Transformation of cellulose into non-ionic surfactants in a one pot catalytic process

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Abstract

Alkyl glucosides surfactants have been synthesized by a cascade process which involves the methanolysis of cellulose into methyl glucosides followed by the transacetalization with n-octanol. The first step was carried out using methanol as solvent and acid catalysts (such as inorganic acids, heteropolyacids, ion-exchange resins or modified carbon materials). Subsequently long chain alkyl glucosides can be obtained in a second step by transacetalization which involves the reaction of methyl glucosides with a fatty alcohol using the same acid catalyst. The overall process was performed under mild conditions. Amorphous sulfonated carbon catalyst achieved the best results for the complete conversion of cellulose in methanol at 200 ^{o}C with yields higher than 80 % of methyl α,β-glucopyranosides. Moreover, this material containing -SO_3H groups is optimal to perform the second step obtaining octyl and decyl glucosides in yields higher than 73 % at 120 ^{o}C. In addition, catalyst reusability has been tested showing that sulfonated carbon catalyst (C-SO_3H) can be reused with only a slightly decrease of its activity after four consecutive cycles.

Keywords: cascade process, cellulose, methyl glucosides, alkyl glucosides surfactants, sulfonated carbon catalyst, heterogeneous acid catalyst, biomass.

1. Introduction

With the world's focus on reducing our dependency on fossil fuel resources, one of the challenges faced by future biorefinery processes will be the development of efficient catalysts for selective transformation of cellulosic biomass into value added compounds.[1] Surfactants are present in many products largely used in our society and they are among the highest volume synthetic chemicals produced globally. Surfactants have traditionally been produced mainly from petrochemicals feedstocks. Recently, increasing interest has been paid on the production of surfactants from oleochemicals and lignocellulosic biomass.[2] We have been working along this line by synthesizing new biodegradable surfactants from lignocellulosic platform molecules such as 5-hydroxymethylfurfural.[3] However, there is no doubt that the preferred process to produce surfactants would be those directly transforming cellulose in a one pot procedure. Among the bio-surfactants, long chain alkyl glucosides are non-ionic surfactants that are employed in manifold applications such as cosmetics, detergents, personal care, foodstuffs, etc.[4] Apart from having favorable physicochemical properties, alkyl glucosides combine biodegradability and low toxicity with chemical stability.[4a] In order to produce alkyl glucosides with surfactant properties from cellulose, existing process rely on the production of glucose units from cellulose by means, for instance, of acid or enzymatic hydrolysis. Further, these glucose units will be coupled with an alcohol to synthesize the corresponding alkyl glucoside. It certainly will be of much interest to produce the alkyl glucoside directly from cellulose. Unfortunately, to do the process in one step is not a simple task. This is because of the hydrolysis of the robust crystalline structure of the cellulose still a challenge.[5] There are many examples reported in several reviews[1a,1b,6] on cellulose hydrolysis to obtain glucose with different acid catalysts such as mineral acids,[7] heteropolyacids,[8] ionic

liquids,[9] supercritical water,[10] zeolites with metal particles,[11] metal oxides,[12] or sulfonated carbons,[13] as well as enzymes.[14] Nevertheless, product yields are often limited and there are several practical inconveniences. The use of sulphuric acid, for example, suffers from energy inefficiency and requires a thorough separation, recycling, and treatment of the acid waste residue. On the other hand, aside from their high cost, enzymes currently need long residence times and a troublesome separation processes.[15] The use of recyclable acid solid catalysts as an alternative to homogeneous acids for the cellulose hydrolysis, offer important advantages such as: their easy and safe handling, avoidance of corrosion problems and neutralization steps, and decrease of waste production. Since the ability to hydrolyse cellulose is directly related to the concentration and pKa of the acid employed, efficient catalysts require a high density of accessible and strong Brönsted acid sites with high stability at higher temperatures.

One way to improve the selectivity of the hydrolysis process, would be to readily react the mono and disaccharides formed giving products of clear added value. In fact, it can be considered that once glucose is obtained from cellulose, the direct incorporation of an alkyl chain can produce long chain alkyl glucosides by reacting with fatty alcohols. The final product would be in this case a non ionic surfactant.

The most simple a low cost method to produce alkyl glucosides is through the Fischer glycosylation.[16] which involves the acid catalysed acetalization of a carbohydrate, usually glucose, in the presence of an alcohol (see Scheme 1). Fischer glycosylation can be carried out by direct acetalization (one-step) or transacetalization (two-step) synthesis. In the two-step process the carbohydrate is first coupled to a short alcohol producing an alkyl glucoside, which subsequently is used as a substrate in the transacetalization with a longer chain alcohol. In both variants the carbohydrate is suspended in an excess of alcohol and the reaction is carried out at temperatures above

100 ºC in the presence of an acidic catalyst.[4b] Concerning the preparation of long chain alkyl glucosides starting from cellulose as a source of glucose in a one-pot system, the number of studies that couple cellulose hydrolysis and Fischer glycosylation is really scarce.[17] In a pioneering work, long chain alkyl glucosides have been obtained in good yields by reacting cellulose and fatty alcohols using Amberlyst-15 (A15) as acid catalyst in ionic liquid media.[17b] The process involves a methodology for the separation of the surfactants from the ionic liquid that allows to recover and reuse 99% of the ionic liquid.[18] On the other hand, the synthesis of alkyl glucosides from cellulose and short chain alcohols such as methanol, ethanol or butanol has been further studied using a variety of acid catalysts such as H_2SO_4, heteropolyacids, A15, Nafion, sulfated zirconia or sulfonated carbons.[17c,19] It is noteworthy that methyl glucosides are obtained from cellulose in reasonable yields, since methyl glucosides in methanol medium are more stable against further degradation than glucose in water.

Taking into account the previous results, herein we report on the use of one catalyst and process that allow the synthesis of long chain alkyl glucoside surfactants by one-pot two-step process using a sulfonated carbon as the only catalyst. Methyl glucosides are prepared by methanolysis of cellulose that is converted in the same reactor into long chain alkyl glucosides by a transacetalization reaction under mild reaction conditions (see Scheme 2). We will also show the importance of the carbon source and activation for preparing an adequate catalyst.

2. Experimentals and methods

2.1. Catalysts

The strongly acidic ion exchange resin Amberlyst-15 and the perfluorinated sulfonic acid resin supported on silica composite catalysts (Nafion SAC-13) were used as

reference catalysts and purchased from Sigma Aldrich whereas Beta zeolite was purchased from PQ Zeolites B.V. The rest of the catalysts used in this work were synthesized as follows:

Zeolites: Beta (Si/Al=12) was received in the acidic form and was calcined at 580 ºC for 3 h before use. A two dimensional (2D) zeolite ITQ-2 catalyst was prepared by expansion and subsequent exfoliation of the corresponding laminar precursors of the MWW structure.[20] Main physicochemical characteristics are included in Table 1.

Carbon material bearing SO_3H groups: The carbon material with SO_3H groups was prepared as reported by Hara et al.[21] Typically, 7 g of amorphous carbon material (Activated Charcoal Norit®) was boiled in 150 mL of fuming sulphuric acid (> 97 %) at 80 ºC under N_2. After heating for 15 h and cooling to room temperature the mixture was filtered, and subsequently the black precipitate was washed repeatedly with hot distilled water until impurities such as sulphate ions were no longer detected in the wash water. After that, the catalyst was calcined before reaction at 150 ºC for 2 h under vacuum. A scheme of catalyst preparation is presented in Figure S1.

Graphene oxide (GO): GO was prepared from graphite by a modified Hummer's method.[22] This method makes use of the Hummer's reagents with additional amounts of $NaNO_3$ and $KMnO_4$. Concentrated H_2SO_4 (360 mL) was added to a mixture of graphite (7.5 g) and $NaNO_3$ (7.5 g), and the mixture was cooled down to 0 °C in an ice bath. $KMnO_4$ (45 g) was added slowly in small doses to keep the reaction temperature below 20 °C. The solution was heated to 35 °C and stirred for 3 h. Then 3 % H_2O_2 (1.5 L) was slowly added. This had a pronounced exothermic effect at 98 °C. The reaction mixture was stirred for 30 min and, finally, the mixture was centrifuged (3700 rpm for 30 min), after which the supernatant was decanted away. The remaining solid material

was then washed with 600 mL of water and centrifuged again, this process being repeated until the pH was neutral.

GO-SO_3H: Functionalization of GO was carried as is described in literature[23] by reduction of GO using $NaBH_4$ followed by diazotization by p-aminobenzenesulfonic acid with $NaNO_2$. In this procedure, 1 g of GO and 200 mL of doubly distilled water were taken into a 500 mL of beaker and sonicated for 30 min. The pH (9-10) was adjusted by adding 5 wt% Na_2CO_3 solution, then 200 mg of $NaBH_4$ (5.2 mmol) was added to the reaction mixture at 80 ºC for 1 h with vigorous stirring. During the reduction, the dispersion turned from dark brown to black and after some time, aggregation of the graphene particles started resulting in the separation of the reduced graphene oxide (rGO). The rGO was separated through centrifugation at 3500 rpm for 5 min and washed 3 times with doubly distilled water (3 x 30 mL). The resulting rGO was re-dispersed in 100 mL of water via mild sonication. The aryl diazonium salt used for sulfonation was prepared by reaction of p-aminobenzenesulfonic acid (900 mg, 5 mmol) and sodium nitrite (360 mg, 5.2 mmol) in 100 mL water and 10 mL 1N HCl solution in an ice bath. The diazonium salt solution was added to the dispersion of the rGO in an ice bath under stirring, and was kept in the ice bath for 2.5 h. After centrifuging, the material was washed with 2-3 times with water and dried at 65 ºC for 2 h.

$H_{0.5}Cs_{2.5}PW_{12}O_{40}$: The acidic salt, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, was prepared as described by Okuhara et al.[24] as follows: 5.15 g of $H_3PW_{12}O_{40}$ was dissolved in 19.5 mL of water and an aqueous solution composed of 0.63 g of Cs_2CO_3 in 15.6 mL of water was gradually added at a rate of 1 mL·min^{-1} under stirring. After complete addition, the water was evaporated at 40 ºC until a dried solid was obtained. Then the solid was calcined at 300 ºC for 3 h under air. The amount of Cs content in the solid was determined by ICP analysis after dissolving the solid in an aqueous NaOH solution.

P-C-SO_3H: The composite catalyst P-C-SO_3H was prepared as reported by Mo et al.[25] An aqueous solution of glucose (1.2 g glucose, 3 mL deionized water) and a small amount of concentrated sulfuric acid (0.2 g) were added to pre-dried (100 ºC air) Amberlite XAD1180 (a porous polyaromatic styrene/divinylbenzene copolymer) to incipient wetness, followed by drying at 100 ºC overnight. Then, the mixture was pyrolyzed under dry N_2 at 300 ºC for 1 h. After that, the precursor polymer was sulfonated using concentrated sulfuric acid (1 g solid/20 mL H_2SO_4) at 160 ºC for 15 h under a dry N_2 atmosphere.

MCM-41-C-SO_3H: This sulfonated carbon-silica composite was prepared following the synthesis carried out by Mo et al.[25] as is described below: aqueous solution of glucose (1.2 g glucose, 3 mL deionized water) and a small amount of concentrated sulfuric acid (0.2 g) was added to pre-dried (100 ºC air) MCM-41 to incipient wetness. Later, this mixture was dried at 100 ºC overnight. After incompletely carbonizing at 400 ºC in flowing N_2 for 15 h, the white glucose/MCM-41 composite changed into brown-black carbon/MCM-41. Then, it was heated in a concentrated H_2SO_4 (>96%) solution at 150 ºC under N_2 for 15 h to introduce –SO_3H into the aromatic carbon rings. After cooling it to room temperature, distilled water was added to the mixture to form a black precipitate, which was then washed repeatedly in hot distilled water until sulfate ions were no longer detected in the filtrate by using a $BaCl_2$ solution. Finally, MCM-41-C-SO_3H was obtained after drying at 100 ºC. A scheme of catalyst preparation is presented in Figure S2. In Figures S3 and S4 are presented the HR-TEM and XRD patterns of the MCM-41-C-SO_3H catalyst.

2.2. Reagents

All reagents, i.e. methanol, α-microcellulose, methyl α-glucopyranoside, n-octanol and n-decanol, were purchased from Sigma Aldrich.

2.3. Catalyst characterization and analytical methods

The main catalyst properties are shown in Table 1. Specific surface areas and pore volume were measured by N_2 adsorption at -196 ºC by using a Micrometrics ASAP 2000 apparatus. The total Brönsted-acid sites in these catalysts were determined by the titration method as follows: a sodium hydroxide aqueous solution (0.01 $mol \cdot L^{-1}$, 20 mL) was added to a catalyst (40 mg), and the mixture was stirred for 2 h at room temperature. After filtration of the solid, the filtrate was titrated by a hydrochloric acid (0.01 $mol \cdot L^{-1}$) aqueous solution using phenolphthalein as indicator to determinate the total acid density. The quantity of sulfonic groups was measured by elemental analysis with an EA-1108 CHNS Fisons analyzer and sulphanilamide as standard. Additionally, for the carbonaceous materials, the quantity of carboxylic groups was determined by titration with $NaHCO_3$ (0.01 $mol \cdot L^{-1}$) and subtracting the $-SO_3H$ content, while the quantity of hydroxyl groups was estimated from the difference between the total, and $-SO_3H$ plus -COOH acid sites (see the results in Table 2). Fourier transform infrared (FTIR) spectra were recorded with a Nicolet iS10 Thermo Scientific. The FTIR spectrums of the sulfonated carbon catalyst as well as the carbonaceous support material are plotted in Figure S5. As can be observed there, absorption bands around 1717 and 1605 cm^{-1} correspond to -C=O (carbonyl) and -OH (hydroxyl groups) bending vibrations respectively, whereas the bands around 3407 and 1605 cm^{-1} can be assigned to C-OH stretching and -OH bending vibration. On the other hand the vibration bands, only showed by the sulfonated catalyst, around 1038 (SO_3^- stretching) and 1357 cm^{-1}

(O=S=O stretching in -SO_3H) in the FTIR spectrum indicate that the resulting material possesses SO_3H groups.

The analysis of the products was performed by a combination of ^{1}H-NMR spectroscopy, ion-exclusion HPLC and GC of silylated samples. Methyl glucosides, alcohols and most of the reaction products were quantified by ^{1}H-NMR (300 MHz Bruker Avance) in d_6-DMSO as solvent. Octyl glucosides were quantified by HPLC analyses of samples diluted with ultrapure water, and acidified with 1.4 M aqueous H_2SO_4 solution, by using a Coregel 87H column (Waters 1525 Binary HPLC Pump, injection volume = 10 mL, column temperature = 70 ^{o}C, eluent = 4 mM aqueous H_2SO_4, flow rate = 0.7 mL·min^{-1}) and a refractive index detector (Waters 2410). Finally, alkyl cellobioside was quantified by GC analyses after silylation of samples with N,O-bis(trimethylsilyl)trifluoroacetamide in pyridine by using a Varian CP-3800 gas chromatograph [on-column injection, injection volume = 0.6 μL, Varian Select Biodiesel column for glycerides with the following temperature program: 50 ^{o}C (1 min), 50-180 ^{o}C (15 ^{o}C·min^{-1}), 180-230 ^{o}C (7 ^{o}C·min^{-1}), 230-370 ^{o}C (10 ^{o}C·min^{-1}), 370 ^{o}C (5 min), carrier gas: N_2, flow = 2.5 min^{-1}, flame ionization detector].

The organic content of the used catalysts was measured by elemental analysis. The thermogravimetric analyses were carried out with a TGA 2050 by TA Instruments, under an air flow and with a heating rate of 10 K·min^{-1}. Mass spectra were performed by GC-MS (HP Agilent 5988 A with a 6980 mass selective detector).

X-ray diffractograms (XRD) were adquired with a CUBIX PANalytical diffractometer equipped with a PW3050 goniometer using monochromatic radiation corresponding to the Kα-Cu line. High resolution transmission electron microscopy (HR-TEM) images were adquired using a microscope JEOL JEM-2100F with field emission gun operating at 200 kV.

Surface tension of the surfactant compounds mixture obtained in the transformation of cellulose: octyl α,β-glucopyranoside + octyl α,β-cellobioside and decyl α,β glucopyranoside + decyl α,β-cellobioside, were measured at concentrations from 4 $g \cdot L^{-1}$ up to 8 $g \cdot L^{-1}$ and from 0.5 $g \cdot L^{-1}$ up to 2 $g \cdot L^{-1}$ respectively at room temperature using the pendant drop method, and compared with solutions of commercial samples: octyl β-glucopyranoside and decyl β-glucopyranoside. The apparatus used was OCA-20 Contact Angle System from DataPhysics Instruments GmbH with a SCA20 software. The drop profile was analyzed by means of a video camera and processed by using the software to obtain the surface tension.

2.4. Reaction Procedures

2.4.1. Methanolysis of cellulose

To perform the methanolysis reaction of cellulose, α-microcellulose (250 mg, 1.55 mmol calculated as anhydroglucose $C_6H_{10}O_5$) and the corresponding catalyst (100 mg) were added into a 15 mL autoclave Engineers. After that, the reactor was charged with methanol (10 mL) and N_2 (30 bar). Then, the reaction mixture was heated at 200 ^oC (ramp: 8 $^oC \cdot min^{-1}$) and left at this temperature for the desired reaction time. At the end of the reaction, the unreacted cellulose, together with the heterogeneous catalyst, was filtered and the reaction solution collected to analyse the products distribution as explained in section 2.3. The solid obtained by filtration was weighed, and the cellulose conversion was calculated by weight difference between total mass of cellulose and catalyst before and after the reaction. During the reaction, besides methyl α,β-glucosides compounds, methyl α,β-cellobioside, 5-hydroxymethylfurfural (HMF), 5-methoxymethylfurfural (MMF) and methyl levulinate (ML) were also detected (see Scheme 3). MMF and ML have also been detected in similar reactions,[19e,26] and are

formed by the subsequent conversions of methyl glucosides to MMF and subsequent hydration into ML.[27]

2.4.2. Transacetalization reaction

The transacetalization process was performed by reacting methyl α-glucopyranoside (300 mg, 1.54 mmol) with n-octanol (3 g, 23 mmol) in the presence of the corresponding acid catalyst (100 mg) at 120 ºC under vigorous stirring, while the methanol was removed by continuous distillation using a N_2 flow and a Dean-Stark system. At the end of the reaction the products were analyzed as explained in section 2.3. The octyl glucosides were purified by an extraction procedure in where the crude of reaction was dissolved in heptane and the octyl glucosides were thoroughly extracted with water. The aqueous fractions were collected and water was eliminated by distillation at reduced pressure. ^{1}H-NMR data of the alkyl glucosides are provided in Supporting Information.

2.4.3. Overall process

The one-pot method was carried out using a mixture of octanol/methanol with molar ratios of 3/1 and 1/3. For this purpose, α-microcellulose (250 mg, 1.55 mmol calculated as anhydroglucose $C_6H_{10}O_5$), C-SO_3H catalyst (100 mg), methanol and octanol (10 mL total volume) and N_2 (30 bar) were added to a 15 mL steel autoclave. Next, the reaction mixture was heated at 200 ^{o}C (ramp: 8 ^{o}C·min^{-1}) and left at this temperature for the desired reaction time. At the end of the reaction, the unreacted cellulose together with the heterogeneous catalyst was filtered and the reaction solution was collected and analysed, (see section 2.3). The solid obtained by filtration was weighed, and the cellulose conversion was calculated by weight difference between total mass of

cellulose and catalyst before and after the reaction. Octyl levulinate (denoted as OL) was also obtained, which can be produced from further reaction of octyl glucosides or by transesterification of methyl levulinate.

One-pot, two-steps method: This strategy was carried out introducing α-microcellulose (250 mg, 1.55 mmol calculated as anhydroglucose $C_6H_{10}O_5$), C-SO_3H catalyst (100 mg), methanol (10 mL) and N_2 (30 bar) in a 15 mL steel autoclave. The reaction mixture was heated at 200 ^oC (ramp: 8 $^oC \cdot min^{-1}$). After the required time, the temperature was decreased up to room temperature and the system was depressurized. After that, n-octanol (3 g, 23 mmol) was added and the reaction mixture was heated at 120 ^oC with a continuous N_2 bubbling in order to remove the methanol from the reaction mixture. At the end of the reaction, the unreacted cellulose together with the heterogeneous catalyst was removed by filtration and the solution was collected and analysed (see section 2.3).

Reaction with recirculation of products: The same methodology as per the two steps method was followed but in this case, after 3 hours of methanolysis of cellulose, the reaction was stopped and the unreacted cellulose along with the catalyst was recovered by filtration. Then, 10 mL of fresh methanol were added to the solid recovered and the mixture was again heated at 200 ºC during 3 hours. This protocol was repeated three times until complete cellulose conversion was achieved. Then, all the filtered solutions containing the methyl glucosides and the catalyst were joined and n-octanol was added. The transacetalization process was performed as indicated in section 2.4.2.

3. Results and discussion

3.1. Transacetalization of methyl α-glucopyranoside into octyl α,β-glucopyranosides.

Taking into account a previous work carried out in our group,[28] the nature of the solid acid catalyst can play a key role in the different reaction steps, i.e. the cellulose hydrolysis, glycosylation and transacetalization. Therefore, the behaviour of several solid acids for the transacetalization step was studied first (Scheme 4). The results obtained in the transacetalization reaction of methyl α-glucopyranoside with n-octanol to obtain octyl α,β-glucopyranosides (α,β-OGP) are given in Table 3 and were very successful in most of the cases. The results presented there clearly show that catalysts with stronger acid sites, i.e. those containing -SO_3H groups are significantly more active than microporous aluminosilicates. In the case of the aluminosilicates the pore dimensions, and therefore the accessibility of reactants to the acid sites and diffusion of the products out of the pores, is a key issue. Indeed, site accessibility would explain the higher activity of the delaminated ITQ-2 with respect to Beta zeolite, despite the lower density of acid sites in the former zeolitic material (see Table 1).

Amberlyst 15 (A15), a polymer containing sulfonic groups, gives interesting results, achieving 94 % conversion of methyl α-glucopyranoside with 85 % yield to α,β-OGP (entry 4, Table 3). An increase of activity together with a decrease of the selectivity of α,β-OGP can be observed at higher reaction temperature (entry 8). Meanwhile, a decrease of the temperature produces a decrease in activity while the selectivity to the desired product is increased (entry 9, Table 3). Notice that selectivity is decreased due to the formation of glucose from alkyl glucoside hydrolysis due to the water produced during the reaction. Finally, carbon materials bearing sulfonic groups (entries 6 and 7, Table 3), give good yields of α,β-OGP. These results indicate that solid acids containing accessible sulfonic groups could be good transacetalization catalysts from

the activity and selectivity point of view, provided that reaction conditions are optimized.

3.2. Hydrolysis of cellulose and methyl α,β-glucopyranosides synthesis

Because the successful results obtained in the transacetalization step, we decided to study the behaviour of the above catalysts for the first step of the global process, i.e., the direct production of methyl α,β-glucopyranosides from cellulose. The results were compared with those obtained using homogeneous acid catalysts such as concentrated H_2SO_4 and the heteropolyacid $H_3PW_{12}O_{40.}$ It can be seen in Table 4 that inorganic acid catalysts such as H_2SO_4 and $H_3PW_{12}O_{40}$ (entries 1 and 2) are active for performing the methanolysis of cellulose, while methyl levulinate, which is formed by dehydration of methyl glucosides and further hydration,[27] was detected as the main byproduct while methyl cellobioside (MCb) was detected at level of traces. The heteropolyacid, $H_3PW_{12}O_{40,}$ was more active than sulphuric acid, giving 87% cellulose conversion with a total yield of methyl glucosides of 64 % after 0.5 h reaction time. These results agree with those previously reported by Shimizu et al.[6a] who showed that heteropolyacids show better hydrolysis activity than mineral acids, effect that is well correlated with the deprotonation enthalpy of these Bronsted acid sites.

Concerning zeolites, neither Beta nor ITQ-2 zeolites (entries 3 and 4, Table 4) were able to perform the cellulose transformation which can be due to mass transfer limitations of the cellulosic molecules, especially in the case of Beta zeolite. After that, and considering the good performances obtained with the homogeneous heteropolyacid (entry 2, Table 4) the high surface area solid heteropolyacid $Cs_{2.5}H_{0.5}W_{12}PO_{40}$[29] (entry 5) was prepared and tested in the reaction but the results were also unsuccessful. Again, this is likely due to the low accessibility to the Bronsted acid sites to the large cellulose

polymeric molecules. Then, taking into account the catalyst requirements: strong solid acid sites and high reactant accessibility, we have explored the catalytic activity of solid acids like Nafion SAC-13 and Amberlyst 15 (A15), with higher accessibility and with sulfonic groups (entries 6 and 7, Table 4). The activity was increased considerably, mainly for the A15 catalyst, confirming the high acid strength of the sulfonic groups and the critical role of acid site accessibility for this reaction. It is important to note that Nafion SAC-13 presents the highest TON number (mmol of anhydroglucose converted per mmol of acid site), so the lower activity of Nafion SAC-13 compared with A15 could be attributed to its smaller acid site concentration, together with the possible blockage of some of the acid sites.

Taking into account the good results provided by sulfonic acid catalysts, and considering the excellent results previously obtained using sulfonated carbon as catalysts for the hydrolysis of cellulose,[13b,19d,19e,30] different catalysts based on sulfonated carbon were tested for the methanolysis of cellulose. Thus, graphene oxide (GO) (as a reference), sulfonated graphene oxide (GO-SO_3H), sulfonated carbon C-SO_3H, sulfonated carbon supported on the polymer matrix Amberlite XAD1180 (P-C-SO_3H) and the sulfonated carbon supported on the mesoporous silica material MCM-41 (MCM-41-C-SO_3H) were selected as catalysts for this transformation. High activity was obtained in all cases (entries 8-12, Table 4). As in the case of cellulose hydrolysis, the remarkable performances exhibited by carbon-based acids in the cellulose methanolysis can be attributed to the ability of hydrophilic molecules to interact with the catalyst, being easy for a cellulose chain in solution to be in contact with the acid sites associated to the carbon material.[31]

3.2.1. Reuse of the most active catalysts

For a potential application of the process presented here for the one-pot conversion of cellulose into alkyl glucosides, the catalyst has to achieve high turnover numbers. Then, taking into account the relatively high loadings of catalyst used, recycling of the catalyst is mandatory. After the first reaction cycle, the cellulose conversion was calculated by weight difference before and after completing the reaction. Then, the mixture of the catalyst and unreacted cellulose together with 10 mL of fresh methanol were introduced into the autoclave again, and the amount of cellulose was adjusted by adding cellulose in an equivalent amount to the cellulose converted in the first cycle. In Table 5, it can be observed that in the case of Amberlyst-15, GO and P-C-SO_3H (entries 1, 2 and 5, Table 5) an important loss of activity occurs during the second cycle. This decrease of activity can be attributed to the low stability of the polymer matrix at high temperatures, and the same occurs with the GO catalyst (entry 2, Table 5). Indeed, it is known that at high temperatures the different oxygen groups present on GO (see Table 2), mainly in the forms of epoxy, -OH and -COOH, change its composition.[32] On the other hand, with GO-SO_3H, C-SO_3H (1) and MCM-41-C-SO_3H (entries 3, 4 and 6, Table 5) the catalyst activity is maintained upon recycling owing to a higher stability of their sulfonic groups.

In a deeper study directed to find what sulfonic material is the most adequate catalyst, the methanolysis of cellulose was carried out up to 3 catalyst reuses using C-SO_3H (1) and MCM-41-C-SO_3H. The objective was to find if the higher surface area (667 $m^2 \cdot g^{-1}$) and large pores of the mesoporous ordered silica support can contribute to enhance the catalyst stabillity.[33] Results in Figure S6 show that a continuous deactivation occurs with both catalysts, with 12 and 11% decrease in conversion after 4 reaction cycles. However, when the sulphur content was analyzed after the fourth use, a

decrease from 2.30 to 1.44 wt % was found in the case of C-SO_3H (1) catalyst. Meanwhile, the sulphur content before and after the use of MCM-41-C-SO_3H was practically the same (1.52 and 1.35 wt % respectively). Moreover, the FTIR spectrum of C-SO_3H (1) (Figure S7) showed that after 4 cycles a decrease in the intensity of the bands at ~1038 and ~1357 cm^{-1}, corresponding to SO_3^- stretching and O=S=O stretching in -SO_3H respectively, clearly takes place, whereas the FTIR spectrum of MCM-41-C-SO_3H (Figure S8) showed that the absortpion bands corresponding to sulfonic groups still appear after four consecutive cycles. Then, taking into account the characterization and catalytic results of the MCM-41-C-SO_3H catalyst fresh and after four cycles, we have to conclude that the deactivation is not associated with a loss of sulfonic groups, but probably to the deposition of products in the mesopores. If this is so, and in order to remove the organic material deposited, the catalyst was treated with air at 450 ºC during 8 hours. After the treatment, the catalyst recovered 39% of the activity, but this was still 8 % lower than for the fresh catalyst. This is due to the fact that the catalyst regeneration treatment also had a negative effect on the sulfonic acids, reducing the sulfur content by 30%, i.e. from 1.52 to 1.03 wt %.

3.2.2. Influence of the sulphur content on the sulfonic carbon catalyst on activity and selectivity

To study the influence of the sulfonic acid sites concentration on the performance of the methanolysis step, the reaction was carried out using various C-SO_3H catalysts with different sulphur content. In Table 6 the results obtained for three C-SO_3H catalysts prepared with different concentration of sulfonic acid sites are presented. To achieve a higher concentration of sulfonic groups on the catalyst, the stirring of the support material in sulphuric solution was maintained for longer time, but sulfonated carbon

catalysts with sulphur content beyond to 3.55 wt % could not be achieved. From the catalytic results presented in Table 6 it can be deduced that the cellulose conversion increases when increasing the concentration of sulfonic groups on the carbon. The same evolution is seeing with respect to the formation of the methyl levulinate byproduct. Therefore, and in order to maximize the yield of depolymerized glucose, a compromise between activity and selectivity could be achieved by using C-SO_3H (1) catalyst with 2.30 wt % of sulphur content.

3.2.3. Influence of the temperature in the methanolysis step using C-SO_3H as catalyst

After selecting the C-SO_3H (1) catalyst as optimum to perform the methanolysis step, the influence of the reaction parameters was studied. The reaction was carried out at 160, 180, 200 and 220 ºC, and the results shown in Table 7 evidence a decrease in selectivity to α,β-MGP when increasing the reaction temperature. In the same way, at lower temperatures a considerable decrease in product yield was observed, even working with double loading of the catalyst (see entry 2, Table 7). In some way working at 200 ºC represents a compromise between product yield and selectivity.

3.3. One-pot process to produce octyl α,β-glucopyranosides (α,β-OGP) from cellulose using C-SO_3H as catalyst

The next challenge was to make the conversion of cellulose into long chain alkyl glucosides using C-SO_3H (1) as catalyst. To achieve this, the whole process, i.e. cellulose hydrolysis, methyl glucosides formation and transacetalization with the fatty alcohol was performed in one pot, in a cascade mode. Thus, cellulose, methanol, fatty alcohol and the catalyst are introduced at the same time in the reactor, under N_2 pressure

(30 bar) at 200 ºC. This attempt was firstly carried out with an n-octanol/methanol ratio of 1/3 and the results are given in Table 8 (entry 1). It can be seen there that, while cellulose conversion is very high, low yields of octyl α,β-glucopyranosides are achieved after 8 hours of reaction. Otherwise, if the same reaction is carried out with an excess of the fatty alcohol, n-octanol/methanol molar ratio of 3/1, incomplete conversion of cellulose is achieved although a slight increase in octyl α,β-glucopyranosides yield are obtained after 8 hours (see entry 2, Table 8). Nevertheless, low yields of octyl α,β-glucopyranosides were reached in both cases.

Due to the inherent difficulty in performing the cascade reaction, the process strategy was changed. Thus, we attempted to convert completely the cellulose in a first step into methyl glucosides, and then, to add the fatty alcohol to the reaction mixture to achieve the surfactant product. The reaction operation would represent a one-pot, two-steps to obtain the alkyl glucoside surfactant from cellulose. To achieve this, firstly the complete cellulose conversion was attempted carrying out the methanolysis step at larger reaction time. The results in Table 8 (entries 3 and 4), show that, indeed, a higher cellulose conversion was achieved after 12 hours, but together with an increase of byproducts formation such as methyl levulinate. At that point n-octanol was added, and the reaction was carried out, removing the methanol from the reaction mixture, while performing the transacetalization reaction (see experimental). A good yield of α,β-OGP was achieved when the methanolysis step was maintained for 12 hours previously, though a considerable yield of octyl levulinate (OL) was also obtained (see entry 4, Table 8).

A third reaction alternative was also attempted to improve the selectivity into octyl glucosides which consists in the conversion of all the cellulose into methyl glucosides in several cycles by recirculating the unconverted cellulose. This attempt was carried out

by converting the cellulose into methyl α,β-glucopyranosides in the same conditions optimized above, and after three hours, the products were filtered to separate the unreacted cellulose and the carbon catalyst from the reaction mixture. Then, fresh methanol was added again and the unreacted cellulose and the carbon catalyst were further reacted for three more hours. This process was repeated up to achieve the complete cellulose conversion. Subsequently, all the filtrates containing the methyl glucosides and the carbon catalyst were put together, n-octanol was added, and the transacetalization reaction was carried out as described in the experimental section. With this strategy, an increase in the yield of surfactant with a considerable decrease of byproducts was obtained (see entry 5, Table 8). When n-decanol was used as fatty alcohol instead n-octanol under the same reaction conditions, similar yield (71 %) was achieved. It is important to note that during the reaction, octyl cellobioside (6% yield) with surfactant properties was also formed being the maximum total surfactant yield (octyl glucosides + octyl cellobiosides) of 79 % when the strategy of recirculation of products is followed. The surface tension of the mixture of surfactants obtained with n-octanol and n-decanol was measured in water solutions at different concentrations in order to determinate the critical micellar concentration in each case. In Table 9 the surface tension values at the critical micellar concentration are shown and, as can be seen, the pure surfactant mixtures obtained by cellulose methanolysis and subsequent transacetalization by n-octanol as well as n-decanol, give just a slightly lower value of surface tension in comparison with the commercial alkyl β-glucopyranosides. This some lower surface tension can probably be due to the presence of a small quantity of alkyl disaccharides in the product coming from the cellulose.

3.5. Catalyst reusability for the one-pot process

Although C-SO_3H (1) stability has already been studied in section 3.2.1 for the first step, i.e. cellulose hydrolysis and methylation, which requires the harshest conditions, the stability of C-SO_3H (1) catalyst was now tested for the overall process following the two strategies presented above, i.e. procedure for achieving the complete conversion of cellulose by prolonging the reaction time, and by doing the complete cellulose conversion into methyl glucosides in 3 cycles. In Table 10 (entries 1 and 2) is showed that during the reuse, the loss of activity is higher when the first step (methanolysis of cellulose) is carried out by prolonging the reaction time, achieving a total yield of α,β-OGP of 51 % (instead of 59 % obtained when using fresh catalyst), while when the methanolysis of cellulose is performed in 3 cycles (entries 3 and 4), the final yield of the α,β-OGP obtained is close in the first and the second use of the catalyst (79 and 73 % respectively). These results indicate that by using the first protocol (prolonging the reaction time of the methanolysis step) there is a largest loss of the sulfonic acid sites from the catalyst due to the longer times of reaction required to achieve similar cellulose conversion. In fact, when the analysis of the S content of the catalysts was measured after the reuse using both protocols, it can be seen that by prolonging the reaction time, the S content decreases from 2.30 up to 1.73 wt%. On the other hand, when the methanolysis of cellulose is performed in 3 cycles, the loss of sulfonic groups was lower and the S content only decreased up to the 2.04 wt %. Taking into account all the results presented up to now, a possible methodology to implant the direct transformation of cellulose into alkyl glucoside surfactants is represented in Scheme 5.

Conclusions

Starting from cellulose, alkyl glucoside surfactants have been synthesized by a cascade process which involves the methanolysis of cellulose into methyl glucosides followed by the transacetalization with a fatty alcohol under mild reaction conditions. High selectivity to long chain alkyl glucosides can be achieved using amorphous sulfonated carbon as acid catalyst and following a protocol that involves as the first step the complete conversion of cellulose into methyl glucosides in several cycles by recirculating the uncorverted cellulose. In a second step, the transacetalization of the methyl glucosides with a fatty alcohol on the same catalyst is performed obtaining a mixture of alkyl glucosides and alkyl cellobiosides. Catalyst stability has been tested showing that sulfonated carbon catalyst (C-SO_3H) can be reused with only a slightly decrease of its activity after four consecutive cycles. Moreover, it is showed that the alkyl glucosides and cellobiosides mixture produced possess a surfactant activity similar to commercial alkyl glucosides. Considering that at an industrial level the production of alkyl glucosides usually involves the use of sulfuric acid as catalyst, which has to be neutralized in situ producing sulphate salts that modifies the surfactant properties, we can conclude that this protocol can be an interesting alternative to produce salt-free alkyl glucosides. Moreover, this process has potential to be used to valorise lignocellulose biomass. Thus, previously to a delignification process, the cellulose-hemicellulose fraction can be a source of cheaper alkyl glucosides and pentosides surfactants.

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Table 1. Main characteristics of the heterogeneous catalysts employed in this research.

Catalyst	**Si/Al**	**Morphology**	**A_{BET} ($m^2 \cdot g^{-1}$)**	**V_p ($cm^3 \cdot g^{-1}$)**	**Acidity[(a)] ($meqH^+ \cdot g^{-1}$)**
Beta	12	3D-12MR	602	0.35	1.19
ITQ-2	15	delaminated	841	0.39	1.04
Nafion SAC-13	-	-	218	0.60	0.13 (0.13)
Amberlyst-15	-	-	35	0.40	5.43 (5.43)
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	-	-	135	0.61	0.15
GO	-	-	566	0.54	2.24
GO-SO_3H	-	-	520	0.47	3.20 (0.87)
C-SO_3H (1)	-	-	529	0.41	2.47 (0.72)
C-SO_3H (2)	-	-	546	0.43	2.18 (0.57)
C-SO_3H (3)	-	-	504	0.40	2.89 (1.11)
P-C-SO_3H	-	-	32	0.37	3.89 (2.52)
MCM-41-C-SO_3H	-	-	667	0.91	2.02 (0.44)

[(a)] Acidity determined by acid-base titration and values in brackets indicate concentration of sulfonic groups calculated by elemental analysis.

Table 2. Acid density of the different carbon catalysts.

	Acid Density ($meqH^{+} \cdot g^{-1}$)			
Catalyst	**Total[(a)]**	**-SO_3H[(b)]**	**-COOH[(c)]**	**-OH[(d)]**
C-SO_3H (1)	2.47	0.72	1.01	0.74
C-SO_3H (2)	2.18	0.57	1.03	0.58
C-SO_3H (3)	2.89	1.11	1.06	0.72
GO	2.24	-	1.58	0.66
GO-SO_3H	3.20	0.87	1.68	0.65

[(a)] Calculated by titration with NaOH (0.01 M); [(b)] Obtained by elemental analysis;
[(c)] Calculated by titration with $NaHCO_3$ (0.01 M) and subtracting the -SO_3H content;
[(d)] Estimated from the difference between the total, and -SO_3H plus -COOH acid sites.

Table 3. Catalytic performances of different solid acid catalysts for the transacetalization reaction between methyl α-glucopyranoside and n-octanol.[a]

Entry	Catalyst	Time (h)	Acidity[b] ($meqH^+ \cdot g^{-1}$)	Conversion α-MGP[c] (%)	Yield α,β-OGP[d] (%)	Selectivity α,β-OGP[e] (%)
1	Beta	8	1.19	62	58	94
2	ITQ-2	8	1.04	81	79	97
3	Nafion SAC-13	8	0.13 (0.13)	85	73	86
4	Amberlyst-15	4	5.43 (5.43)	94	85	90
5	GO	4	2.24	84	79	94
6	GO-SO_3H	4	3.20 (0.87)	88	82	93
7	C-SO_3H (1)	4	2.47 (0.72)	92	85	93
8	Amberlyst-15[f]	3	5.43 (5.43)	99	83	84
9	Amberlyst-15[g]	8	5.43 (5.43)	77	75	98

[a] Reaction conditions: methyl α-glucopyranoside, 1.53 mmol; n-octanol, 23 mmol; catalyst, 100 mg; 120 ^oC. Dean Stark system and N_2 bubbling. [b] Acidic groups as determined by acid-base titration and values in brackets indicate concentration of sulfonic groups calculated by elemental analysis. [c] α-MGP denotes methyl α-glucopyranoside. [d] α,β-OGP denotes the total amount of octyl α-glucopyranoside and octyl β-glucopyranoside. [e] Selectivity values at 60 % of methyl α-glucopyranoside conversion. [f] Reaction carried out at 140 ^oC. [g] Reaction carried out at 100 ^oC.

Table 4. Catalytic performances of different solid acid catalysts for the conversion of cellulose into methyl glucosides in methanol.[a]

Entry	Catalyst	Time (h)	Acidity[b] ($meqH^+ \cdot g^{-1}$)	Conversion[c] (%)	TON[d]	Yield (%)				Selectivity α,β-MGP (%)
						α-MGP[e]	β-MGP[e]	MCb[e]	ML[e]	
1	H_2SO_4[f]	1	9.90	82	1.81	38	21	1	11	72
2	$H_3PW_{12}O_{40}$[f]	0.5	1.02	87	1.92	40	24	1	9	74
3	Beta	3	1.19	3	0.39	1	1	-	-	82
4	ITQ-2	3	1.04	7	1.04	4	2	-	-	85
5	$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	3	0.15	11	11.32	7	4	-	-	89
6	Nafion SAC-13	3	0.13 (0.13)	27	32.05	14	9	1	2	85
7	Amberlyst-15	1	5.43 (5.43)	92	2.61	49	27	2	8	82
8	GO	3	2.24	62	6.25	32	19	1	5	93
9	GO-SO_3H	3	3.20 (0.87)	51	4.06	30	17	3	6	92
10	C-SO_3H (1)	3	2.47 (0.72)	58	3.07	29	17	5	4	79
11	P-C-SO_3H	1	3.89 (2.52)	82	2.85	38	22	2	11	76
12	MCM-41-C-SO_3H	3	2.02 (0.44)	47	3.53	25	14	2	3	83

[a] Reaction conditions: cellulose, 250 mg; methanol, 10 mL; catalyst, 100 mg; 200 °C; N_2 (30 bar). [b] Acidic groups as determined by acid-base titration and values in brackets indicate concentration of sulfonic groups calculated by elemental analysis. [c] Cellulose conversion. [d] Determined as mmol of anhydroglucose converted per mmol of nominal Brönsted acid sites. [e] α-MGP (methyl α-glucopyranoside), β-MGP (methyl β-glucopyranoside), MCb (methyl cellobioside) and ML (methyl levulinate). [f] $[H^+]$, 7.0 $mmol \cdot L^{-1}$.

Table 5. Catalytic performances of various acid catalysts for the reuse in the conversion of cellulose to methyl glucosides in methanol.[a]

Entry	Catalyst	Time (h)	Acidity[b],[c] ($meqH^+ \cdot g^{-1}$)	Conversion[d],[e] (%)	Yield (%)			Selectivity α,β-MGP (%)
					α,β-MGP[e],[f]	MCb[e]	ML[e],[f]	
1	Amberlyst-15	1	5.43	29 (92)	20 (76)	1 (2)	4 (8)	69 (82)
2	GO	3	2.24 (1.16)	22 (62)	17 (51)	1 (1)	2 (5)	77 (93)
3	GO-SO_3H	3	3.20 (3.04)	45 (51)	39 (47)	2 (3)	3 (6)	86 (92)
4	C-SO_3H (1)	3	2.47 (2.38)	55 (58)	43 (46)	5 (5)	4 (4)	78 (79)
5	P-C-SO_3H	1	3.89	15 (82)	11 (60)	1 (2)	2 (11)	73 (76)
6	MCM-41-C-SO_3H	3	2.02 (1.91)	43 (47)	35 (39)	2 (2)	4 (3)	80 (83)

[a] Reaction conditions: cellulose, 250 mg; methanol, 10 mL; catalyst, 100 mg; 200 ^oC; N_2 (30 bar). The second use of the catalyst was carried out at the same reaction conditions, reloading the cellulose converted into the solid mixture and adding others 10 mL of methanol. [b] Total acidity determined by acid-base titration. [c] Values in brackets indicate the acidity after its use. [d] Cellulose conversion. [e] Values in brackets indicate the results of the first use. [f] α,β-MGP (methyl α,β-glucopyranoside), MCb (methyl cellobioside) and ML (methyl levulinate).

Table 6. Results of C-SO_3H catalysts with different sulphur content in the methanolysis reaction step of cellulose.[a]

Catalyst	S content (wt%)	Acidity[b] ($meqH^+ \cdot g^{-1}$)	Conversion[c] (%)	Yield (%)				Selectivity α,β-MGP (%)
				α-MGP[d]	β-MGP[d]	MCb[d]	ML[d]	
C-SO_3H (1)	2.30	2.47 (0.72)	58	29	17	5	4	79
C-SO_3H (2)	1.83	2.18 (0.57)	48	27	16	4	3	89
C-SO_3H (3)	3.55	2.89 (1.11)	63	30	19	3	11	76

[a] Reaction conditions: cellulose, 250 mg; methanol, 10 mL; catalyst, 100 mg; 200 ^oC; N_2 (30 bar); 3h. [b] Acidic groups as determined by acid-base titration and values in brackets indicate concentration of sulfonic groups calculated by elemental analysis. [c] Cellulose conversion. [d] α-MGP (methyl α-glucopyranoside), β-MGP (methyl β-glucopyranoside), MCb (methyl cellobioside) and ML (methyl levulinate).

Table 7. Results of the methanolysis reaction step of cellulose using C-SO_3H (1) catalyst at different temperatures.[a]

Entry	Temperature (ºC)	Conversion (%)	Yield (%)				Selectivity α,β-MGP (%)
			α-MGP[b]	β-MGP[b]	MCb[b]	ML[b]	
1	160	18	9	5	6	1	89
2[c]	160	24	13	8	4	2	87
3	180	37	20	12	5	3	86
4	200	58	29	17	5	4	79
5	220	70	33	19	3	9	74

[a] Reaction conditions: cellulose, 250 mg; methanol, 10 mL; C-SO_3H (1), 100 mg; 200 ^oC; N_2 (30 bar); 3h. (b) α-MGP (methyl α-glucopyranoside), β-MGP (methyl β-glucopyranoside), MCb (methyl cellobioside) and ML (methyl levulinate). (c) Reaction carried out with the double weight of the catalyst.

Table 8. Results of the different strategies performed to synthesize octyl α,β-glucopyranosides from cellulose in the presence of C-SO_3H (1).

		Methanolysis Step					Transacetalization Step				
Entry	**Strategy**	**Time (h)**	**Cellulose Conversion (%)**	**α,β-MGP[(e)] Yield (%)**	**MCb[(e)] Yield (%)**	**ML[(e)] Yield (%)**	**Time (h)**	**α,β-MGP[(e)] Conversion (%)**	**α,β-OGP[(e)] Yield (%)**	**OCb[(e)] Yield (%)**	**OL[(e)] Yield (%)**
1	Cascade[(a)]	8	93	51	4	14	-	-	16	1	3
2	Cascade[(b)]	8	87	36	3	6	-	-	26	2	8
3	One-pot, two-steps[(c)]	3	58	46	5	4	4	90	41	4	2
4	One-pot, two-steps[(c)]	12	97	72	3	17	4	88	59	2	13
5	Reaction with recirculation of cellulose[(d)]	3x3	97	84	7	6	4	94	73	6	5

[(a)] Reaction conditions: cellulose, 250 mg; methanol, 7.5 mL; n-octanol, 2.5 mL; C-SO_3H (1), 100 mg; 200 ^oC; N_2 (30 bar); 3h. [(b)] Reaction conditions: cellulose, 250 mg; methanol, 2.5 mL; n-octanol, 7.5 mL; C-SO_3H (1), 100 mg; 200 ^oC; N_2 (30 bar); 3h. [(c)] Reaction conditions: 1st step, cellulose, 250 mg; methanol, 10 mL; C-SO_3H (1), 100 mg; 200 ^oC; N_2 (30 bar); 3h. 2nd step, n-octanol, 3000 mg; 120 ^oC; N_2 bubbling. [(d)] Reaction conditions: 1st step, cellulose, 250 mg; methanol, 10 mL; C-SO_3H (1), 100 mg; 200 ^oC; N_2 (30 bar). After 3 hours, the catalyst together with the unreacted cellulose are separated and taken to react again adding 10 mL of fresh methanol. This action is made 3 times. 2nd step: n-octanol, 3000 mg; 120 ^oC; N_2 bubbling. [(e)] α,β-MGP (methyl α,β-glucopyranoside), α,β-OGP (octyl α,β-glucopyranoside), MCb (methyl cellobioside), Ocb (octyl cellobioside), ML (methyl levulinate) and OL (octyl levulinate).

Table 9. Interfacial properties of the surfactants products obtained from cellulose.

Surfactant	**cmc[(a)] ($g \cdot L^{-1}$)**	**$\gamma_{surf\text{-}cmc}$[(b)] ($mN \cdot m^{-1}$)**
α,β-OctylGP + α,β-Octyloligosaccharides	5.70	31.68
Commercial β-OctylGP	6.07	33.71
α,β-DecylGP + α,βDecyloligosaccharides	0.76	25.09
Commercial β-DecylGP	0.82	27.34

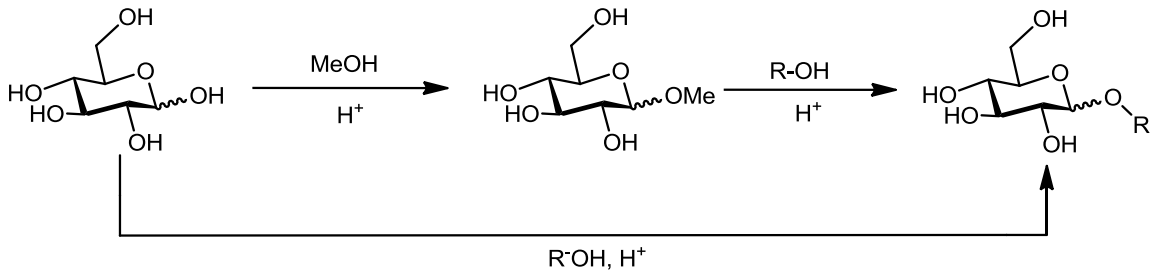
[(a)] Critical micelle concentration (cmc) was calculated at an ambient temperature using surface tension (γ_{surf})-concentration profiles. [(b)] Surface tension value measured at the cmc by the pendant drop method.

Table 10. Results of the reuse by two different strategies performed in order to synthesize octyl α,β-glucopyranosides from cellulose using C-SO_3H (1) as catalyst.

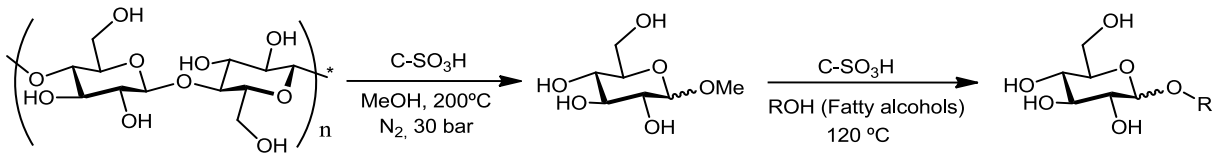
		Methanolysis Step					Transacetalization Step				
Entry	**Strategy**	**Time (h)**	**Cellulose Conversion (%)**	**α,β-MGP[(c)] Yield (%)**	**MCb[(c)] Yield (%)**	**ML[(c)] Yield (%)**	**Time (h)**	**α,β-MGP[(c)] Conversion (%)**	**α,β-OGP[(c)] Yield (%)**	**OCb[(c)] Yield (%)**	**OL[(c)] Yield (%)**
1	Two steps, 1st use[(a)]	12	97	72	3	17	4	88	59	2	13
2	Two steps, 2nd use[(a)]	24	83	58	3	19	4	83	51	3	13
3	Cycles, 1st use[(b)]	3x3	97	84	7	6	4	94	73	6	5
4	Cycles, 2nd use[(b)]	4x3	93	81	8	9	4	88	67	6	6

[(a)] Reaction conditions: 1st step, cellulose, 250 mg; methanol, 10 mL; C-SO_3H (1), 100 mg; 200 ^oC; N_2 (30 bar); 3h. 2nd step, n-octanol, 3000 mg; 120 ^oC; N_2 bubbling. [(b)] Reaction conditions: 1st step, cellulose, 250 mg; methanol, 10 mL; C-SO_3H (1), 100 mg; 200 ^oC; N_2 (30 bar). After 3 hours, the catalyst together with the unreacted cellulose are separated and taken to react again adding 10 mL of fresh methanol. This action is made 3 times. 2nd step: n-octanol, 3000 mg; 120 ^oC; N_2 bubbling. [(c)] α,β-MGP (methyl α,β-glucopyranoside), α,β-OGP (octyl α,β-glucopyranoside), MCb (methyl cellobioside), Ocb (octyl cellobioside), ML (methyl levulinate) and OL (octyl levulinate).

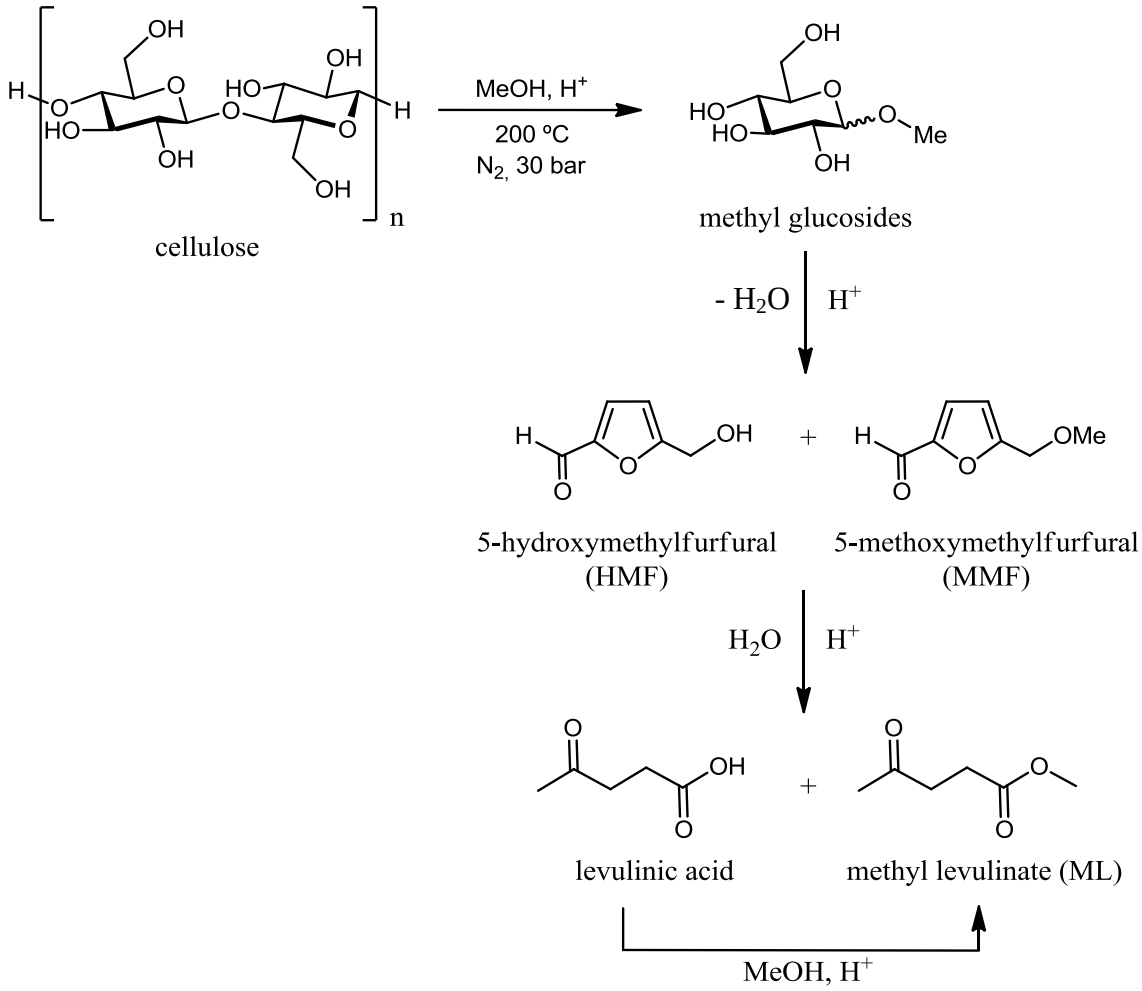
SCHEMES



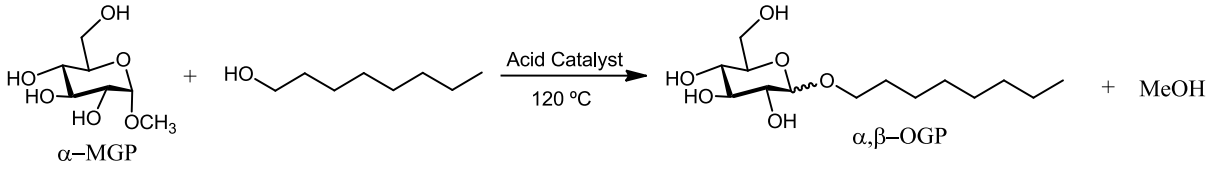
Scheme 1. Synthesis of long chain alkyl glucosides via Fischer glycosylation.



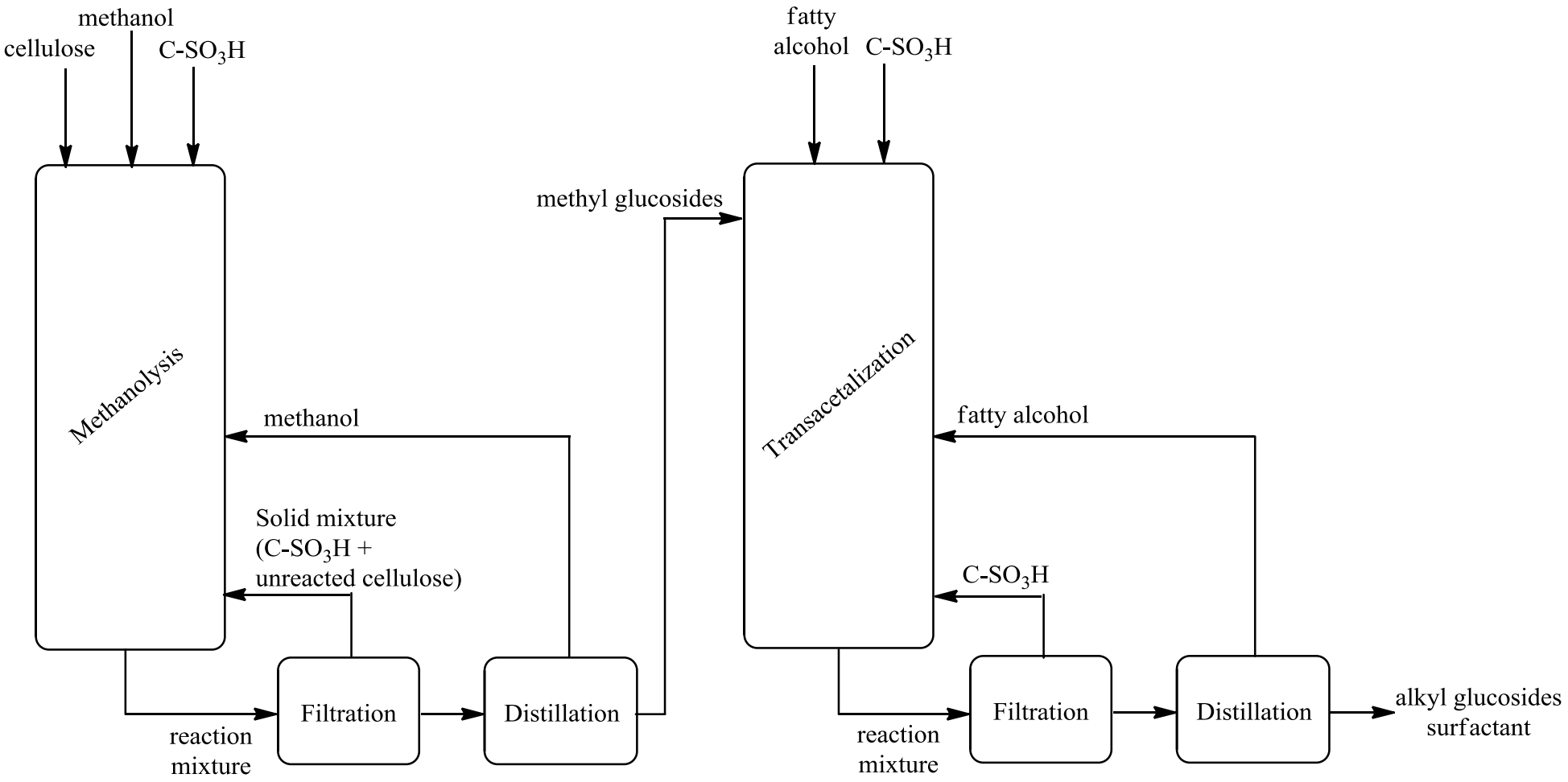
Scheme 2. Synthesis of long chain alkyl glucosides from cellulose via methanolysis of cellulose followed by transacetalization of the methyl glucosides obtained with a fatty alcohol.



Scheme 3. Reaction mecanism of the methanolysis of cellulose.



Scheme 4. Transacetalization reaction between methyl α-glucopyranoside and n-octanol.



Scheme 5. Diagram of the overall process conversion of cellulose into alkyl glucoside surfactants.

Supporting Information

Transformation of cellulose into non-ionic surfactants in a one pot catalytic process

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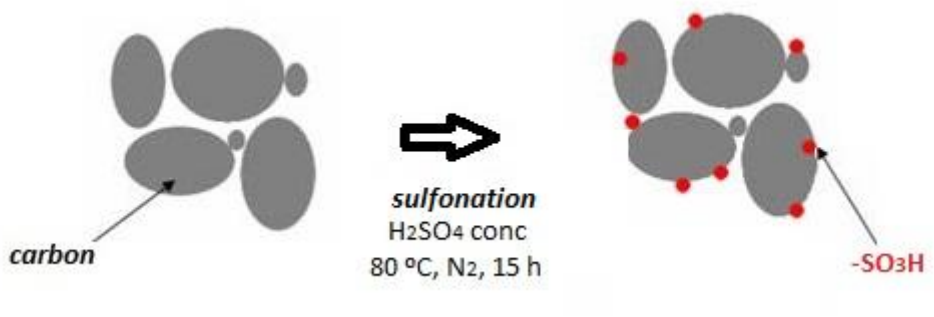


Figure S1. Scheme of preparation of C-SO_3H catalyst

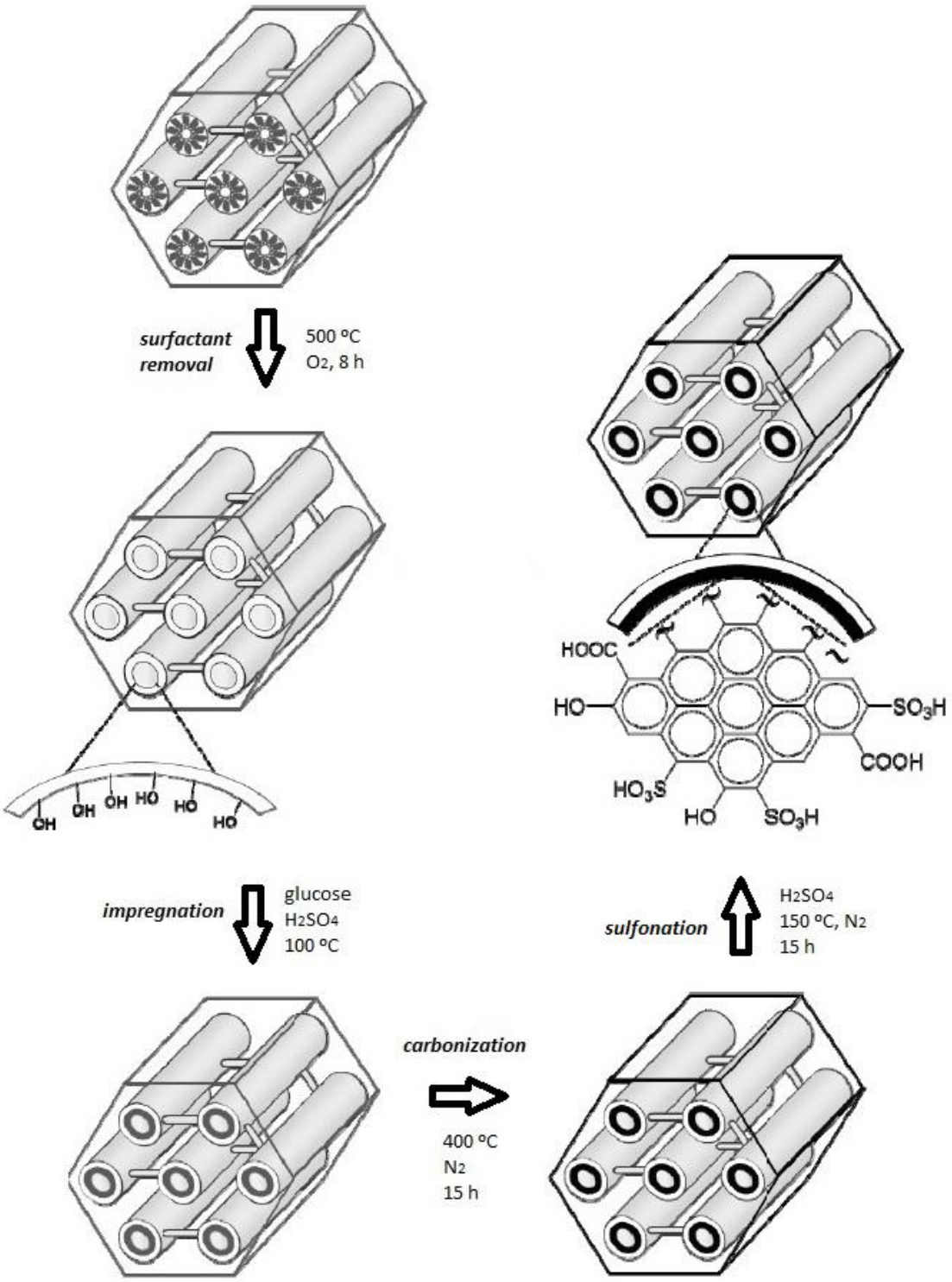


Figure S2. Scheme of preparation of MCM-41-C-SO_3H.

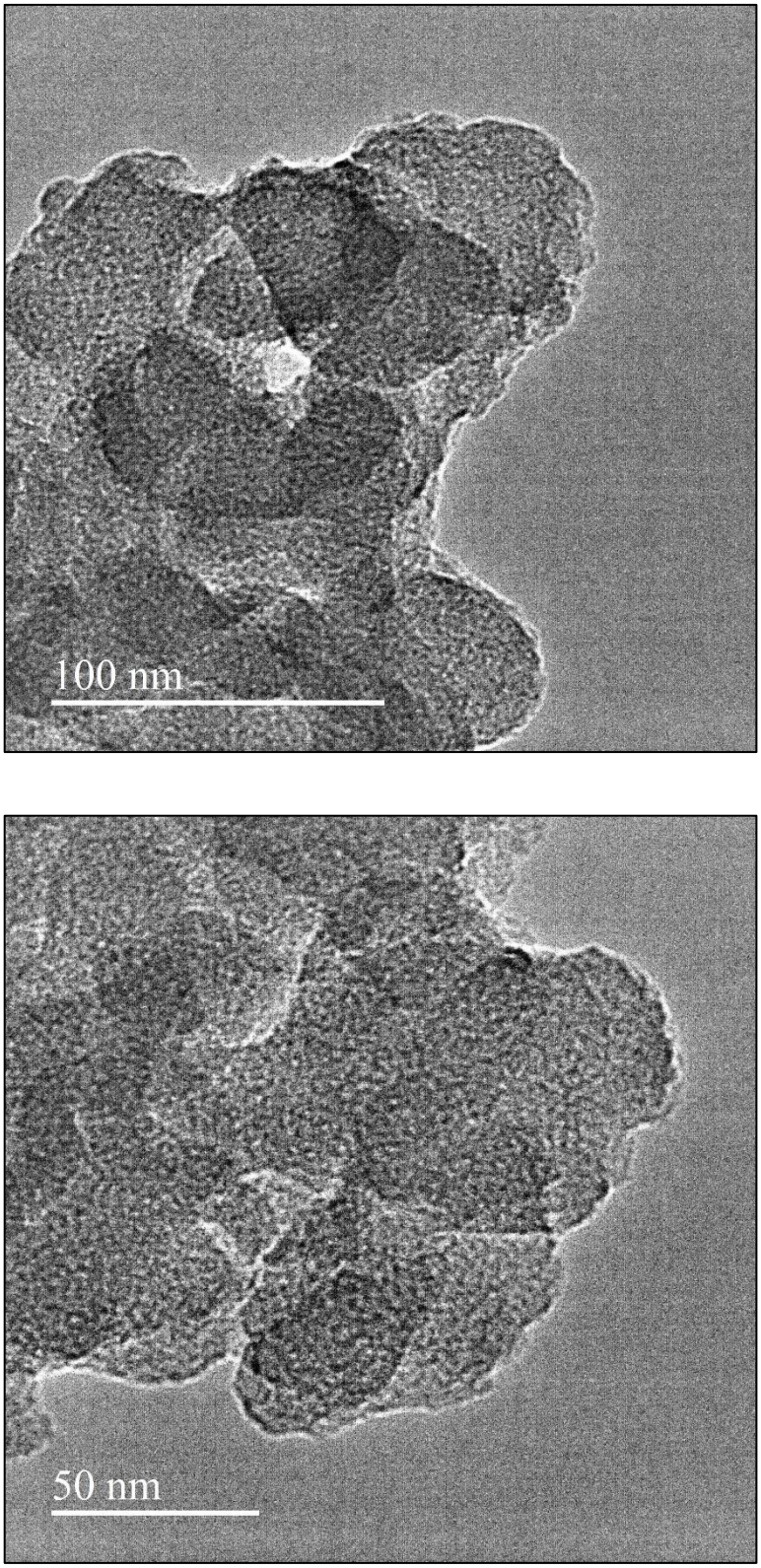


Figure S3. HR-TEM images of MCM-41-C-SO_3H.

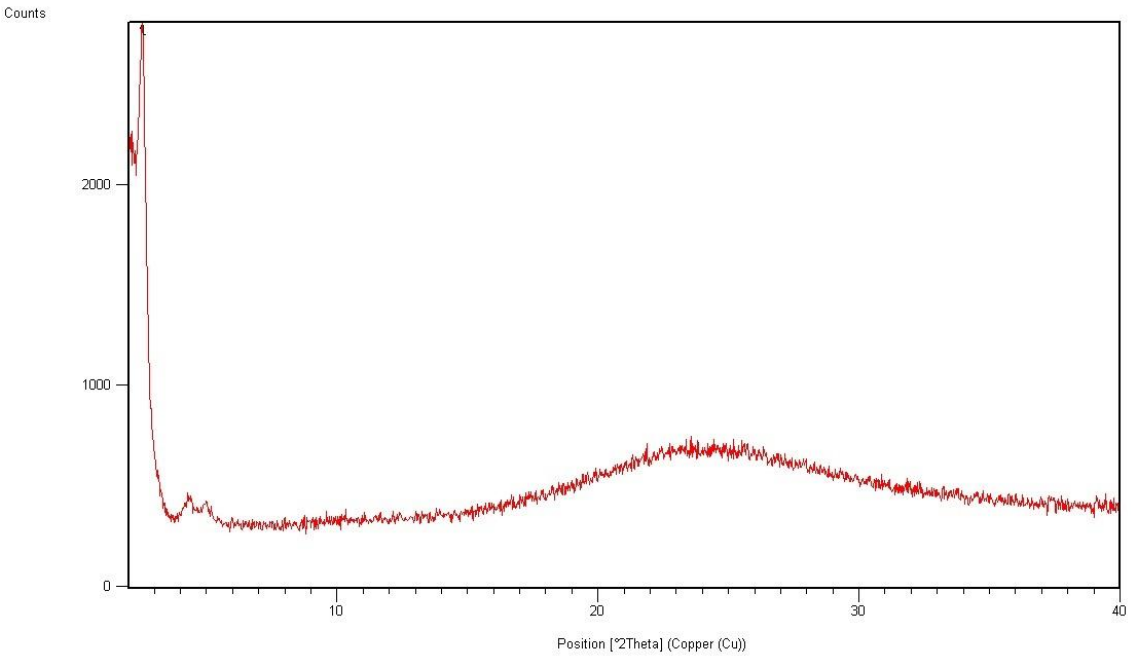


Figure S4. XRD spectra of MCM-41-C-SO_3H.

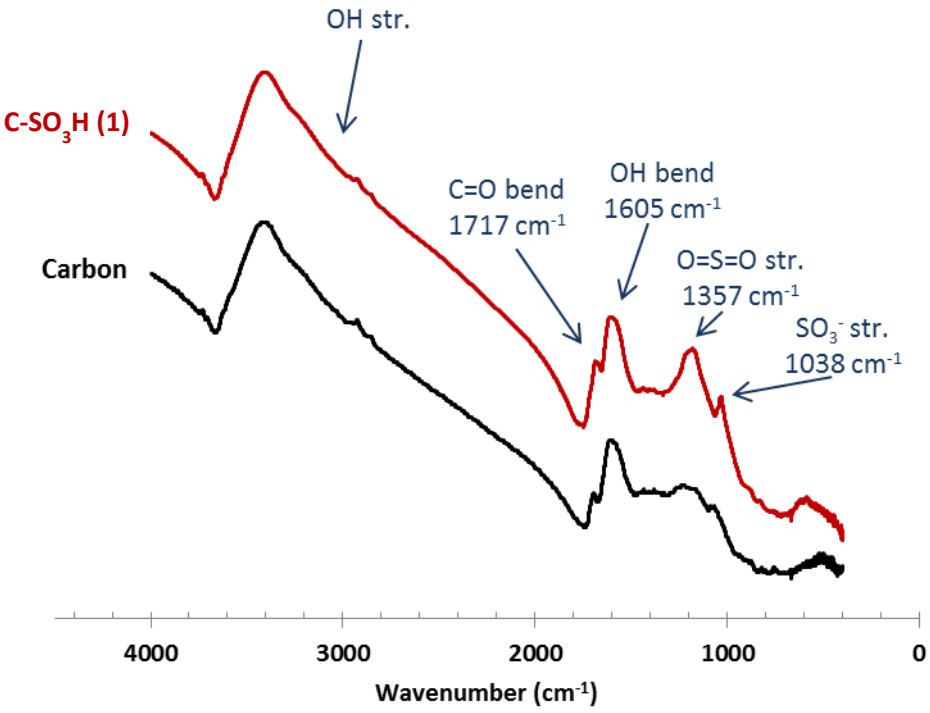


Figure S5. FTIR spectrum for the active carbon material before and after sulfonation treatment.

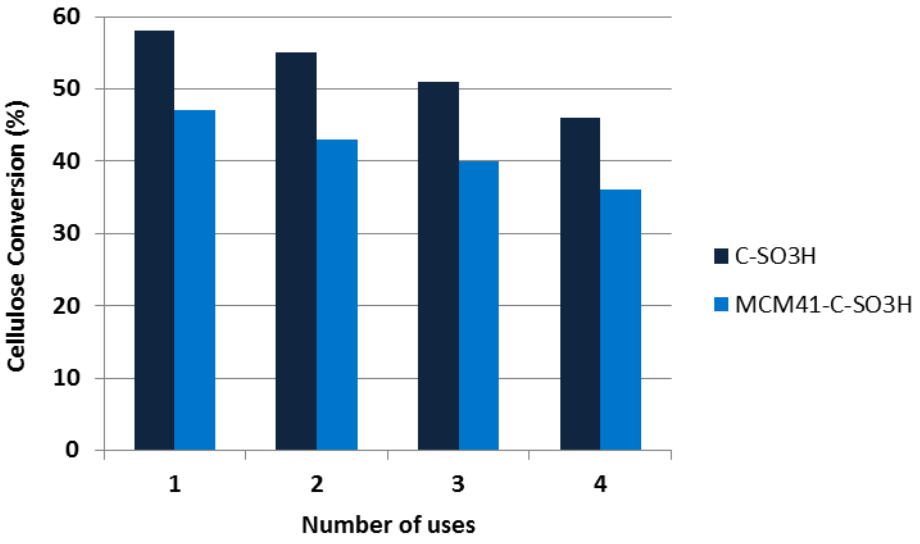


Figure S6. Stability of C-SO_3H (1) and MCM-41-C-SO_3H catalysts for the methanolysis step after successive uses. Reaction conditions: cellulose, 250 mg; methanol, 10 mL; catalyst, 100 mg; 200 ^{o}C; N_2 (30 bar); 3h.

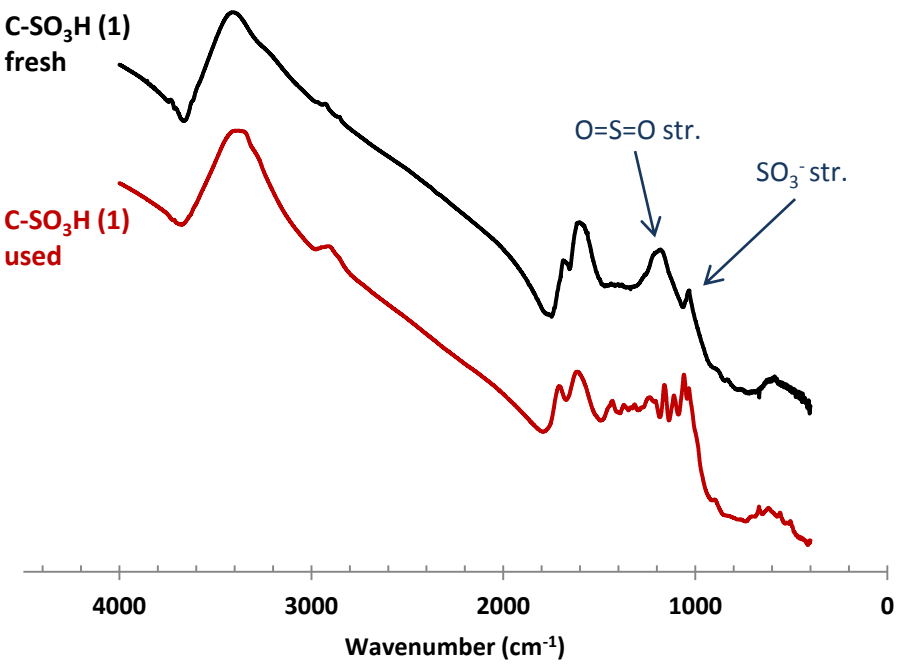


Figure S7. FTIR spectrum for fresh C-SO_3H (1) compared to the same catalyst after 4 cycles in the methanolysis step of cellulose.

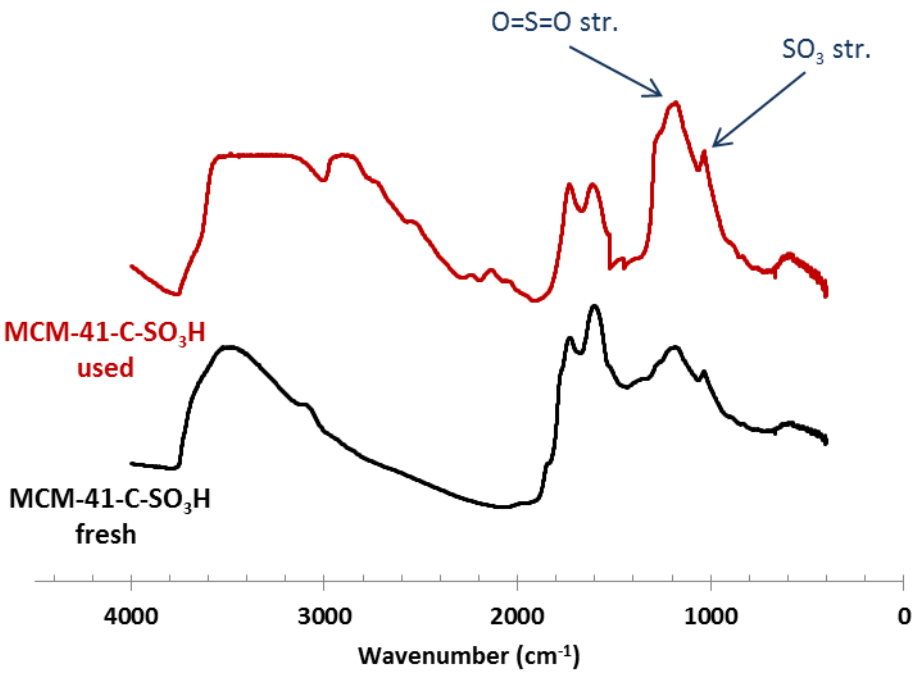
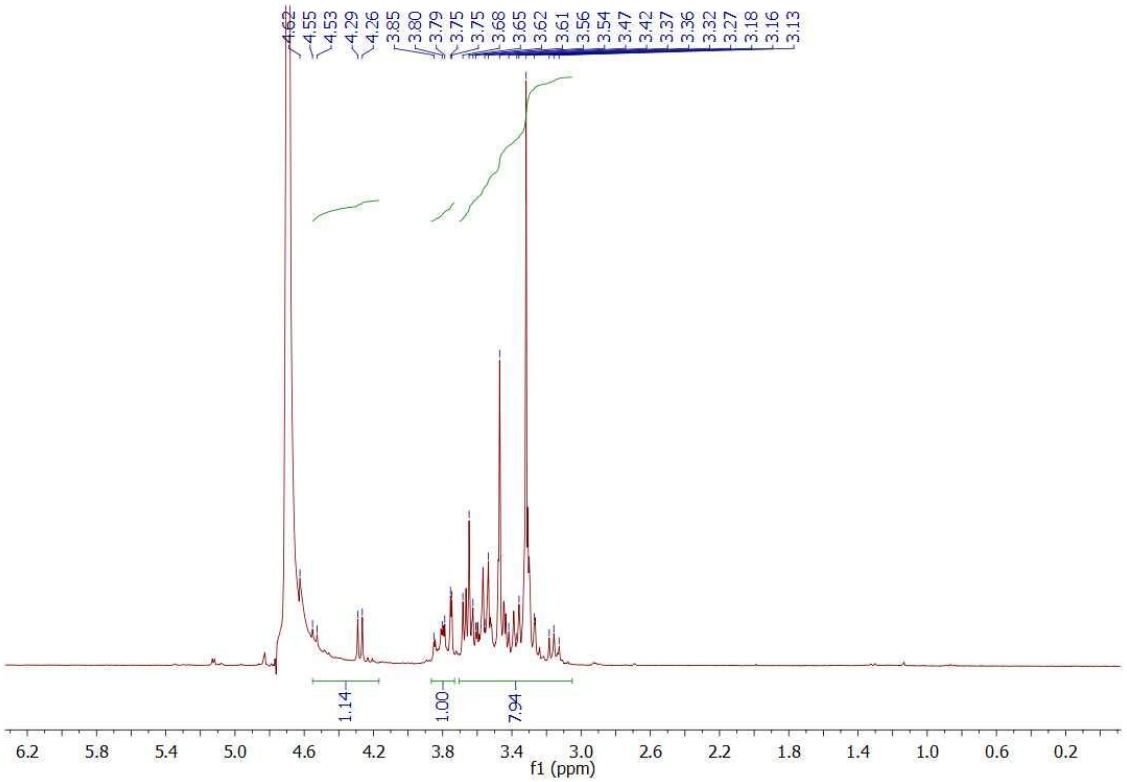


Figure S8. FTIR spectrum for fresh MCM-41-C-SO_3H compared to the same catalyst used 4 times in the methanolysis step of cellulose. Reaction conditions: cellulose, 250 mg; methanol, 10 mL; MCM-41-C-SO_3H catalyst, 100 mg; 200 ^{o}C; N_2 (30 bar); 3h. The successive uses of the catalyst were carried out at the same reaction conditions, reloading the cellulose converted into the solid mixture and adding others 10 mL of methanol.

NMR data of the alkyl glucosides

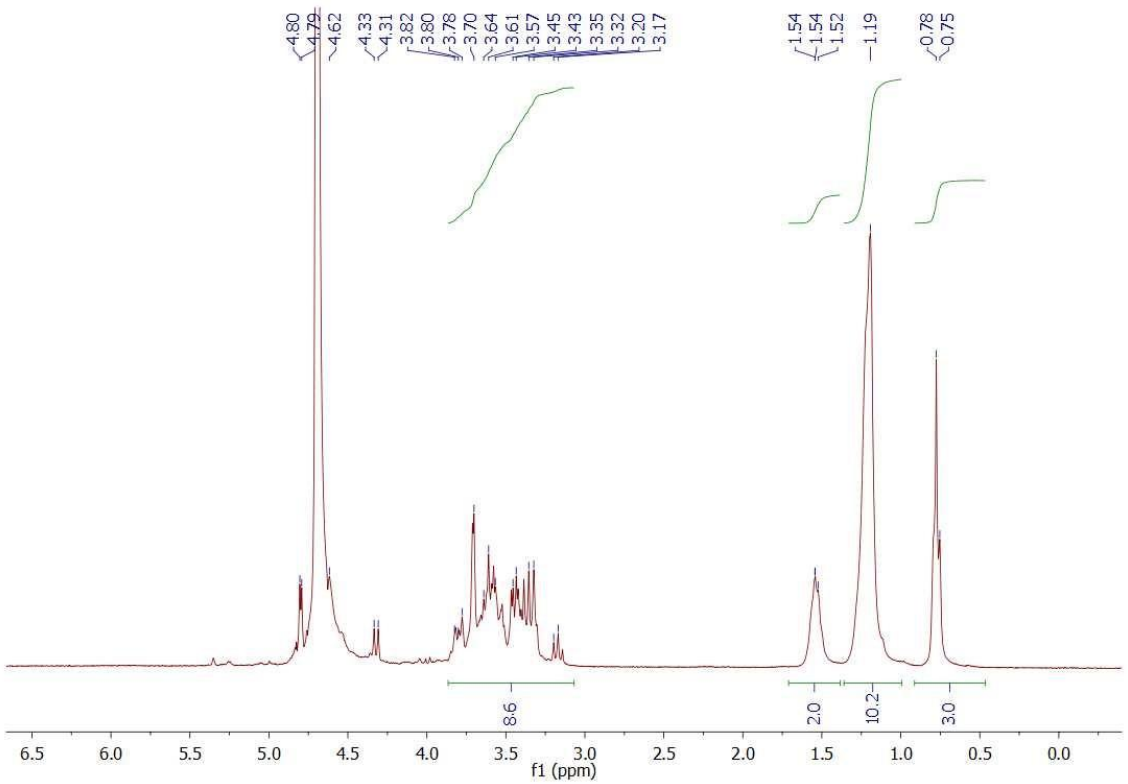
α,β-methylglucopyranoside

^{1}H NMR (300 MHz, D_2O), δ: 3.1-3.7 (m, 8H), 3.7-3.9 (m, 1H), 4.2-4.6 (dd, 1H) ppm.



α,β-octylglucopyranoside

^{1}H NMR (300 MHz, D_2O), δ: 0.6-0.8 (t, 3H), 1.2 (br s, 10H), 1.4-1.6 (t, 2H), 3.1-3.8 (m, 8H), 4.3-4.8 (dd, 1H) ppm.



α,β-decylglucopyranoside

^{1}H NMR (300 MHz, D_2O), δ: 0.8 (br s, 3H), 1.2 (br s, 14H), 1.5 (br s, 2H), 3.2-3.8 (m, 8H), 4.3-4.9 (m, 1H) ppm.