

SYNTHESIS OF ALKYL POLYGLUCOSIDE FROM DEXTROSE-DECANOL IN THE PRESENCE OF SILICOTUNGSTIC ACID SOL-GEL CATALYST

(Sintesis Alkilpoliglukosida Daripada Dekstrosa-Dekanol Dengan Kehadiran Katalis Asid
Silikotungstik Sol-Gel)

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Abstract

The purpose of this study is to synthesis alkylpolyglucoside via condensation of decanol with dextrose in the presence of heterogenous catalyst. In this study, silicotungstic acid sol-gel (STSG) prepared using sol-gel was used as solid acid catalyst. The catalyst was characterized using BET surface area measurement, X-ray Diffraction (XRD) and X-ray Photoelectron Spectroscopy (XPS) surface analysis. The final product was easy to be separated from catalyst without the need of a further neutralization. Silicotungstic acid sol-gel has been found efficient to be solid catalyst for synthesis alkylpolyglucosides. Condensation reaction was carried out 8 hours at 110°C-120°C under vacuum condition at 10mmHg. The determination of decylglucoside has been achieved by LC/ESI-MS/MS (ToF) giving a mass peak at $m/z = 343.2$ correspond to the m/z of $[M + Na]^+$. Alkylpolyglucoside produced was analysed by FTIR, 1H and ^{13}C NMR spectrometric technique.

Keywords: silicotungstic acid sol-gel, alkylpolyglucosides, XPS, LC/ESI-MS/MS

Abstrak

Tujuan penyelidikan ini dilakukan adalah untuk menghasilkan alkilpoliglukosida melalui proses kondensasi di antara dekanol dan dekstrosa, dengan kehadiran mangkin heterogen. Dalam penyelidikan ini, mangkin asid silikotungstik sol-gel digunakan, yang mana disediakan menggunakan teknik sol-gel. Mangkin dicirikan menggunakan kaedah pengukuran luas permukaan BET, Pembelauan Sinar X (XRD) dan analisis permukaan Spektroskopi Fotoelektron Sinar X (XPS). Produk akhir yang diperolehi mudah untuk diasingkan daripada mangkin yang digunakan tanpa proses penutralan. Didapati, mangkin asid silikotungstik sol-gel boleh digunakan sebagai katalis pepejal untuk penghasilan alkilpoliglukosida. Tindakbalas kondensasi dilakukan selama 8 jam pada suhu 110°C-120°C pada keadaan vakum 10mmHg. Penentuan dekilglukosida berjaya diperolehi menggunakan LC/ESI-MS/MS, yang mana memberikan nilai puncak $m/z = 343.2$, yang mana merujuk kepada $[M + Na]^+$. Alkilpoliglukosida yang dihasilkan dianalisa menggunakan spektrometri FTIR, 1H dan ^{13}C NMR.

Katakunci: asid silikotungstik sol-gel, alkilpoliglukosida, BET, XPS, LC/ESI-MS/MS

Introduction

Alkylpolyglucosides (APGs) are non-ionic surfactants developed based on carbohydrate and fatty alcohol and categorized as environmentally non-toxic surfactant as it based on renewable resources [1]. Fischer glycosidation, a method identified by Emil Fischer more than 100 years ago, have been used widely to synthesis alkylpolyglucosides [2]. However, the method exist many drawbacks, especially the needs of final neutralization and a separation step of

the acid catalyst after the reaction [3]. Homogenous catalysts and strong mineral acids for example dinonyl naphthalenesulfonic acid, *p*-toluene sulfonic acid, and sulphuric acid have been used in tradition as acid catalyst for the synthesis of alkylpolyglucosides because of their good catalytic properties [4].

Strong acid catalyst usage also can produces alkylpolyglucosides which dark in colour and offensive smell, generate a waste that need to be managed, as well as gives a corrosion to the equipment [5]. Therefore, in order to overcome the drawbacks and achieve a green chemistry process, a solid acid catalyst has to replace the conventional liquid acid catalysts [6]. Heterogenous catalyst receives an attention due to easy separate from final products as well as gives a good catalytic [7]. Few studies have been reported on the synthesis of alkylpolyglucosides using heterogenous catalyst such as acid zeolites [8], MCM-41 [9] and dealuminated HY faujasites [10]. Y.Wu et al. (2008) reported the synthesis of alkylpolyglucosides in the presence of solid acid catalyst ($\text{H}_2\text{SO}_4/\text{SiO}_2$) offers high conversion and minimal environmental effect [11]. In this paper, we present the studies of the usage of silicotungstic acid sol-gel (STSG) as catalyst for synthesis of alkylpolyglucosides. Alkylpolyglucosides is produce when glucose is reacting with fatty alcohol through ether bond as shown in Figure 1.

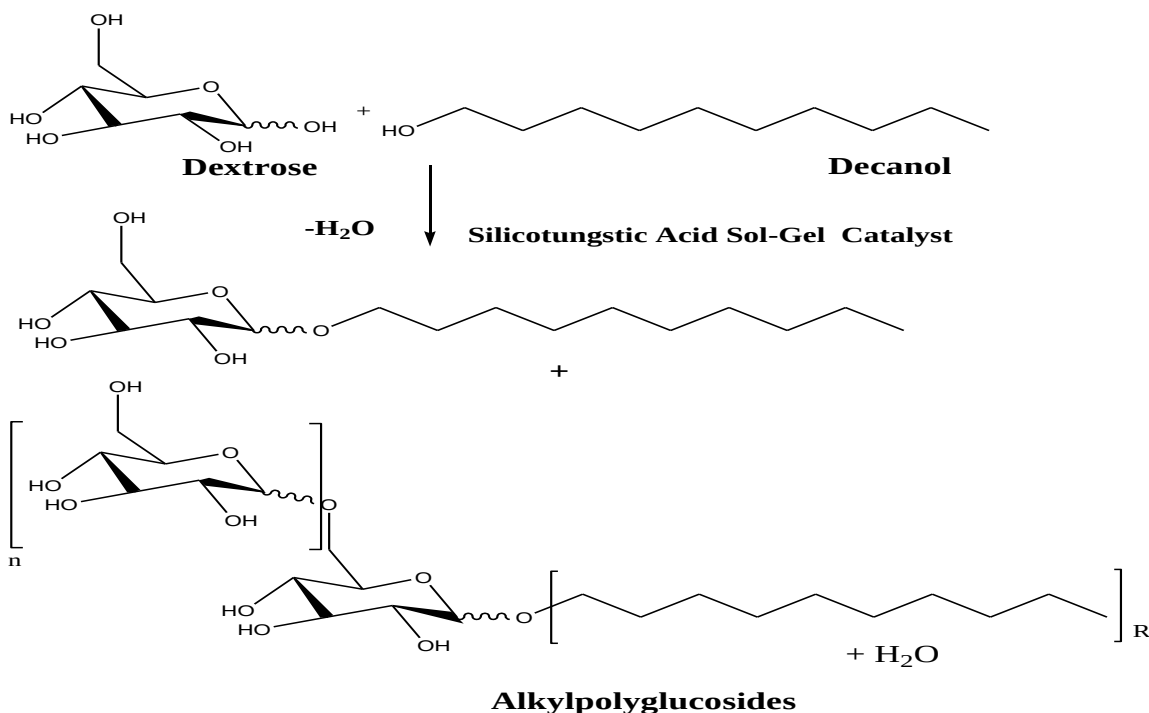


Figure 1. Synthesis of Alkylpolyglucosides [12, 13, 14]

Materials and Methods

Materials

All chemicals used are of A.R grade. TEOS is a product supplied by Merck-Schuchardt, Hohenbrunn, Germany. $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ supplied by Fluka Sigma-Aldrich Chemie Gmbh, Japan.

Synthesis of silicotungstic acid sol-gel (STSG)

The preparation of STSG was carried out based on method by Izumi et al. [15] with some modification. A mixture of water (2 mol, 36.00g), 1-butanol (0.2 mol, 14.28g), and 12-silicotungstic acid hydrate ($\text{H}_4\text{SiW}_{12}\text{O}_{40}$, 5.0×10^{-4} mol, 1.440g) was added to tetraethyl orthosilicate (TEOS, 0.2 mol, 41.60g) and stirred for 3 hours at 80°C . A

hydrogel was obtained and was dehydrated in reflux apparatus with methanol at 65°C-70°C for 72 hours, and then was heated to let the methanol to dry completely.

Catalyst Characterization

The specific surface area, S_{BET} of the catalyst was measured using a Gemini apparatus Micromeritics model ASAP 2010 and the analysis adsorptive was done at liquid nitrogen at 77 K. XRD analysis was performed on Bruker AXS D8 Advance X-ray Powder Diffractometer with Cu K α (40 kV, 40 mA, $\lambda=0.15406$ nm) to record angle 2θ from 10° to 60°. The X-ray Photoelectron Spectroscopy (XPS) surface analysis was performed on XPS Axis Ultra from Kratos equipped along with monochromatic Al K α radiation. The catalyst was analyzed in the analysis chamber pressure at 1×10^{-10} Pa. The binding energy of C1s, 284.5 eV was used as reference.

Synthesis of alkylpolyglucosides

The Fischer direct glycosidation process was carried out by reacting excess decanol and dextrose in a mol ratio of 4:1 and the presence of meoporous silica sol-gel (10%wt of reactant) as catalyst. The reaction was carried out at 110°C-120°C and connected to the vacuum in order to remove water as by product which can cause hydrolysis of product [11]. After 8 hours, the reaction was terminated and the reaction product was dissolve in methanol; the catalyst was removed by simple filtration. Purification was carried using solid-liquid chromatography to isolate the alkylpolyglucosides from excess alcohol and unreacted dextrose [16].

Analysis and Characterization of Alkylpolyglucosides

The structure of the prepared alkylpolyglucosides was confirmed by:

1. The presence of ether linkage was confirmed by Fourier transform infrared spectroscopy (FTIR) model Perkin Elmer Model GC 1605.
2. ^1H and ^{13}C Nuclear Magnetic Resonance (NMR) was measured in DMSO- d_6 on on FT-NMR 600MHz Cryoprobe Model Bruker/Advance III 600 MHz equipped with TOPSPIN 2.1 software and pulse programme zg30 for proton and zgpg 30 for ^{13}C .
3. LC/ESI-MS/MS (ToF) analysis was performed on a Dionex Ultimate 3000 separation module filter with an auto injector (20- μL injection loop), coupled via an electrospray interface and a Bruker micrOTOF-Q mass spectrometer. A C18-reversed phase column chromatography was carried out with a column (150 mm x 3.9 mm, RP18) supplied by XTerra. Parameter for separation method; gradient of water and methanol was applied, the linear gradient started from 30% of methanol reaching 100% of methanol after 10 min. The latter concentration was maintained for 10 min; with the mobile phase flow rate was 0.5 ml min $^{-1}$. The electrospray source potentials were: capillary 4 kV, end plate offset -0.5 kV, collision cell RF 250.0 Vpp; the source temperature was 190°C. Nitrogen was used as the nebulizing and at flow rates of 0.6 l/h.

Results and Discussion

Surface Area Analysis by BET

The surface area analysis of showed that the surface area of STSG catalyst was 794.1 m 2 /g while raw material, silicotungstic acid bulk (STAB) was 0.98 m 2 /g. By using the sol-gel technique, STSG catalyst prepared gave a higher surface area with higher porosity. These properties will give a catalyst result in higher adsorption and higher catalytic activity. Figure 2 shows the sorption of the STSG which exhibited a type-IV isotherm and a presence of hysteresis loop indicated a capillary condensation in mesoporous material.

Crystalline Determination by XRD.

From Figure 3, the XRD patterns of STSG catalysts show an amorphous phase, no crystalline material characteristic due to the presence of SiO $_2$ layers. Broader diffraction peaks at 25° correspond to the Si-O-Si bond.

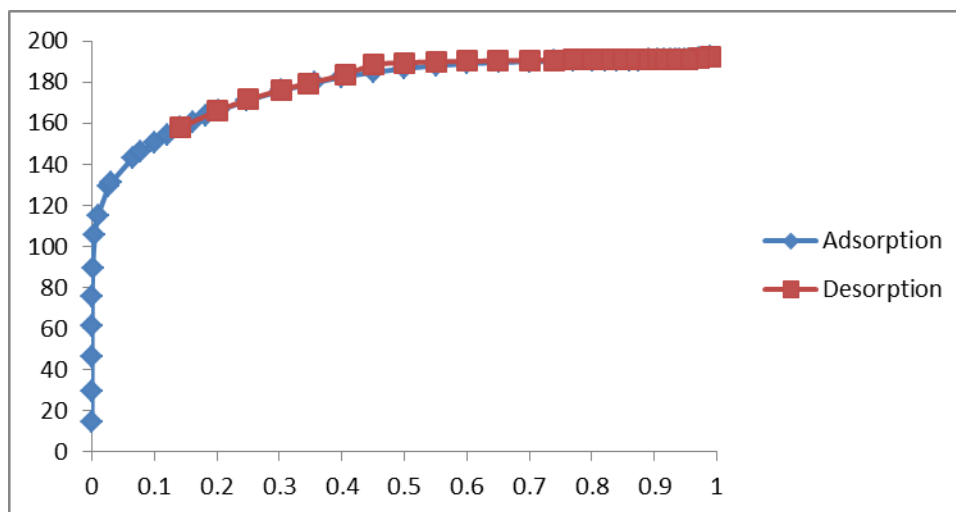


Figure 2. Nitrogen sorption of STSG catalyst

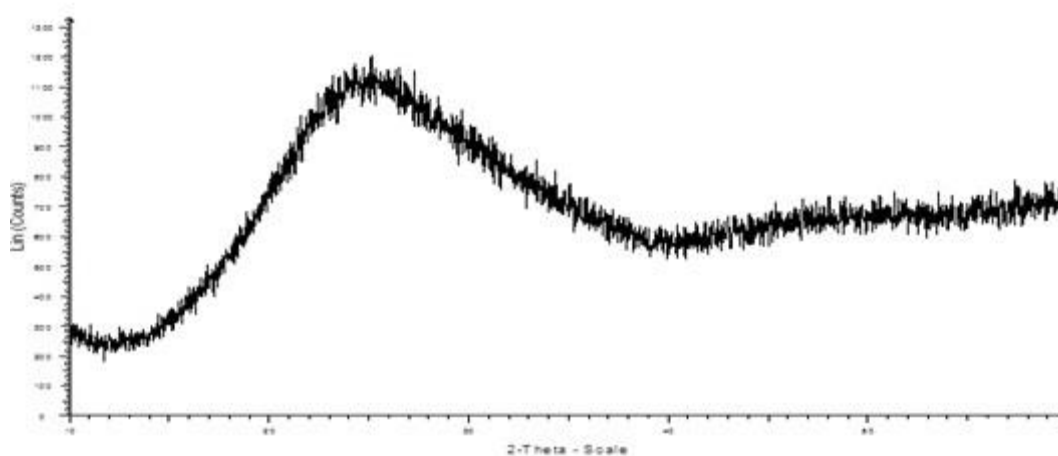


Figure 3. XRD patterns of STSG

Surface Analysis by XPS

The surface composition and binding energy (BE) of the C1s, O1s, and Si2p of STSG and STAB were obtained using XPS analysis. Figure 4 shows the XPS wide scan spectra of STSG and STAB. The photoelectron peaks show the presence of C1s, O1s, Si2p and W4f as expected. The percentage of mass concentration and binding energy of C1s, O1s, and Si2p of STSG obtained were summarized in Table 1.

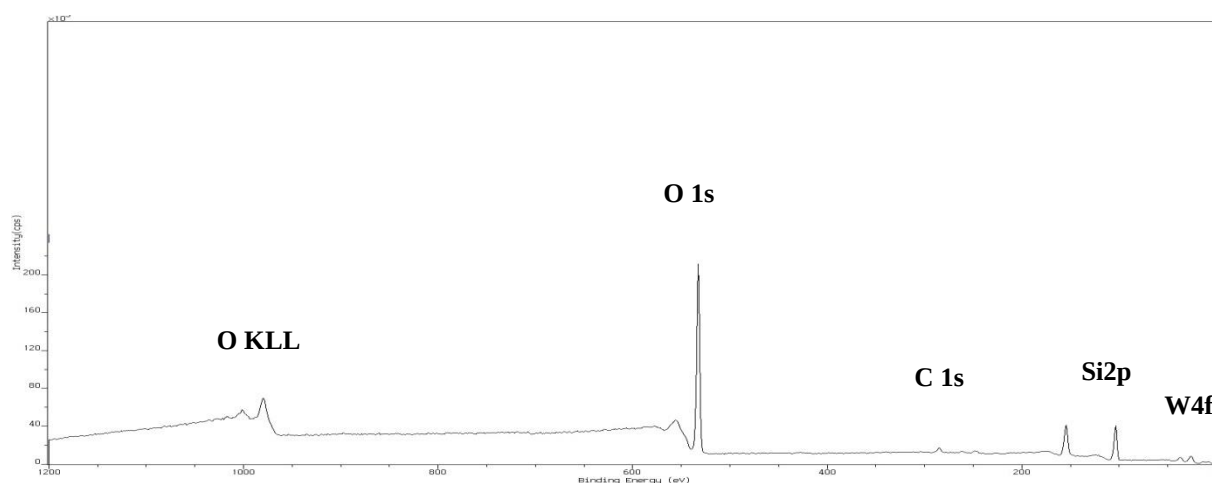


Figure 4. XPS wide scan spectra of STSG

Table 1. Binding energy (eV) and mass concentration (%) from wide scan analysis of the elements of STSG.

Catalyst	O1s		Si2p		W4f	
	Binding energy, eV	Mass concentration, %	Binding energy, eV	Mass concentration, %	Binding energy, eV	Mass concentration, %
STSG	532.9	56.41	103.8	31.8	26.9	8.01

Figure 5(a) shows XPS narrow scan for O1s of STSG and found that O1s binding energy of STAG, 534.0 eV and 535.6 eV. It is due to the adsorbed water, SiOH_2^+ .

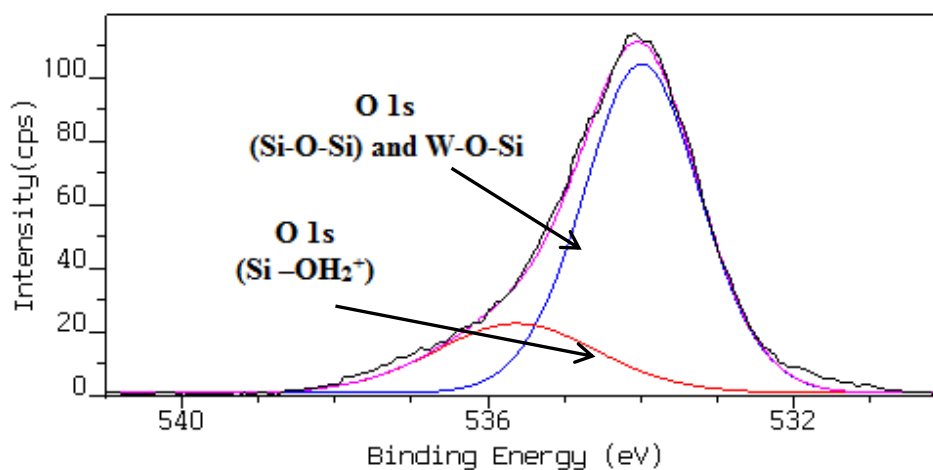


Figure 5(a). Narrow scan for O1s of STSG

Figure 5(b) shows XPS narrow scan for Si2p of STSG and found that Si2p binding energy of STSG, 103.0 eV and 104.1 eV. The Si2p binding energy, 103.0 eV corresponds to the Si in the matrix SiO_2 while 104.1 eV correspond to the appearance of SiOH_2^+ .

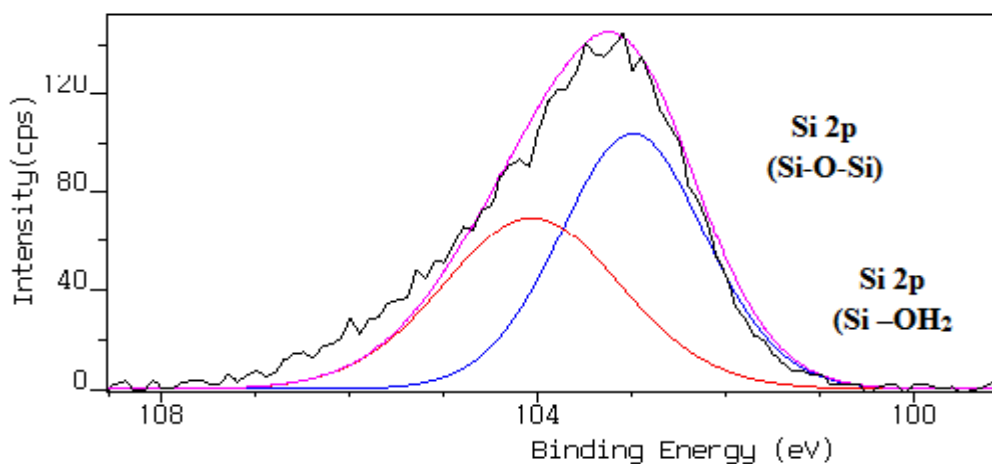


Figure 5(b). Narrow scan for Si2p of STSG

Figure 5(c) shows XPS narrow scan for W4f of STSG. Found that W4f binding energy corresponds to two different W contributions, a spin doublet at 35.9 eV ($\text{W}4f_{7/2}$) and 37.6 eV ($\text{W}4f_{5/2}$) respectively. The binding energy 37.6 eV corresponds to the formation of an oxide, WO_x .

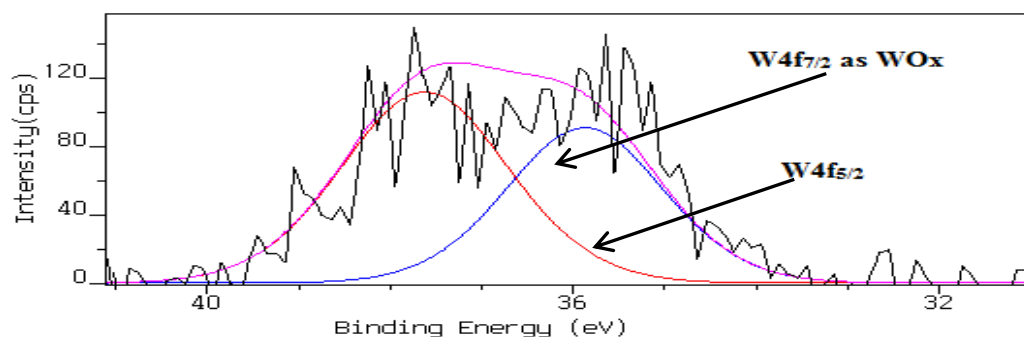


Figure 5(c). Narrow scan for W4f of STSG

FTIR spectroscopy of alkylpolyglucosides.

Ether linkage formed as condensation among OH groups of trehalose and decanol happen. This showed by existence of prominent band at wavenumber $1034\text{--}1051\text{ cm}^{-1}$ for the ether linkage (C-O-C), while at 3391 cm^{-1} for the OH bond, $2924\text{--}2855\text{ cm}^{-1}$ for CH bond in $-\text{CH}_2$ or $-\text{CH}_3$, 1458 cm^{-1} for $-\text{CH}_2$, 1378 cm^{-1} for CH_3 , and 721 cm^{-1} for $(\text{CH}_2)_2$ as shown in Figure 6.

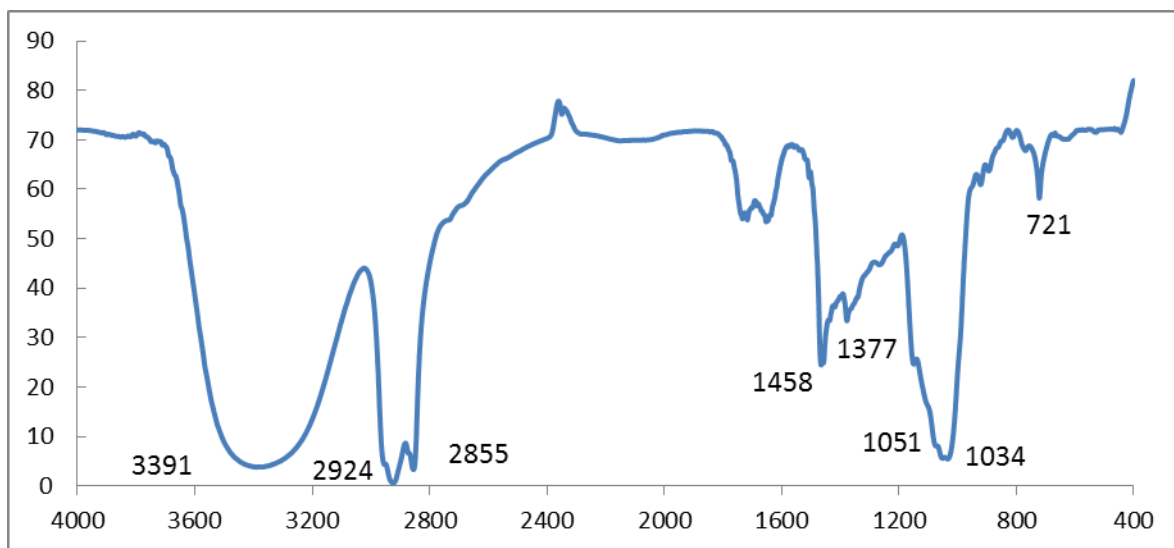


Figure 6. FTIR spectroscopy spectra of alkylpolyglucosides

NMR spectroscopy of alkylpolyglucosides.

Figure 7(a) shows the ^1H -NMR spectrum. It showed protons of the alkyl CH_3 groups (t, 3H, $\text{CH}_3(\text{CH}_2)_9$), at $\delta = 0.85$ ppm, the CH_2 protons of alkyl chain (16H, $\text{CH}_3(\text{CH}_2)_8$) dominated the spectrum at $\delta = 1.24$ - 1.52 ppm. The protons of the hydroxyl groups (OH) of dextrose are found at $\delta = 4.3$ ppm. The alkyl CH_2 protons attached to dextrose (m, 2H, $\text{O}-\text{CH}_2(\text{CH}_2)_8$), are found at $\delta = 3.35$ ppm and CH protons of the dextrose moieties are found as multiplet at $\delta = 3.38$ ppm.

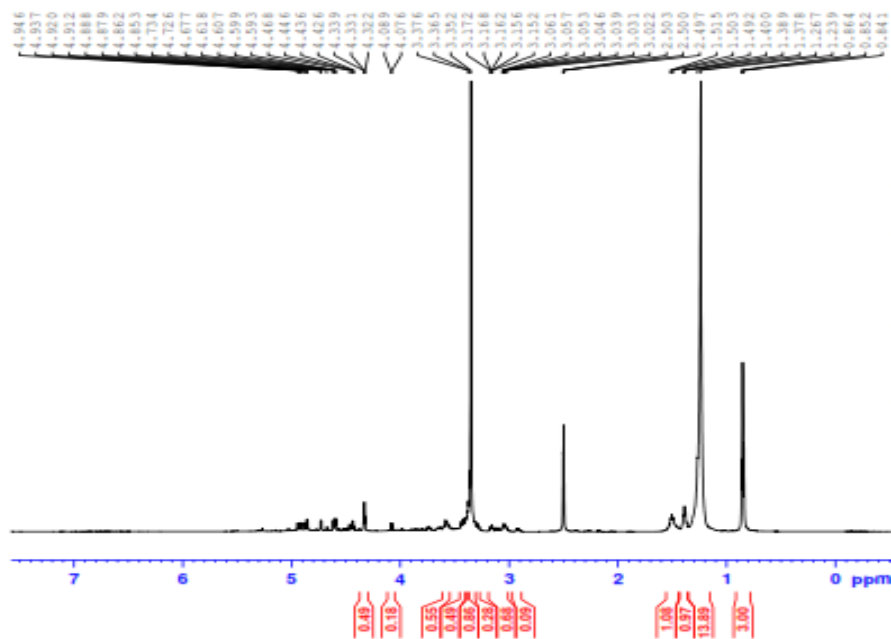


Figure 7(a). ^1H NMR spectroscopy spectrum of alkylpolyglucosides

Figure 7(b) shows the ^{13}C -NMR spectrum. It showed the terminal CH_3 are found at $\delta = 14$ ppm, the methylene carbons are found between $\delta = 22$ ppm and $\delta = 33$ ppm, the peak at $\delta = 61$ ppm is carbon atom of CH_2OH (of glucose ring). The remaining peak at $\delta = 67$ - 77 ppm are the carbon atom of CH-O which directly attached to the dextrose ring and the carbon atoms of the dextrose ring, with the exception of the anomeric carbon. Anomeric carbon attached to two oxygen atoms and deshielded at $\delta = 99$ ppm and $\delta = 103$ ppm, each for α - and β -anomer respectively.

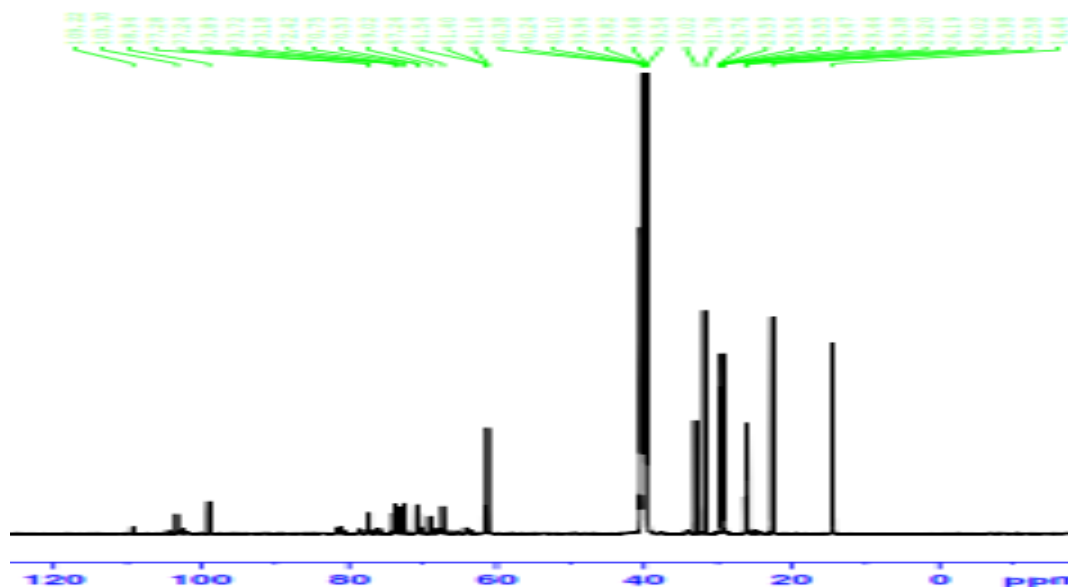


Figure 7(b). ^{13}C NMR spectroscopy spectrum of alkylpolyglucosides

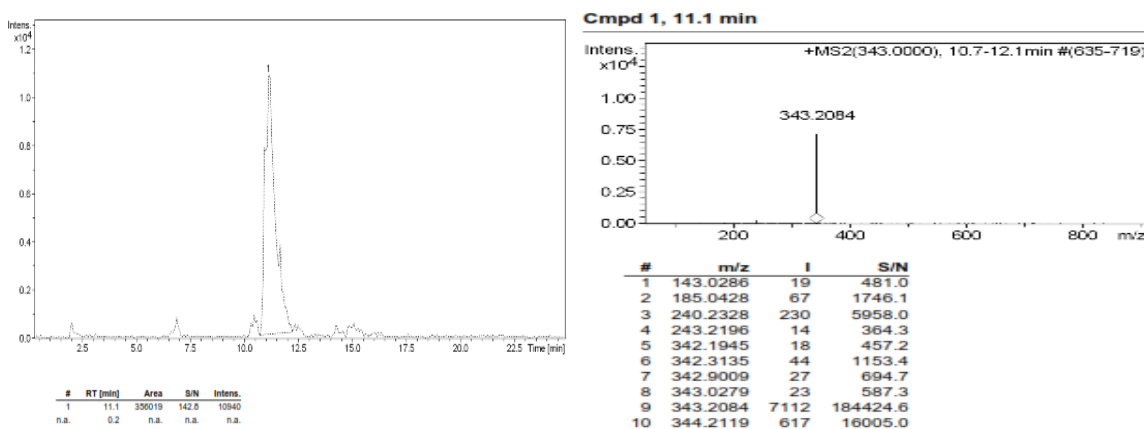


Figure 8. LC/ ESI-MS-MS (ToF) chromatogram of decylmonoglucoside

LC/ESI-MS/MS of alkylpolyglucosides

Alkylpolyglucosides were characterized by positive-mode LC/ESI-MS/MS (ToF) spectra. Alkylpolyglucosides was identified by their protonated molecules, the m/z value of the adduct ions $[M + Na]^+$. At retention time 11.1 min corresponding to alkylmonoglucosides, $m/z = 343.21$ as $[M + Na]^+$. The mass spectrum confirms the structure based on the proposed fragmentation mechanism pathway. Mass spectrum of alkylpolyglucosides is shown in Figure 8. Molecular ion peak at m/z 343.2 correspond to the protonated parent ions $[M + Na]^+$, which confirmed the structure as decylglucoside. Elimination of one proton generated positive ions at m/z 342.9. Elimination of C_nH_{2n} and one protons generate the positive ions at $m/z = 243.2$, followed by elimination of three protons to give the positive ions at $m/z = 240.2$. Elimination of $O-C_nH_n$ generated the ions at $m/z = 185.0$ and elimination of two molecule water and 6 protons generated positive ions at $m/z = 143.0$. Figure 9 shows the proposed fragmentation mechanisms pathway of decylpolyglucoside [1].

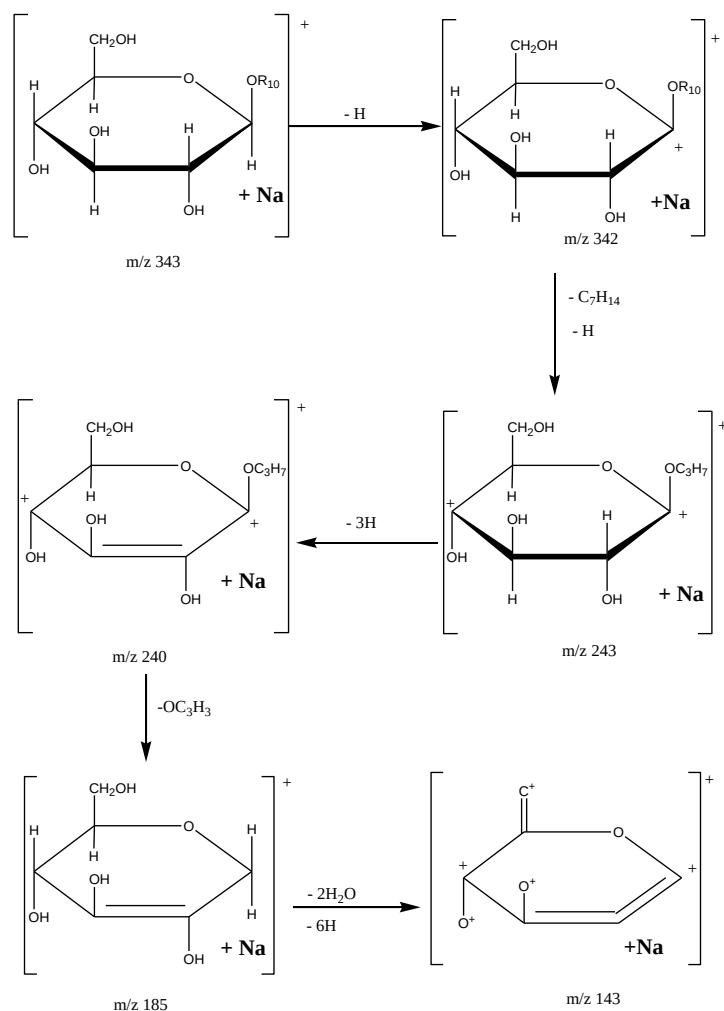


Figure 9. Proposed fragmentation mechanism pathway of decylglucoside

Conclusion

From this study, showed that the silicotungstic acid sol-gel (STSG) catalyst prepared by sol-gel technique has a catalytic activity as well as can be used as a catalyst to prepare alkylpolyglucoside by glycosidation, without the need of a further neutralization and separation process. This sol-gel catalyst can be applied as an alternative heterogenous catalyst instead of using homogenous acid catalyst. Decylglucoside, $m/z = 343.2$ as $[M+Na]^+$ have been successfully synthesis from dextrose and decanol in the presence of silicotungstic acid sol-gel (STSG) catalyst.

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