Screening of mono- and bi-functional catalysts for the one-pot conversion of cellobiose into sorbitol.

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Abstract

With the ultimate goal of producing robust catalysts for the one-pot conversion of cellulose to sorbitol, a number of solid acids were first investigated for the hydrolysis of cellobiose (model compound). In particular, acid functionalization, catalyst recyclability and hydrothermal stability were evaluated for SBA-15. In the second part of the work, the impregnation of Ru nanoparticles (RuNPs) on the Amberlyst 15 (A15) for the preparation of the bi-functional catalyst 3% RuNPs/A15 for the one-pot conversion of cellobiose into sorbitol is described. The performances of the bi-functional catalyst, 5% Ru/C and the physical mixture of the 5% Ru/C and A15 were evaluated for the conversion of cellobiose to sorbitol. When the bi-functional catalyst was employed, 81% yield of sorbitol was obtained after 5 h of reaction. In contrast, the best result with the physical mixture gave less than 53% yield of sorbitol after 5 h, indicating that the bi-functionality of the 3% RuNPs/Amberlyst 15 catalyst plays a major role in this reaction.

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1. Introduction

The uncertainty regarding the future supply of oil, the increasing energy demand per capita and the need for reducing the environmental impact of processes and products has been the driving force behind the development of a new industry based on renewables. In this present scenario, the efficient use of lignocellulosic biomass and its conversion in high value products has become one of biggest challenges for both the academia and industry [1].

In the past ten years, a lot of work has been done in optimizing conditions for hydrothermal hydrolysis of both cellulose and hemicellulose [2-4]. However, even with these optimized conditions a broad distribution of by-products is obtained. On the other hand, the hydrogenation of sugars is already a well-established industrial process, but the severe reaction conditions along with the possibility of producing sugar alcohols from different feedstocks undoubtedly offer room for improvement. In this context, the one-pot conversion of polysaccharides into sugar alcohols is a very interesting route as the sugar monomers (glucose and xylose) are hydrogenated to more stable products (e.g. sorbitol & xylitol), producing higher value products and minimizing the formation of by-products in the hydrolysis step [5, 6].

Most of the literature on the topic describes the one pot conversion of polysaccharides into sugar alcohols. The catalysts employed in these studies can be classified in two groups: metallic and bifunctional catalysts. Within the metallic group, the most used catalysts are the ruthenium based ones [5-9] due to their ability to promote both hydrogenolysis and hydrogenation. In these systems, the polysaccharide is believed to be broken into sugars by hydrolysis (catalyzed or not) and by hydrogenolysis catalyzed by the Ru catalysts. When aiming to produce sugar alcohols such as sorbitol and xylitol using metal catalysts one of the challenges is to avoid further hydrogenolysis of the products [10-14]. Bi-functional catalysts can provide both acid sites and metallic sites [15-20]. The acid sites promote the hydrolysis whereas the metallic sites mostly promote sugar hydrogenation. Such catalysts typically comprise a solid acid support decorated with metallic sites.

It is well known that in the coupled hydrolysis-hydrogenation of polysaccharides the hydrolysis is usually the rate determining step [5, 21, 22]. Therefore, the choice of the solid acid for the preparation of a bi-functional catalyst is very important. Ideally, the solid acid should not only be able to catalyze the hydrolysis of the substrate but also ought to be very stable under reaction conditions; otherwise, the leaching of the acid sites would result in a decrease of activity in the hydrolysis [10, 20, 23-26]. Furthermore, the leaching of the acid sites can increase the rate of the metal leaching which is further detrimental.

In the present work, a series of solid acids has been screened for cellobiose hydrolysis. The performance of these materials was evaluated in terms of glucose yield, catalyst stability and recyclability. In the second part of the work, A15 is impregnated with pre-formed ruthenium nanoparticles, to form the bi-functional catalyst: 3% RuNPs/A15. After that, the performances of this bi-functional catalyst, a catalyst 5% Ru/C and the physical mixture (5%Ru/C + A15) were compared for the one pot conversion of cellobiose to sorbitol, highlighting and discussing the superior results obtained with this bi-functional catalyst.

2 Experimental

2.1 Materials

Tetraethyl-orthosilicate (TEOS), 3-mercaptopropyltrimethoxysilane (3-MPTMS), cellobiose, 5-hydroxymethyl furfural (HMF), glucose, Amberlyst-15 (A15), D-(+)-cellobiose, ruthenium on carbon (5% Ru/C), ruthenium (III) chloride hydrate, acetone

(HPLC grade), ethylene glycol anhydrous and polyvinylpyrrolidone (PVP) 10,000 MW were purchased from Sigma Aldrich and used without further purification.

Analytical grade reagents hydrochloric acid (HCl 37% w/w), hydrogen peroxide (H_2O_2 30% w/w), sulfuric acid (H_2SO_4 96% w/w), phosphoric acid (H_3PO_4 85% w/w) were purchased and used without further purification.

2.2 Catalyst preparation

2.2.1 Bi-functional catalyst preparation

The 3% RuNPs/A15 catalyst was prepared according to the following procedure: PVP stabilized ruthenium nanoparticles were synthetized using a procedure adapted from the work of Yan et al. [27]. Typically, RuCl3·nH2O (0.0371 g, 1.5 x 10-4 mol) and PVP (MW = 10000, 0.1667 g, 1.5 x 10-3 mol) were dissolved in ethylene glycol (150 mL) giving a dark red solution. This solution was then heated to reflux (198 °C) with vigorous stirring. After 3 hours, a dark brown colloidal solution containing the RuNps was obtained. To the solution, 750 ml of acetone were added and left to stir for 12h. The RuNps were recovered by centrifugation and re-dispersed in water. Finally, RuNps were impregnated to A15 by wetness impregnation using a w/v (g/ml) ratio of 10.

2.2.2 SBA-15 synthesis

The protocol used in this study was adapted from Meynen *et al.* [28] , a solution of concentrated HCl 37% w/w (20 ml) and H_2O (130 ml) was prepared and 4 g of P123 were added and the solution was left to stir until complete dissolution of the templating agent. Subsequently, TEOS (9.14 ml) was added to the P123 acid solution and the mixture was left to stir for 7.5 h at 45°C. The formed mesoporous material was left aging for 15.5 h at 80°C under static conditions. At the end of the aging step, the mixture was cooled down to room temperature, and the white solid precipitate was filtered and washed 3 times with distilled water and dried at room temperature overnight. The templating agent was removed by calcination by treating the material at 550°C.

2.2.3 Sulfonic acid functionalized SBA-15 via post surface grafting

SBA-15 was then functionalized with propyl-sulfonic acid groups following the protocol reported by Siril et al [29]. SBA-15-SO_3H catalysts was prepared with S/Si ratio of 0.30 (SBA-15-S-0.3). Typically, SBA-15 (1.5 g) was suspended in toluene (15 mL) and refluxed for one hour at 115 °C under stirring. Subsequently, the appropriate amount of 3-MPTMS was added to the suspended solid and the mixture was kept at 115 °C for 24 hours under stirring. The mixture was then left to cool down to room temperature and the recovered solid was filtered, washed 3 times with distilled water and dried overnight at room temperature. The dry solid was then suspended in 30% w/w H_2O_2 solution and left under stirring for 1 hour in a closed vessel. The recovered solid was then filtered, washed with water and left to dry overnight at room temperature. Finally, SBA-15 acid treated with a 10% v/v H_2SO_4 solution for 1 hour under stirring, and then filtered, washed 3 times with distilled water and left to dry at room temperature overnight.

2.2.3 Phosphoric acid functionalized SBA-15 via post surface grafting

The phosphoric acid functionalized catalyst was synthesized according to the method reported by Wu et al. [30]. Typically, SBA-15 (1 g) was suspended in acetone (40 ml) and the appropriate amount of H_3PO_4 (85% w/w) was added. The suspended catalyst was stirred at room temperature for 6 hours. The solvent was removed with a rotary evaporator at 60 °C, and the recovered solid calcined at 500 °C (4 h^1). Subsequently, the material was left to cool down. The materials were denoted SBA-15-P-X where X states for the P/Si molar ratio values used for the preparation, namely: 0.15, 0.3, 0.6.

2.3 Characterization

TEM characterization was performed on the supported 3% RuNPs/A15 catalyst using a JEOL JEM 2100 LaB6 instrument at 200kV accelerating voltage. Catalysts were sonicated in methanol and supported on holey carbon film on copper grids (300 mesh) Particle size distributions were determined from 300 particles.

Powder X-ray diffraction patterns (PXRD) were recorded in transmission mode with a PANalytical X'Pert Pro HTS diffractometer with a slit of 0.04° from 0.5 to 70 º2θ using a Cu Kα radiation.

UV-Vis spectroscopy was used to monitor the synthesis of the PVP stabilized ruthenium nanoparticles using the Thermo Scientific evolution 260 spectrophotometer. The Brønsted-acidity of the catalysts was determined by titration method described elsewhere [31] using the Mettler Toledo G20 Compact Tritrator. The surface area and pore volume values of A15 and 3% RuNPs/A15 were measured by N_2 BET analysis on a Micromeritics ASAP 2420 and the samples were degassed overnight at 90°C prior to the analysis. The ICP-OES of reaction medium were performed using the instrument ICP-OES-SoP, Spectro Ciros CCD.

2.4 Catalytic Testing

In the screening of the solid acids for hydrolysis of cellobiose the reactions were carried out in a 5000 multiple Parr reactor system which consists of 6 vessels of 75ml. 30 ml of a 30 mmol cellobiose solution with 25 mg of catalyst were introduced in the vessel. The reactor was heated up to 150 ºC with a stirring of 700 rpm for two hours under autogenous pressure.

The one-pot conversion of cellobiose into sorbitol experiments were carried out in a 50 mL Parr reactor. The reaction mixture was added to the vessel then the reactor was flushed three times with nitrogen before being heated up to the desired temperature. When the correct temperature was reached hydrogen gas was charged into the reactor to a pressure of 40 bar under stirring of 800 rpm (t=0 h).

25 mL of 30 mmol L^{-1} cellobiose solution was used in all experiments. For the physical mixture, 50 and 83 mg of 5% Ru/C and A15 catalysts were used respectively. In the case of 5% Ru/C, the amount of catalyst used in the experiment is 50 mg. In the case of the bi-functional catalyst (RuNPs/A-15) the amount used was 83 mg. Therefore, the total metal content on a weight basis is constant. The experiments were performed in triplicates and the largest deviation within the yield values was less than 5%. The reaction products were analyzed by HPLC coupled with a diode array detector (DAD), a refractive index detector (RID) and an Aminex-HPX-87H column using a 25 mmol L^{-1} H_2SO_4 solution. Relative standard deviation on calibration curves was found to be less than 1% across all concentration range.

3 Results and Discussion

3.1 Characterization

3.1.1 Acidity of the solid acids

The Brønsted acidity of the materials were characterized by titration method, the results are displayed in Table 1. In the case of SBA-15-P-X, the measured acidity values are close to the theoretical ones with exception of the SBA-15-P-0.6, where the acid functionalization value is 42% lower than the theoretical one. As expected, in the case of the SBA-15-S-0.3, the Brønsted acidity value was much lower than the theoretical one because in that case the synthesis relies on two low efficiency steps: silane grafting, and subsequent oxidation of the immobilized mercaptopropyl for generating the acid sites. The acidity of the bifunctional catalyst, 3% RuNPs/A15, is 4.63 meq/g, which represents 96.4% of the acidity of A15. Therefore, considering that the catalyst has 3% in mass of ruthenium there was no significant effect on the acidity of the support after the impregnation procedure.

Table 1

Table 1 Brønsted Acidity values obtained for the acid functionalized catalysts with the titration method reported by Onda et al. [31]

3.1.2 UV–Vis spectroscopy

The synthesis of the PVP stabilized ruthenium nanoparticles was monitored with UV-vis spectroscopy to assure complete reduction of the precursor. A number of colour changes were observed, first from dark red to yellow, then to dark green and finally to dark brown; a sample was taken at each color change for analysis by UV-vis spectroscopy. After a total reaction time of 3 hours, a dark brown homogeneous colloidal dispersion was obtained. Figure 1 shows the UV-Vis spectra obtained during the synthesis. At the beginning, a characteristic peak at 351 nm may be observed, confirming the presence of Ru^{3+}, which gradually disappears as the synthesis proceeds, indicating the complete reduction of the precursor.

Figure 1

Fig.1 UV-Vis spectra of the RuNps colloidal solution during synthesis taken at increasing time until full reduction.

3.1.3 XRD

The XRD pattern (Figure 2) of the bi-functional catalyst 3% RuNPs/A15 shows a diffuse peak at $2\theta = 42.2^{o}$ assigned to Ru (002) reflection. The low intensity of the peak is due to the small crystallite size of the ruthenium nanoparticles.

Figure 2

Fig. 2 XRD pattern of 3% RuNPs/A15.

3.1.4 TEM

The TEM (Figure 3) of the bi-functional catalyst 3% RuNPs/A15 shows that supported ruthenium nanoparticles have a mean particle size of 4.25 nm with a standard deviation (SD) of 1.08 nm. Furthermore, lattice measurements of the RuNPs/A15 provided in Figure S.1 of the supplementary material do not match ruthenium oxide or ruthenium chloride, indicating that the nanoparticles consist mainly of Ru^0, which, notwithstanding, can be oxidized forming ruthenium oxide. Nevertheless, it is worth highlighting that the oxide layer can be readily reduced under the tested reaction conditions.

Figure 3

Fig. 3 Transmission electron microscopy for the 3% RuNPs/A15 catalyst: (a) micrograph showing nanometer-size Ru particles distributed on the support; (b) particle size distribution histogram for 300 particles.

3.1.5 Textural analysis

The textural analysis of both the bifunctional catalyst and A15 are presented in Table S.1. We could observe that there were no significant changes in the total surface area after impregnation procedure. The differences in the total surface area by BET are less 6%, being this discrete increase in the specific surface area within the experimental error.

3.2 Catalysts screening

Figure 4 shows the results for the screening of different acid catalysts in the hydrolysis of cellobiose into glucose carried out at 150 °C for 2 hours.

Figure 4

Fig 4. Glucose yield and selectivity (%)

The phosphoric acid functionalized SBA-15 materials appear to be the most active catalysts if compared with Amberlyst 15. By varying the nominal P/Si molar-ratio from 0.15 to 0.6, the catalytic activity of SBA-15-P-X increases and even the catalyst with a lower P/Si molar ratio is more active than the sulfonic acid functionalized SBA-15 which shows the worst performance. However, it is worth highlighting that this result was expected since the SBA-15-P-X materials exhibit a much higher concentration of Brønsted acid sites than both A15 and SBA-15-S-0.15.

A blank test shows that less than 10% of cellobiose is converted into glucose when no catalyst and untreated SBA-15 are used.

3.3 Recycling

SBA-15-P-0.6 was the most active catalyst in the hydrolysis of cellobiose to glucose, so we decided to carry out recycling and leaching tests to compare with the commercial Amberlyst 15. In a typical recycling experiment, the catalyst is recovered by filtration after reaction and then washed thoroughly with water, dried in air and tested again with fresh reactants. Recycling tests are shown in figure 5.

Figure 5

Fig 5. Recycling test: Comparison of glucose yield and cellobiose conversion for SBA-15-P-0.6 and A15.

Despite the SBA-15-P-0.6 high initial catalytic efficiency, after only one recycling run both the glucose yield and selectivity drop dramatically. The yield in the second run (6%) is comparable to the one observed in the one observed in the test with the non-functionalized SBA-15. This fact leads us to suspect that total leaching of the acid sites was taking place.

A15 also showed a loss of activity between the first and second run due to the leaching of acid sites previously reported [32]. On the other hand, the loss of activity in the others runs was very small proving that A15 is a better catalyst over multiple re-uses under these reaction conditions.

3.4 Leaching test

One of the main cause of grafted catalysts deactivation is the leaching of acid groups [24]. In order to confirm that the deactivation of SBA-15-P-0.6 was mainly due to the leaching of phosphoric groups and that the reaction is homogeneously catalyzed, one experiment was carried out with SBA-15-P-0.6 as follows: the catalyst was washed with water in a reactor simulating the reaction conditions and then recovered by centrifugation at 4000 rpm for 10 min.

After that, both the liquid and the solid phase were separated and then used in two different reactors for cellobiose hydrolysis. The same experiment was carried out with SBA-15-S-0.3 as well to confirm that the leaching occurs also for sulfonated SBA-15 at these conditions. The results of both experiments are shown in Table 2.

Table 2

Table 2. Conversion of cellobiose and glucose yield.

After washing, both solid catalysts converted only 14% and 16 % of cellobiose whereas the liquid phase gave 94% and 41 % conversion of cellobiose and 88 and 37 % yield of glucose for SBA-15-P-0.6 and SBA-15-S-0.3 respectively. These results confirm that the phosphoric and sulfonic groups have been leached almost completely to the liquid phase during the pre-treatment of the catalysts, causing a permanent loss of catalytic activity. Also, data indicate that the reaction is homogeneously catalyzed by either the phosphoric acid or the sulfuric acid promptly formed in solution.

Therefore, due to the lack of stability of SBA-15-P-0.6 and SBA-15-S-0.3 one decided to move back to the more stable A15 as catalyst of choice for the one-pot conversion of cellobiose into sorbitol.

3.5 One-pot conversion of cellobiose to sorbitol

For the one-pot reaction, pre-formed RuNps were supported on A15 and used as a bi-functional catalyst containing both acid and metallic sites. The performance of this bi-functional catalyst was then compared with the performance of the commercial hydrogenating catalyst 5%Ru/C and the physical mixture of 5% Ru/C and A15. Figure 6 shows that the behavior of the reaction is completely different depending on the catalytic system employed. This is mainly due to the different possible reaction pathways displayed in the figure 7, so different catalytic systems favor different pathways.

For instance, when 5% Ru/C is used, cellobiose is selectively converted to its hydrogenated form cellobiitol. In the first hour of reaction the yield of cellobiitol achieves 94%. A small amount of sorbitol (<5%) is also formed. This implies that the hydrogenation activity of the catalyst is far superior to its ability to promote the hydrolysis of the dimers. The yield of cellobiitol gradually drops from 94 to 72 % with increasing time on line as further hydrogenolysis products are formed (others). On the other hand, a physical mixture of 5%Ru/C and Amberlyst15 yields sorbitol preferentially. The sorbitol yield rises reaching a maximum of 53% at 3h, but for longer reaction times the yield slowly drops due to the conversion of sorbitol into degradation products, as reported previously by other authors [10-14]. Finally, in the test with the bi-functional catalyst consisting of 3% Ru nanoparticles impregnated in Amberlyst15 cellobiose is fully converted after 4h. Furthermore, the yield of sorbitol steadily increases until it reaches 81.6% after 5 hours. Moreover, in order to assess the reproducibility of the bi-functional catalyst preparation a second batch was prepared and tested under same conditions. After 5 hours of reaction we obtained the 76.9% yield in sorbitol and a very similar product distribution. This result is presented in the Supplementary Material in Figure S.2.

The results obtained with the bi-functional catalyst are in accordance with the observations of W. Zhu et al. [17] that sorbitol selectivity is determined by its stability under catalytic conditions. Moreover, it seems that the superior performance of the bi-functional catalyst resides in the fact that 3% RuNPs/A15 appears to be less active towards the hydrogenolysis of sorbitol, thus less degradation products are observed. ICP analysis of the reaction medium was performed and no ruthenium leaching was detected. However, we have indeed observed S leaching (~10%) which confirms that the A15 acid sites underwent leaching.

Figure 6

Fig 6. One pot hydrogenolysis of cellobiose into sorbitol: cellobiose conversion and product yield distribution for 3% RuNPs/A15, 5% Ru/C and the physical mixture of 5% Ru/C + A15.

Figure 7

Fig. 7 Global reaction scheme for the hydrogenation of cellobiose to sorbitol along with the undesired glucose dehydration side reaction with the production of HMF and the further hydrogenation of sorbitol to smaller sugar alcohols [17].

4 Outlook and Conclusions

We have evaluated the performance of different acid functionalized SBA-15 materials for the hydrolysis of cellobiose and concluded that all these materials suffer from severe leaching. This fact is often neglected in similar studies for the conversion of biomass employing acid functionalized silica-type material. The loss of these sites makes these materials not desirable for our target reaction, whereas we have shown that A15 is much more stable under the same conditions, thus being more adequate for the preparation of a bifunctional catalyst for the direct one-pot conversion of cellobiose to sorbitol. However, even A15 presents a significant deactivation due to leaching of sulfonic groups.

We have found that a bi-functional catalyst product of the impregnation of A15 with RuNPs (3% RuNps/A15) is a very active and selective catalyst for the one pot conversion of cellobiose into sorbitol, affording a yield of sorbitol higher than 80% in 5 h. This value is much higher than the 53% yield obtained when a physical mixture of the solid acid and the hydrogenation catalyst is used, indicating that the bifunctionality of the catalyst plays a major role in the one pot conversion of cellobiose into sorbitol.

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6 References

[1] E.F. Sousa-Aguiar, L.G. Appel, P.C. Zonetti, A.d.C. Fraga, A.A. Bicudo, I. Fonseca, Some important catalytic challenges in the bioethanol integrated biorefinery, Catal Today, 234 (2014) 13-23.
[2] Y.-B. Huang, Y. Fu, Hydrolysis of cellulose to glucose by solid acid catalysts, Green Chem, 15 (2013) 1095.
[3] L. Hu, L. Lin, Z. Wu, S. Zhou, S. Liu, Chemocatalytic hydrolysis of cellulose into glucose over solid acid catalysts, Appl Catal B-Environ, 174-175 (2015) 225-243.
[4] F. Chambon, F. Rataboul, C. Pinel, A. Cabiac, E. Guillon, N. Essayem, Cellulose hydrothermal conversion promoted by heterogeneous Brønsted and Lewis acids: Remarkable efficiency of solid Lewis acids to produce lactic acid, Appl Catal B-Environ, 105 (2011) 171-181.
[5] J. Li, H.S.M.P. Soares, J.A. Moulijn, M. Makkee, Simultaneous hydrolysis and hydrogenation of cellobiose to sorbitol in molten salt hydrate media, Catal Sci Technol, 3 (2013) 1565.
[6] J. Hilgert, N. Meine, R. Rinaldi, F. Schüth, Mechanocatalytic depolymerization of cellulose combined with hydrogenolysis as a highly efficient pathway to sugar alcohols, Energy Environ. Sci., 6 (2013) 92-96.
[7] D.Y. Murzin, E.V. Murzina, A. Tokarev, N.D. Shcherban, J. Wärnå, T. Salmi, Arabinogalactan hydrolysis and hydrolytic hydrogenation using functionalized carbon materials, Catal Today, 257 (2015) 169-176.
[8] L. S. Ribeiro, J.J.M. Órfão, M.F. R. Pereira, Enhanced direct production of sorbitol by cellulose ball-milling, Green Chem., 17 (2015) 2973-2980.
[9] L. Negahdar, P.J.C. Hausoul, S. Palkovits, R. Palkovits, Direct cleavage of sorbitol from oligosaccharides via a sequential hydrogenation-hydrolysis pathway, Appl Catal B-Environ, 166-167 (2015) 460-464.

[10] P.A. Lazaridis, S. Karakoulia, A. Delimitis, S.M. Coman, V.I. Parvulescu, K.S. Triantafyllidis, d-Glucose hydrogenation/hydrogenolysis reactions on noble metal (Ru, Pt)/activated carbon supported catalysts, Catal Today, 257 (2015) 281-290.
[11] I.M. Leo, M.L. Granados, J.L.G. Fierro, R. Mariscal, Sorbitol hydrogenolysis to glycols by supported ruthenium catalysts, Chinese J Catal, 35 (2014) 614-621.
[12] H. Wang, Y. Guo, D. Zheng, J. Han, Direct incorporation of tungsten into ordered mesoporous alumina and enhanced selectivity for converting cellulose to ethylene glycol, J Porous Mat, 22 (2015) 919-925.
[13] P.J. Hausoul, L. Negahdar, K. Schute, R. Palkovits, Unravelling the Ru-Catalyzed Hydrogenolysis of Biomass-Based Polyols under Neutral and Acidic Conditions, ChemSusChem, 8 (2015) 3323-3330.
[14] Y. Jia, H. Liu, Selective hydrogenolysis of sorbitol to ethylene glycol and propylene glycol on ZrO2-supported bimetallic Pd-Cu catalysts, Chinese J Catal, 36 (2015) 1552-1559.
[15] Y. Li, Y. Liao, X. Cao, T. Wang, L. Ma, J. Long, Q. Liu, Y. Xua, Advances in hexitol and ethylene glycol production by one-pot hydrolytic hydrogenation and hydrogenolysis of cellulose, Biomass Bioenerg, 74 (2015) 148-161.
[16] M. Liu, W. Deng, Q. Zhang, Y. Wang, Y. Wang, Polyoxometalate-supported ruthenium nanoparticles as bifunctional heterogeneous catalysts for the conversions of cellobiose and cellulose into sorbitol under mild conditions, Chem Comm, 47 (2011) 9717-9719.
[17] W. Zhu, H. Yang, J. Chen, C. Chen, L. Guo, H. Gan, X. Zhao, Z. Hou, Efficient hydrogenolysis of cellulose into sorbitol catalyzed by a bifunctional catalyst, Green Chem, 16 (2014) 1534.
[18] H. Wang, J. Lv, X. Zhu, X. Liu, J. Han, Q. Ge, Efficient Hydrolytic Hydrogenation of Cellulose on Mesoporous HZSM-5 Supported Ru Catalysts, Top Catal, 58 (2015) 623-632.
[19] A.P. Tathod, P.L. Dhepe, Efficient method for the conversion of agricultural waste into sugar alcohols over supported bimetallic catalysts, Bioressource Technol, 178 (2015) 36-44.
[20] A. Negoi, K. Triantafyllidis, V.I. Parvulescu, S.M. Coman, The hydrolytic hydrogenation of cellulose to sorbitol over M (Ru, Ir, Pd, Rh)-BEA-zeolite catalysts, Catal Today, 223 (2014) 122-128.
[21] H. Kobayashi, Y. Ito, T. Komanoya, Y. Hosaka, P.L. Dhepe, K. Kasai, K. Hara, A. Fukuoka, Synthesis of sugar alcohols by hydrolytic hydrogenation of cellulose over supported metal catalysts, Green Chem., 13 (2011) 326-333.
[22] H. Kobayashi, A. Fukuoka, Chapter 2 - Current Catalytic Processes for Biomass Conversion, in: S.L. Suib (Ed.) New and Future Developments in Catalysis, Elsevier, Amsterdam, 2013, pp. 29-52.
[23] S.-Y. Chen, S. Lao-ubol, T. Mochizuki, Y. Abe, M. Toba, Y. Yoshimura, Transformation of non-edible vegetable oils into biodiesel fuels catalyzed by unconventional sulfonic acid-functionalized SBA-15, Appl Catal A-Gen, 485 (2014) 28-39.
[24] M. Karaki, A. Karout, J. Toufaily, F. Rataboul, N. Essayem, B. Lebeau, Synthesis and characterization of acidic ordered mesoporous organosilica SBA-15: Application to the hydrolysis of cellobiose and insight into the stability of the acidic functions, J Catal, 305 (2013) 204-216.
[25] A.C. Alba-Rubio, F. Vila, D.M. Alonso, M. Ojeda, R. Mariscal, M. López Granados, Deactivation of organosulfonic acid functionalized silica catalysts during biodiesel synthesis, Appl Catal B-Environ, 95 (2010) 279-287.

[26] D. Zuo, J. Lane, D. Culy, M. Schultz, A. Pullar, M. Waxman, Sulfonic acid functionalized mesoporous SBA-15 catalysts for biodiesel production, Appl Catal B-Environ, 129 (2013) 342-350.
[27] X. Yan, H. Liu, K.Y. Liew, Size control of polymer-stabilized ruthenium nanoparticles by polyol reduction, Journal of Materials Chemistry, 11 (2001) 3387-3391.
[28] V. Meynen, P. Cool, E.F. Vansant, Verified syntheses of mesoporous materials, Micropor Mesopor Mat, 125 (2009) 170-223.
[29] P.F. Siril, N.R. Shiju, D.R. Brown, K. Wilson, Optimising catalytic properties of supported sulfonic acid catalysts, Appl Catal A-Gen, 364 (2009) 95-100.
[30] B. Wu, Z. Tong, X. Yuan, Synthesis, characterization and catalytic application of mesoporous molecular sieves SBA-15 functionalized with phosphoric acid, J Porous Mat, 19 (2011) 641-647.
[32] P.F. Siril, H.E. Cross, D.R. Brown, New polystyrene sulfonic acid resin catalysts with enhanced acidic and catalytic properties, J. Mol. Catal. A - Chemical, 279 (2008) 63-68.