfate ions was 15% wt, then dried at 120 °C for 24 h.

(iii) Preparation of xWO₃/SO_4^{2-}/SnO₂ catalysts: the carrier S.Sn was impregnated with appropriate amounts of ammonium tungestate $[(NH_4)_{10}W_{12}O_{41}.5H_2O]$ solution to obtain percentage ratios of x loaded of about 5, 15, 25, 35 and 45 % wt of WO₃, with vigorous stirring for 4 h, then dried at 120 °C for 24 h. All prepared catalysts 5%W-S.Sn, 15%W-S.Sn, 25%W-S.Sn, 35%W-S.Sn and 45%W-S.Sn were calcined in air at 400 °C for 4 h. The specific surface areas, S_{BET}, were determined from nitrogen adsorption at 77 K and the total surface acidity was measured by potentiometric titration in non-aqueous solution [8].

Direct etherification using WO₃/SnO₂ catalyst:

Anhydrous glycerol (2.30 gr; equivalent to 25 mmol) was placed in a round-bottom, double-neck reaction flask, placed on electrical heater under stirring at 600 rpm and equipped with heat sensor to control temperature reaction. After the glycerol was heated to 100 °C, 0.1 gr of WO₃/SnO₂ catalyst was added and the mixture was kept under an atmosphere of dry argon for 10 minutes. D-glucopyranose (0.54 gr; equivalent to 3 mmol) was inserted through the other neck of the flask and the mixture was stirred for 1 h at 100 °C with continuous flow of dry argon.

Direct etherification using 15%W-S.Sn catalyst:

As mentioned above in the general procedure; after the glycerol was heated; 0.05 gr of 15%W-S.Sn catalyst was added and the reaction was continued under an atmosphere of dry argon for 10 minutes. D-glucopyranose (0.54 gr; equivalent to 3 mmol) was inserted and the mixture was stirred for 1, 2, 3 and 4 hours for each specific temperature 105 °C, 115 °C and 125 °C with continuous flow of dry argon. We repeated the above procedure for each weight of the catalyst: 0.1, 0.15 and 0.2 grams. We investigated these differences to assign the catalytic activity and to achieve the best yield of the glycerol glycoside diastereomers.

Silylation of the reaction mixture:

The trimethylsilylation indicate that is fairly generally applicable in the polyhydric organic compounds to their trimethylsilyl ethers. The reactions progress were monitored by gas chromatography-mass spectrometry GC-MS, and the products therefore, were silylated by silylation reaction and injected for ease separation and identification. The silylation reaction was carried out as follows: to the 25 µL of the mixture; a 500 µL of pyridine was added, then we added 400 µL of hexamethyldisilazane and 200 µL of trimethylchlorosilane. The resulting mixture was stirred at room temperature for 5 minutes, then centrifuged and filtered in order to remove the pyridinium salts before injection. GC Agilent 7890A equipped with auto sampler (split/splitless) and a HP-5MS column (30 m × 0.25 mm; phase thickness: 0.25 µm) and connected with MS Agilent 5975C. Injector temperature 290 °C and ionization source 230 °C.

Characterization of the reaction mixture:

The chromatographic peaks of the glycerol glycoside diastereomers, the related isomerization reaction peaks and the side oligomerization reaction peaks were identified by NIST data available in GC-MS program and according to Sakuma [11].

RESULTS AND DISCUSSION

Etherification reaction:

This study affords, a process and without addition of any organic solvent, a divers α- and β-diastereomers of glycerol-based organic structures in moderate to excellent yields. It is noteworthy that this study opens, for the first time, environmentally friendly and easy routes for the transformation of glycerol to higher value added chemicals. Indeed, glycerol glycoside (o-glycerol -α- or -β-glucopyranoside) from these transformations are highly valuable chemicals since they exhibit a wide spectrum of biological activities such as dermatological preparations and cosmetics [12]. They are also important precursors for the preparation of green degradable surfactants [13].

Table (**1**) shows some of the acidic properties of the prepared catalysts, where the specific surface areas S_{BET} exhibit maximum values at 400°C for all catalysts. This related to the increasing pore areas of the surface of the catalysts, and this is because of losing of H_2O molecules and OH groups. E_i (mv) values revealed that the prepared catalysts possess very strong acid sites, ($E_i > 100$ mv), and total amounts of surface acidity assign to the thermal treatment and loading ratios.

Table (1), illustrates the total amounts of surface acidity of catalysts x%W-S.Sn determined potentiometrically and volumetric titrations

Catalyst NO.	Catalyst symbol/ thermally treated at 400°C	Specific surface areas S_{BET} (m^2/g)	Electrode potentiality E_i (mv)	Total amounts of surface acidity, (mmol/g)	
				Potentiometrically titration*	Volumetric titration
(I)	5%W-S.Sn	126	518	0.204	0.084
(II)	15%W-S.Sn	114	473	0.162	0.094
(III)	25%W-S.Sn	96.7	482	0.055	0.049
(IV)	35%W-S.Sn	86.9	465	0.140	0.059
(V)	45%W-S.Sn	62.6	383	0.060	0.055

* potentiometrically titration was considered for the comparison between catalysts x%W-S.Sn, because it represents Lewis and Brønsted acidity. While volumetric titration represent mmoles number of H$^+$.

It is obvious that heating the mixture reaction more than 50 °C caused inter-conversion for D-glucopyranose to its diastereomers; α- and β-D-glucopyranose, which react later with glycerol to form α- and β-D-glucopyranosyl glycerol. Indeed 3 mmol of D-glucopyranose react with 25 mmol of glycerol, without using organic solvent, at 100 °C and catalyzed with 0.1 gr of acidic solid catalyst (**I**) for 1 hour under stirring at 600 rpm, and subsequently the formation of mixture of α- and β- D-glucopyranosyl glycerol as shown in the chromatogram of figure (**1**) to gave a yield of about 49% of the etherification.

The yield of the etherification reaction and the side reactions were determined according to the surface areas of the peaks, Whereas the separated chromatographic peaks of the six diastereomers α- and β-D-glucopyranosyl glycerol and side reaction peaks (related isomerization and oligomerization) were all identified by GC-MS.

In the figure (**1**), the peaks (No.: **4, 8, 9, 10, 11** and **12**) represent α- and β-D-glucopyranosyl glycerol, and the peaks (No.: **1, 5, 6** and **7**) represent related isomerization products. The oligomerization products are in the range of the retention times of about 37 min to 39 min). while peaks **2** and **3** represent unreacted α- and β-D-glucopyranose.
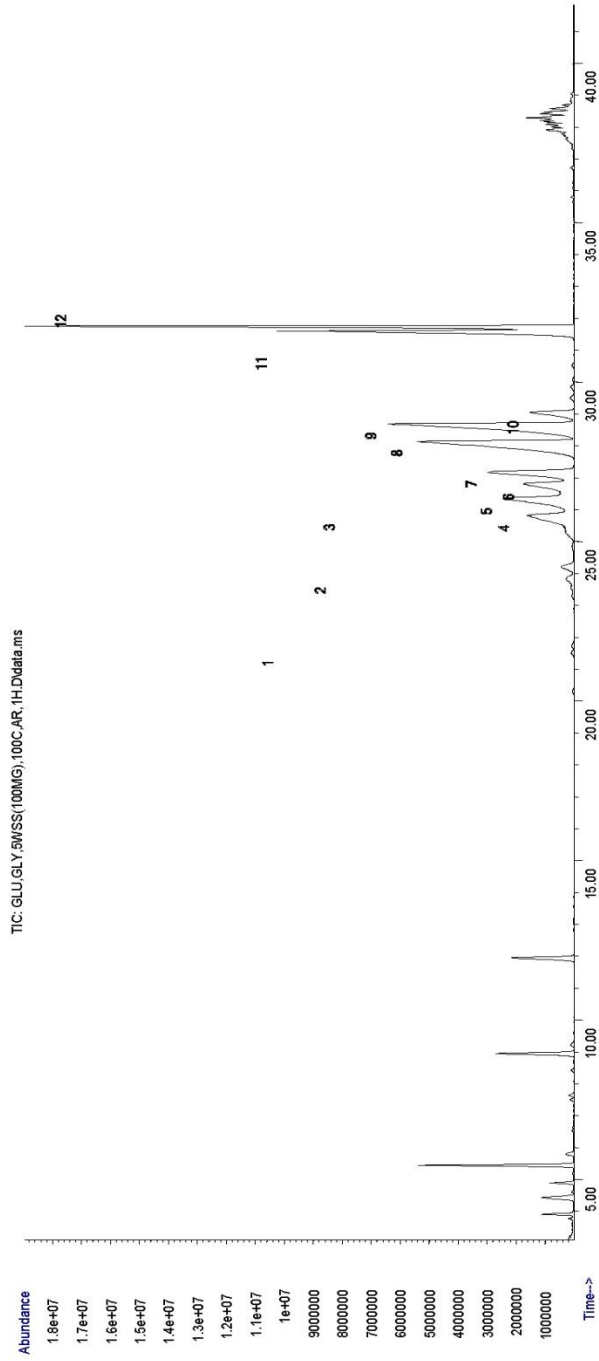
TIC: GLU,GLY,5WSS(100MG),100C,AR,1H.D\data.ms

Figure (1), shows GC-MS chromatogram of the silylated mixture reaction, reaction temp. at 100 °C.

Figure (**2**) illustrates mass spectrum of one of the six silylated diastereomers at which it's mass fragments *m/z* complies with NIST data referential. No molecular ions M$^{.+}$ were observed in the mass spectra of the TMSi derivatives of glycerol glycoside. The loss of the glucose-TMSi with charge retention on the glucose portion and the cleavage of the C-O glycosidic bond produces an ion at *m/z* 451 with low abundance, which subsequently loses trimethylsilanol [Me$_3$Si-OH] to produce another ion at *m/z* 361, which is prominent in all spectra. The ions at *m/z* 451 and 361 are also characteristic of the TMSi- derivatives of many other types of natural hexose glycosides. The TMSi- groups also give rise to an intense ion at *m/z* 73 and to an ion at *m/z* 147 formed by cleavage of two vicinal TMSi- groups [**14**].
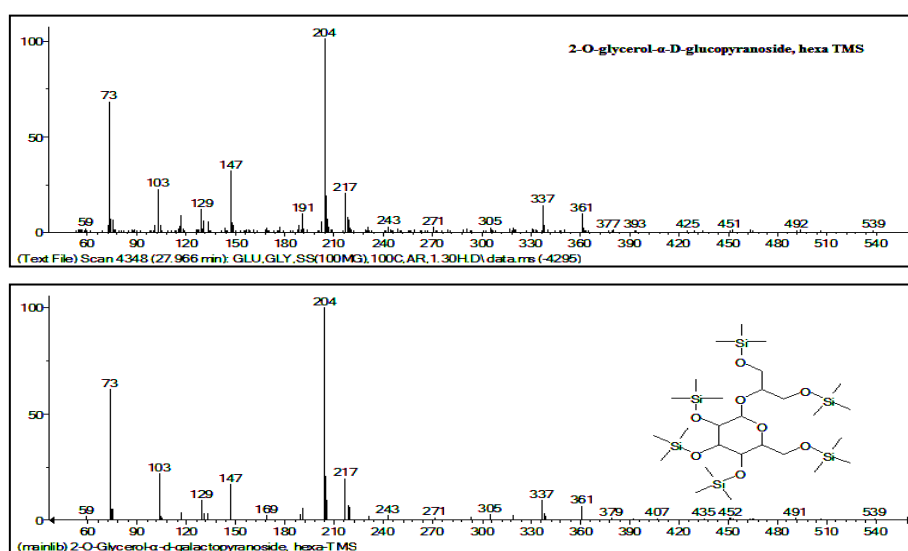

Figure (2), shows mass spectrum of silylated 2-O-glycerol-α-D-glucopyranoside, the main and sub-fragments

It's documented that the main fragment at *m/z* 204 contains two carbons of silylated glucose, formed due to the cleavage at C$_2$ and C$_3$ in the glucose-TMSi. And the cleavage at C$_1$ and C$_2$ produce fragment at *m/z* 337, and the cleavage at C$_2$ and C$_4$ produce fragment at *m/z* 306 [15]. The abundance of the fragment at *m/z* 103 produced due to the cleavage at C$_1$ and C$_2$ in the glycerol-TMSi. Finally, the high relative intensity of the fragment ion at *m/z* 204 and the lower abundance of that at *m/z* 217 confirms a pyranoside configuration, which is readily distinguishable from the furanoside one in which the fragment at *m/z* 217 is more prominent than the fragment at *m/z* 204 [**15**].

Purification of the glycerol glycosides:

It's notably, that most reviews referred to the removal of free glycerol by vacuum distillation, but in this work, we could purified glycerol glycosides from free glycerol by extraction method using the solvent 2-methyl-2-butanol, as follow**:** we added 10 mL of methanol to dissolve the viscous glycerol glycosides liquid, filtered by 0.45 µm nylon filter to remove the catalyst and evaporated of methanol by evaporator to get colorless viscous liquid. Then we added 10 mL of the solvent 2-methyl-2-butanol to the crude mixture under stirring in water bath at 40 °C for 5 minutes then decanted the extracted glycerol solution. We repeated the procedure three times consecutively using 5 mL of the solvent in each extraction. The isolated glycerol glycosides were identified by IR absorption spectrum, which showed characteristic band at 3388 cm^{-1} for hydroxyl group and bands at 1040 cm^{-1}, 1106 cm^{-1} and 1150 cm^{-1} for glycosidic linkage.

The effect of the WO$_3$/SnO$_2$ catalysts on the yield of the etherification reaction:

It is clear that increasing time reaction, using catalyst (**I**), to improve the yield of α- and β-D-glucopyranosyl glycerol was not enough or sufficient, because of the related isomerization products in the reaction mixture to D- glucofuranose and to ethyl-D-glucopyranose in a ratio of 41.1%, while the other side products is the oligomerization reaction of D-glucopyranose in a ratio of 8.18%, as shown in table (**2**).

Table (2), illustrates the yields of the direct etherification, related isomerization and side oligomerization products, by using *x*%W-S.Sn catalysts.

Catalyst NO.	Catalyst symbol/ thermally treated at 400°C	% *, Unreacted of α- and β-D-glucopyranose	% *, Side reactions		% *, Yield
			Isomerization products of α- and β-D-glucofuranose	Oligomerization products	α- and β-D-glucopyranosyl glycerol
(I)	5%W-S.Sn	1.70	41.1	8.18	49.1
(II)	15%W-S.Sn	0.83	27.76	9.64	61.77
(III)	25%W-S.Sn	1.54	57.84	7.76	32.86
(IV)	35%W-S.Sn	1.15	40.11	9.91	48.84
(V)	45%W-S.Sn	1.21	52.98	7.97	37.85

* To achieve the yield we compared between the five catalysts according to the reaction conditions: glycerol 25 mmol, D-glucopyranose 3 mmol, catalyst (0.1 gr ~ 1 mol%), temperature reaction 100°C, stirring 600 rpm and atmosphere of dry argon.

Fortunately, the yield of the diastereomers was improved better when we used the acidic solid catalyst (**II**) in the same conditions reaction and the yield was reached to 61.77% with low percentage of related isomerization products 27.67% and side oligomerization products 9.64%. On the other hand the other three catalysts **III**, **IV** and **V** were less selective in which the yields were 32.86%, 48.84% and 37.85%; respectively and with percentages of isomerization products 57.84%, 40.11%, 52.98%; and oligomerization products 7.76%, 9.91% and 7.97%; respectively.

When we compared between these acidic solid catalysts as shown in the table (**2**), we noticed that the yield of the etherification increased for the catalyst (**II**), then it decreased clearly for the catalyst (**III**) and returned to increased for the catalyst (**IV**). These results coincide with the investigated total surface acidity and this could be explained, back to table (**1**), to the percentages of tungsten oxide loaded at less than 15% or more than 15%, which lead to decrease in the catalytic selectivity towards direct etherification and increase the selectivity for isomerization. This means that catalyst (**II**) , which is loaded with 15% of WO_3, possess the best porosity, specific surface area and high Brønsted acidity, that facilitate glycerol molecule to attack, as a nucleophile, the adsorbed D-glucopyranose molecule on the surface of the catalyst to form the etherification and the related isomerization and the side oligomerization products. Subsequently, the reaction is directed towards etherification more than towards the related isomerization and side oligomerization.

Figure (**3**) shows the expected mechanism scheme of the etherification reaction which took place on the Brønsted sites of the surfaces of the combined mixed oxides and the expected mechanism scheme of the related isomerization took place on the Lewis sites of the same surfaces. Another explanation could be, that the 15wt% $WO_3/SO_4^{2-}/SnO_2$ provides Brønsted sites which lead to the etherification more than Lewis sites that lead to isomerization. The other three catalysts **III**, **IV** and **V** that loaded with the ratio of 25%, 35% and 45% WO_3 are directing the reaction towards the related isomerization more than that to etherification, and this is because of the decreasing of the specific surface area and pore volume as well as Brønsted sites, so they have Lewis sites more than Brønsted ones. It is noteworthy, that the chemical structures of the produced diastereomers for all five catalysts are the same through the coincidence of their retention times by GC-MS, but in different yields.
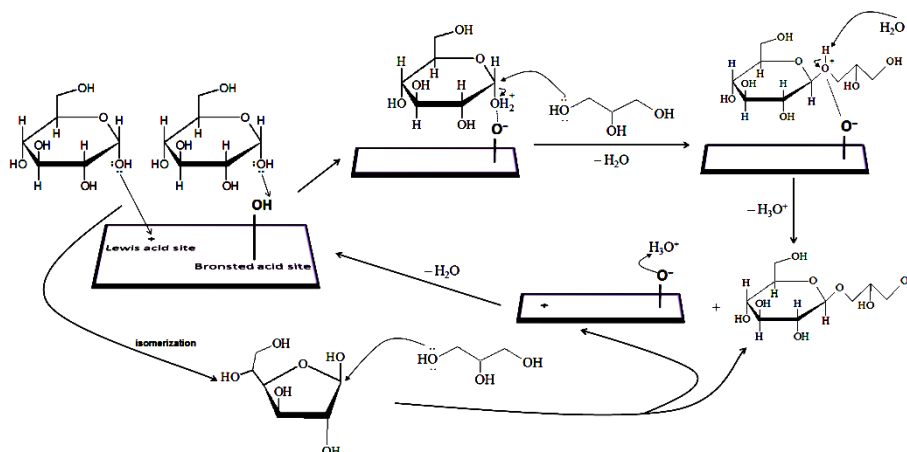
Figure (3), explains the expected catalytic reaction scheme on the surface of the acidic solid catalysts WO_3/SnO_2 through Brønsted and Lewis sites on the same surface.

Determination the typical reaction conditions using the specified catalyst (II):

It's observed that the catalytic activity was clearly influenced by the very simple changes of the temperature reaction, so the yield of the etherification at 105 °C was reached to about 84.14%, but higher ratio of the side oligomerization 13.06%. Consequently, in order to improve the yield and catalytic activity of catalyst (**II**) we will study some parameters that affected the catalytic activity.

Changing the quantity of the catalyst (II):

Different quantities of catalyst (**II**) was investigated, equivalent to 0.05, 0.10, 0.15 and 0.2 gr. We noticed that 0.05 gr of catalyst (**II**) produced glycerol glycoside ethers in yield 78.26% with higher percentages of the unreacted α- and β-D-glucopyranose in yield 10.04% and less percentages of related isomerization and side oligomerization in yields 5.92% and 5.79%, respectively. Remarkably, we also noticed that increasing the catalyst (**II**) quantity from 0.05 gr to 0.10 gr caused clear increasing in the yield from 78.26% to 93.23% and also clear decreasing in the yield of unreacted α- and β-D-glucopyranose from 10.04% to 0.36%. besides the decreasing in the percentages of related isomerization products from 5.92% to 0.57%. We should mention that there was no significant change on the yields of etherification products when the quantity of the catalyst was more than 0.20 gr, so this amount of catalyst was very adequate to increase the catalytic activity to produce etherification products in yield of 93.23%.

Changing the temperature reaction using 0.20 gr of the catalyst (II):

We have investigated the reaction in the range of temperatures between 105 °C and 125 °C with molar ratio (glycerol: 25 mmol and D-glucopyranose 3

mmol). The reaction progress was monitored by GC-MS during time extended from 1 h to 4 h for each applied temperature. We observed, as shown in table (**3**), that the yield of the glycerol glycoside ethers were increased slowly as temperature reaction increased from 105 °C to 115 °C and after that it decreased slightly. Regarding the temperatures reactions 105 °C, 115 °C and 125 °C, the yields were exceeded 90.0% after the first hour of the catalyzed reaction coupled with less percentages of the related isomerization.

Table (3), illustrates the effect of changed temperature reactions, catalyze by catalyst (II), on the yields of all reactions, extended from 1 h to 4 h.

Temperature reaction °C	Duration reaction, h	%, Unreacted of α- and β-D-glucopyranose	%, Side reactions		%, Yield α- and β-D-glucopyranosyl glycerol
			Isomerization products of α- and β-D-glucofuranose	Oligomerization products	
105°C	1	2.16	0.65	3.61	93.58
	2	0.11	0.92	3.99	94.98
	3	0.04	0.12	4.91	94.93
	4	0.03	0.09	5.24	94.63
115°C	1	0.06	0.09	4.32	95.82
	2	0.04	0.07	4.53	95.36
	3	0.04	0.22	4.37	95.84
	4	0.03	0.20	4.41	95.50
125°C	1	0.20	0.52	6.41	92.88
	2	0.30	0.60	5.41	93.0
	3	0.80	0.82	4.64	93.70
	4	0.95	0.90	5.0	93.89

Typical reaction conditions: glycerol 25 mmol, D-glucopyranose 3 mmol, catalyst (II) (0.2 gr ~ 2 mol%), different temperatures reaction (115°C is the best), stirring 600 rpm and atmosphere of dry argon.

It is clear that the temperature reaction 115 °C, compared to the 125 °C, has less percentage of related isomerization 0.07% and side oligomerization 4.32% with higher yield in the etherification 95.82% and very low percentages (0.03%) of unreacted α- and β-D-glucopyranose. Finally when we investigated the catalytic

reaction at 125 °C we noticed re-increasing the yields of unreacted α- and β-D-glucopyranose from 0.2% to 0.8%, also a slight increasing of the related isomerization from 0.52% to 0.82% and relative decreasing in the yield of etherification to about 92.88%. We could concluded that the catalytic reaction at 115 °C is the best to produce higher yield of etherification diastereomers 95.82%, less related isomerization products 0.09% and side oligomerization products 4.32%. And it's recommended to proceed catalytic reaction for 1 h only, as shown in the chromatogram of figure (**4**).
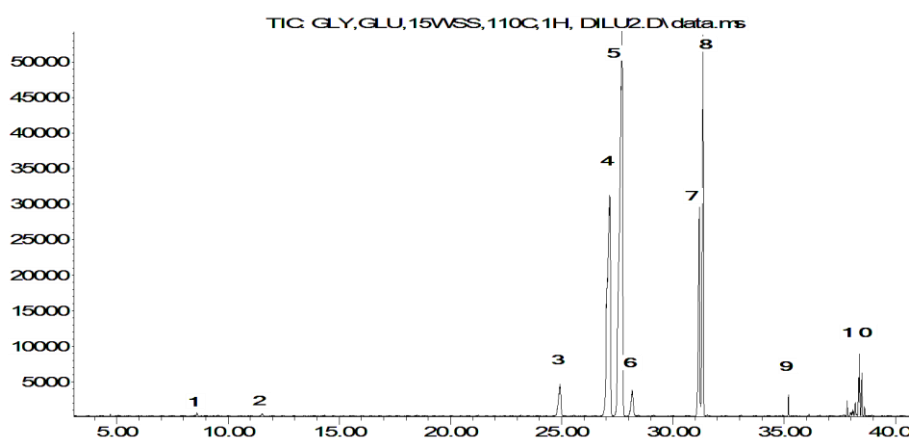

Figure (4), shows GC-MS chromatogram of the silylated reaction mixture, reaction temp. at 115 °C.

In this figure peak No. **9** represents the silylated standard of lactose (clue of dimer glucose molecule) and there are no chromatographic peaks for related isomerization products (disappeared) because of the completely transformation to glycerol glycoside diastereomers.

Finally, Amberlyst-15 catalyst (**VII**) was chosen as a reference solid acid catalyst because of its strong acidity, middle thermal stability (up to 120 °C) and high proton exchange capacity (4.7 mmol g^{-1}). With other known solid acid catalyst such as the silicate one MCM-41 (**VI**) which was prepared in our Lab [**16**], to compare them with our catalyst (**II**), Table (**4**) showed that the catalyst (**VI**) has less tendency for the etherification in yield 23.68% than the others and is directed to the related isomerization in yield 60.87%, while the catalyst (**VII**) is close in yield of the etherification to the catalyst (**II**). Therefore, to the best of our knowledge the prepared catalyst **II** is favorable, more than the known compared ones, toward the etherification reaction.

Table (4), illustrates the yields of the direct etherification, related isomerization and side oligomerization, by using known acid solid catalysts.

Catalyst NO.	Catalyst symbol/ thermally treated at 400°C	% *, Unreacted of α- and β-D-glucopyranose	% *, Side reactions		% *, Yield α- and β-D-glucopyranosyl glycerol
			Isomerization products of α- and β-D-glucofuranose	Oligomerization products	
(II)	15%W-S.Sn	0.83	27.76	9.64	61.77
(VI)	MCM-41	10.40	60.87	5.05	23.68
(VII)	Amberlyst-15	2.10	34.61	8.54	54.68

* The results are compared according to the reaction conditions: glycerol 25 mmol, D-glucopyranose 3 mmol, catalyst (0.1 gr ~ 1 mol%), temperature reaction 100 °C, stirring 600 rpm and atmosphere of dry argon.

CONCLUSION

Glycerol plays two main roles in the direct etherification, as a green solvent and as the glyceryl donor. The higher performance of the 15%W-S.Sn catalyst might be ascribed to its strong affinity for glycerol. Indeed, this catalyst is highly polar super acid and probably interact stronger with glycerol to produce good yields. The catalytic activity of the catalyst (**II**) showed a clear improvement, in a slightly increasing of temperature reaction, that helps of easy leaving of intermediate products from the catalyst surface. The catalyst(**II**) have a good performance, in moderately high temperatures, through its efficients for directing towards main etherification reaction more than the side ones. In addition, the study illustrates that loading of sulfate SO_4^{2-} on a WO_3/SnO_2 caused improving, clearly, of the yield of etherification products much more than loading WO_3 on SSn, in the same ratio, which attributed to the increasing of acidic Brønsted sites directivity to the etherification reaction. Finally, the used catalysts gave higher etherification yields when compared with other known solid catalysts.

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استخدام حفّازات مبتكرة xWO₃/SO₄²⁻/SnO₂ لتطوير تفاعل أيترة الغليسيرول مع D–غلوكوز بدون استخدام أي محل عضوي

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ملخص البحث. قُمنا باصطناع مُماكبات فراغيّة مختلفة من α– وβ–D–غلوكوبيرانوزيل غليسيرول باستخدام حفّازات الأكسيد المشترك لأكسيد القصدير المحمّل بالكبريتات 15wt%SO₄²⁻/SnO₂ وبنسب مختلفة من أكسيد التنغستين، حيث كُلِّست الحفّازات المحضّرة عند الدرجة 400 °C.

تُعدُّ هذه العمليّة الحفزية خطوة جديدة في اتجاه تفاعل الإضافة النيكليوفيليّة، إضافة مركّب متعدّد الغول إلى سكريد أحادي، المباشر والانتقائيَّ وغير المترافق بتشكيل أملاح معدنيّة.

تمّت دراسة الشروط المثلى للتّفاعل والتي أعطت أعلى مردود وبنسبة حوالي 95.82% من إيترات الغليسيرول (α– وβ–D–غلوكوبيرانوزيل غليسيرول).

تمّ في هذا العمل دراسة الأداء الحفزي لهذه الحفّازات الحمضيّة الصلبة WO₃/SO₄²⁻/SnO₂ في تفاعل أيترة الغليسيرول مع D–غلوكوز، حيث أظهرت دراسة الفعاليّة الحفزيّة لهذه الحفّازات المطوّرة انتقائيّة حفزيّة ممتازة لتفاعل أيترة الغليسيرول مقارنةً مع حفّازات أخرى معروفة.

تُعدُّ مركّبات α– وβ–D–غلوكوبيرانوزيل المصنّعة أساس تحضير المركّبات الفعّالة سطحيّاً المحبّه للماء.

لقد تمّت مراقبة سير التفاعل من خلال شروط الفصل الكروماتوغرافيَّة المثلى عبر تقنية الكروماتوغرافيا الغازيّة المرتبطة بمطيافيّة الكتلة بعد إجراء تفاعل سيللة (اشتقاق) لنواتج التفاعل من أجل سهولة فصلها وتحديد هويتها.

الكلمات المفتاحية: α– وβ–D–غلوكوبيرانوزيل غليسيرول، حفّازات، تماكب، أيترة، غلمرة، سيللة، مُحبّه للماء.