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THE ROLE OF SULFONATED ACTIVATED CARBONS AS CATALYSTS FOR THE HYDROLYSIS OF CELLOBIOSE

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Abstract - In this work the production of glucose via hydrolysis of cellobiose using sulfonated active carbons as catalysts was studied. Commercial carbons presenting different types of porous system (micropores and mesopores) have been treated with sulfuric acid at different temperatures, being characterized afterwards. Such carbons have been tested as catalysts in the reaction of cellobiose hydrolysis. The results indicated that the type and density of sulfonic sites are not the only parameters responsible for the activity of the catalysts. Indeed, the porosity of the catalysts also plays an important role in the determination of the catalyst activity.

Keywords: Hydrolysis; Sulfonated carbon; Cellobiose; Glucose.

INTRODUCTION

The uncertainty regarding the future supply of oil, along with the increasing energy demand per capita and the necessity of reducing the environmental impact of hazardous process effluents and products have been the driving force for the development of an innovative industry based on renewables. In this rather stringent scenario, the efficient deployment of biomass as well as the conversion thereof into high value products has become one of most important challenges for both the academia and industry (Sousa-Aguiar et al., 2014a).

Biomass is a rather encompassing concept. Nevertheless, it is well established that the so-called “second generation biomass” regards the biomass existing in residues originated from both the agribusiness and the agroindustry (Romano et al., 2016). Such biomass is essentially lignocellulosic; hence, in the past ten years, a lot of work has been done trying to optimize conditions for hydrothermal hydrolysis of both cellulose and hemicellulose. In fact, cellulose, along with hemicellulose and lignin, are the major components of lignocellulosic materials. Cellulose is a polymer containing monosaccharides as building blocks; therefore, the hydrolysis thereof will produce glucose monomers, which may undergo several chemical modifications.

Various papers have been published concerning the hydrolysis of cellulose using sulfuric acid as catalyst. Sulfuric acid, however, presents several drawbacks such as its corrosive characteristics, which require further neutralization, and the difficult separation of the products. Also, enzymes (cellulases) have been tried as biological catalysts (Carvalho et al., 2017). Nevertheless, high production costs of such enzymes, along with low conversions obtained in enzymatic processes, and the impossibility of recovering them, have brought about a growing loss of interest in enzymatic processes.

The search for solid acid catalysts has been growing steadily (Almeida et al., 2016). Among several potential solid acids, sulfonated activated carbons seem to be an excellent alternative (Sousa-Aguiar et al., 2014 b). Indeed, sulfonated activated carbons

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present high activity, high utilization capacity, as well as easy separation from the products, not to mention the fact that such carbons are sustainable, since they are obtained from biomass residues (Kobayashi et al., 2011).

The present article describes the use of sulfonated active carbons in the hydrolysis of cellobiose, which has been previously used as a model molecule to describe the behavior of cellulose under hydrolysis conditions (Zhou et al., 2011; Almeida et al*.,* 2016). The influence of two parameters is discussed. First, the influence of the porous system of the parent carbons on the conversion is determined. Second, a study of the sulfonating temperature of the different activated carbons was carried out, aiming at varying the amount of acid sites generated, thereby changing the activity of the catalysts. In fact, the main target of our paper is to study the concept of accessibility. Accessibility is an important concept in Catalysis which has been proposed not long ago. The first publications concerned FCC catalysts (Sousa-Aguiar et al., 1995a; Sousa-Aguiar et al., 1995b; Cavalcante Jr. et al., 2003). However, the concept has become more encompassing, being nowadays applied to several catalytic systems in which voluminous molecules undergo reaction.

EXPERIMENTAL

Carbon selection

The commercial samples of the carbons were provided by Indústrias Químicas Carbomafra. All carbons were of vegetal origin. Two carbons (C-141-S and C-147), were chosen as the parent materials. The choice of the parent carbons was based upon the different porosity thereof. Main characteristics of such carbons are depicted in Table 1. C-141-S is a microporous carbon, whereas C-147 is a mesoporous one, although they have similar total specific surfaces. The parent carbons were ground and sieved, thereby obtaining powders whose particle size varied from 0.150mm to 0.090mm.

Sulfonation step

Both parent carbons underwent sulfonation with 95-97% sulfuric acid, in three different temperatures (120, 160 and 200°C) being washed with deionized water afterwards. 10g of carbon were agitated with 100g of sulfuric acid for 6h. The material was then filtered and washed. All catalysts were treated in hot water before drying, aiming at eliminating unstable acidic groups. Immediately before use in reactions the catalysts were dried at 110ºC for 4h.

Cellobiose hydrolysis

Hydrolysis reactions were carried out using cellobiose as reactant (Vetec Química Fina, 98%) as well as deionized water. 10g of cellobiose were added to 100g of deionized water, being heated until complete dissolution of cellobiose. Then, 4.5g of catalyst were added and the suspension was kept under agitation for 24h at 110°C, aliquots being collected at different times and analyzed via an Agilent 1260 HPLC. Two different detectors have been used. The first one was a Refractive Index Detector (RID), which was employed to determine carbohydrates. The other one was a Diode Array Detector, used to detect degradation products such as HMF.

The pH of the cellobiose solution after reaction was measured and no appreciable change was detected in such pH, as a clear indication that the pre-treatment with hot water was able to eliminate unstable acidic groups.

Characterization

The following characterization was performed:

a) Ash content – Carbons were calcined at temperatures around 600 ºC for 4 hours. The remaining material was considered the ash content;

b) pH measurement – 0.5g of the carbon was placed in a flask with 5g of deionized water (10g/1g). The flask was closed and, after 24h, pH was measured using a Hanna Instruments HI 253; The surface pH represents the sum of the contributions of several groups; however, it must be borne in mind that the method determines groups that undergo considerable ionization in the presence of water (strong and medium acid and base sites). Weak sites might not represent a significant contribution to the pH value determination.

c) Determination of acid groups – 0.04g of carbon was mixed with 20ml of a 0.01M solution of NaOH, being stirred for 4h. Then, an aliquot was titrated with HCl 0,01M, using phenolphthalein as indicator; the titration method employs a traditional titration using a strong base (NaOH). Hence, all acidic sites are measured, or rather, both weak and strong acidic groups are determined.

d) Nitrogen adsorption – adsorption was carried out in aa ASAP 2400 (Micromeritics) using the t-plot method to determine microporosity;

e) Elemental analysis - ThermoFinnigan FLASH EA1112 was employed to determine CHNSO elements, X-ray fluorescence (PANAlytical MagiX PRO) also being used;

f) Crystallinity – a Rigaku Miniflex II equipment was used to determine crystallinities;

g) Thermogravimetric analysis - ASTM E1131 method was employed.

Conversion

Conversions were calculated using the following equation:

$$X_{CB} = 100\frac{\left(C_{CBi} - C_{CBf}\right)}{C_{CBi}} \qquad (1)$$

where C_{CBi} and C_{CBf} are the initial and final concentrations of cellobiose.

RESULTS AND DISCUSSION

Main characteristics of the parent carbons

Samples (C-141-S and C-147) were analyzed using X-ray diffraction. Both samples were amorphous, showing no diffraction peaks. Furthermore, chemical analysis revealed that the ash content was very similar for both carbons, C-141-S having 2.11wt% ash content, whereas for C-147 the content was 3.23wt%. Regarding the surface pH of the samples, however, completely different values were determined. C-141-S has a very basic surface (pH=10.62), whereas C-147 was mildly acidic (pH=5.67). Nevertheless, after acid treatment with sulfuric acid, the surface pH became acid for all samples, as will be discussed later. Thermogravimetric analysis showed that both carbons were stable up to 500°C in inert atmosphere.

Both carbons had acid groups on the surface, C-147 having 0.60 mmol/g and C-141-S 0.49 mmol/g. Since no sulfur was introduced in the samples, such acid sites are probably due to the existence of OH and COOH on the carbon surface.

Porosity

As depicted in Table 1, the two carbons employed in this study had different characteristics in terms of porous system. Indeed, C-141-S is a typical microporous carbon (high micropore volume), whereas C-147 presents mesopores.

Figure 1 shows the nitrogen adsorption isotherms. As expected, C-141-S presents a type I isotherm, that is to say, it is a typical microporous material. On the other hand, C-147 displays a Type IV isotherm, with a hysteresis loop, confirming the existence of mesopores.

The process of sulfonation brings about textural modifications in the carbons. An increase in the external surface area was observed for the microporous carbon when a lower temperature of sulfonation was employed (Table 2); however, as the sulfonation temperature increases, a steep drop in microporosity is observed. Moreover, as far as the microporous sample is concerned (C-141-S), the sulfonation step clearly generates mesoporosity. In fact, as depicted in Figure 2, all isotherms are Type IV after treatment with sulfuric acid. Regarding the isotherms presented for the sulfonated carbons, it can be noted that although both are type IV the hysteresis type differs. For sulfonated carbon C-147, hysteresis type H3 was observed, characteristic of slit-shaped pores in plate-like structures. The hysteresis observed for carbon C-141-S sulfonated were type H4, related to narrow slit-shaped pores (Sing, 1985).

Table 1. Porous system of C-147 and C-141-S.

Sample	BET Surface (m²/g)	t-plot micropore area (cm²/g)	Total pore volume (cm³/g)
C-147	670	365	0.56
C-141-S	780	684	0.30

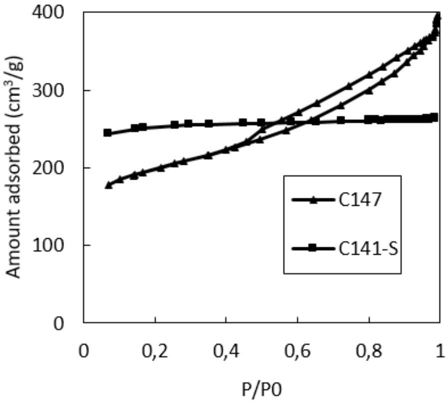

Figure 1. Nitrogen adsorption isotherms for parent carbons C-141-S and C-147.

Table 2. Nitrogen adsorption isotherms for sulfonated carbons.

Sample	Temperature of sulfonation (ºC)	Specific surface (m²/g)	Micropore area (m²/g)	Average pore size (Å)
C-141-S	120	846	724	19.9
C-141-S	160	628	526	20.2
C-141-S	200	562	465	20.4
C-147	120	363	157	35.6
C-147	160	551	293	32.6
C-147	200	559	297	32.3

The analysis of the ash content after treatment with sulfuric acid revealed that the ash content drops with sulfonation (Table 3). Sulfuric acid is probably dissolving inorganic compounds which give rise to ashes. The removal of such inorganic compounds may be responsible for the generation of mesopores, since sample C-141-S, which clearly presented a microporous texture, became mesoporous after acid treatment. This fact is corroborated by the decrease in both the total surface area and the micropore area. It must be borne in mind, however, that for samples already exhibiting mesoporosity, the removal of inorganic compounds does not affect the porous system. An influence of temperature was also observed, the ash contents decreasing as sulfonation temperature increases. At higher temperatures, as previously reported (Zhu et al., 2015), sulfuric acid leaching of inorganic compounds is more effective.

Notwithstanding, as far as textural properties are concerned, the mesoporous carbon (C-147) presents

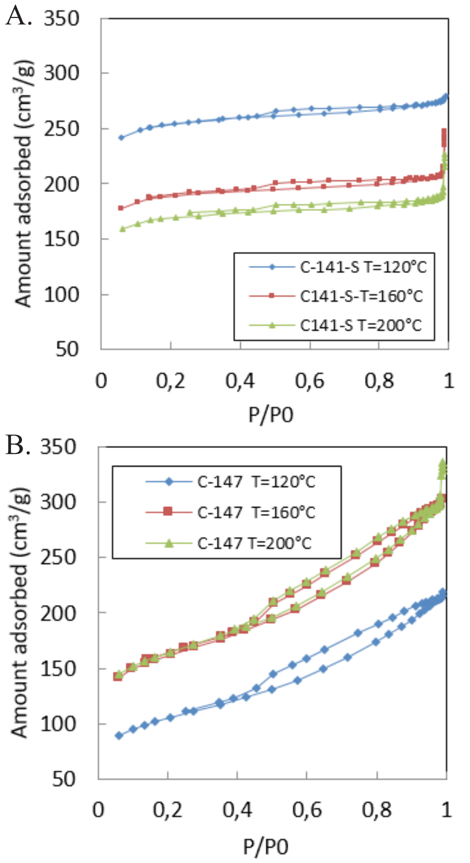

Figure 2. Nitrogen adsorption isotherms for different sulfonated carbons.

Table 3. Ash content of sulfonated carbons.

Sample	Sulfonation temperature (ºC)	Ash content (wt%)
C-141-S untreated	-	2.11
C-141-S	120	1.82
C-141-S	160	0.69
C-141-S	200	1.52
C-147 untreated	-	3.23
C-147	120	2.68
C-147	160	2.42
C-147	200	2.02

a completely different behavior. Micropore area increases as temperature of sulfonation increases, although such influence is rather small for higher temperatures.

Sulfonation and generation of acid sites

Table 4 depicts the sulfur content of the sulfonated samples as a function of temperature. Also, the surface pH is presented. The concentration of sulfonic groups was calculated using sulfur content determination and considering that all the sulfur present is in the form of sulfonic groups. This is a traditional assumption often used in published papers. Non-sulfonic acid sites were calculated by subtracting the amount of sulfonic groups from the total amount of acid sites.

Data presented in Table 4 show that, regardless of the surface pH of the parent carbon, the drastic treatment with sulfuric acid causes a steep reduction in the surface pH. This rather acidic surface occurs thanks to the generation of new SO_3H groups, which are acidic. Such groups were identified by means of FTIR. Also, the generation of sulfonic groups is a function of temperature. Indeed, less sulfur is incorporated on the surface as the temperature increases. The influence of temperature on sulfur incorporation on sulfuric acid-treated carbons had already been observed (Sousa-Aguiar et al*.,* 2014b). For the non-sulfonic acid sites, a different behavior was observed. The sulfonation temperature increase caused a higher density of such sites, probably due to an extended surface oxidation.

Also, it is important to highlight that all catalysts underwent hot water treatment. Such treatment aimed at removing unstable acidic sites, whose leaching is considered the main reason for the deactivation of such carbons. (Van Pelt, 2012; Chen et al*.*, 2018)

Cellobiose conversion

Table 5 depicts the results of cellobiose conversion for carbons which have been sulfonated at different temperatures. Only glucose was obtained as a reaction product. Potential sub products generated from reactions of glucose degradation were not detected.

Interestingly, conversion drops with increasing sulfonation temperature, a linear correlation being observed. In fact, if conversion data are plotted against the content of sulfonic groups (Figure 3), straight lines are obtained, as a clear indication that sulfonic groups are the active sites responsible for the catalytic activity. Similar results have been previously reported for sulfonated carbons obtained directly from raw biomass (Fraga et al., 2016).

Table 4. Effect of sulfonation temperature on sulfur content and surface pH.

Sample	Sulfonation temperature (ºC)	Sulfonic groups (mmol/g)	Surface pH	Non-sulfonic acid sites (mmol/g)
C-141-S untreated	-	-	10.62	0.49
C-141-S	120	0.33	2.50	0.51
C-141-S	160	0.29	2.37	0.56
C-141-S	200	0.24	3.18	0.88
C-147 untreated	-	-	5.67	0.60
C-147	120	0.81	2.06	0.27
C-147	160	0.53	2.05	0.50
C-147	200	0.31	2.29	1.00

Table 5. Cellobiose conversion data for different temperatures calculated at 24h reaction time.

Sample	Sulfonation temperature (ºC)	Conversion* (%)
C-141-S	120	58.6
C-141-S	160	37.8
C-141-S	200	22.0
C-147	120	55.6
C-147	160	51.5
C-147	200	41.3

* Standard deviation of cellobiose hydrolysis tests is 1.99%.

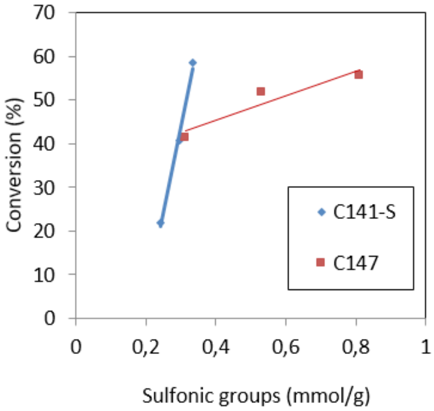

Figure 3. Influence of sulfonic groups on the conversion of cellobiose into glucose.

Based upon conversion curves and the density of active sites, turn-over numbers were calculated. The influence of site density on the turn-over number is presented in Figure 4. Peculiarly, completely different curves are obtained. Indeed, for carbon C-141-S the turn-over number increases with increasing density of sites, whereas the opposite occurs for carbon C-147.

Usually, such peculiar behavior is associated with two characteristics. First, there is the concept of accessibility, in which, depending on the porous characteristics of the material, reactant molecules are unable to reach active sites located in rather inaccessible (more internal) positions. Second, there is the concept of acid strength. As a matter of fact, not all sites have the same strength, hence some acidic sites are not sufficiently strong to catalyze the desired reaction. The individual role of these two effects may not be easily discriminated, requiring very sophisticated characterization techniques, as well as diffusion studies.

However, when the turn-over number is plotted against specific surface or mesopore area (Figure 5) it becomes clear that there is a relation between textural properties and the apparent activity of sulfonic sites.

For both carbons, increasing mesopore area led to higher turn-over numbers (more molecules converted per active site). This is related to the better accessibility to the sulfonic sites provided by the new mesopores present in the carbon matrix. Interestingly, although clear relations between turn-over numbers and mesopore area could be observed, they differ in the ranges of the effects. Carbon C-147 has almost twice the mesopore area of C-141-S, but this is not reflected in higher turn-over numbers, compared to C-141-S. This is an indication that, despite the fact of mesopore presence being relevant for the apparent activity of sulfonic sites, there are other properties that play an important role in hydrolysis reactions by sulfonated activated carbons.

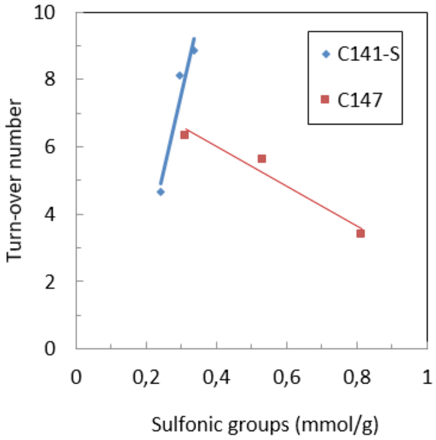

Figure 4. Influence of site density on the turn-over number.

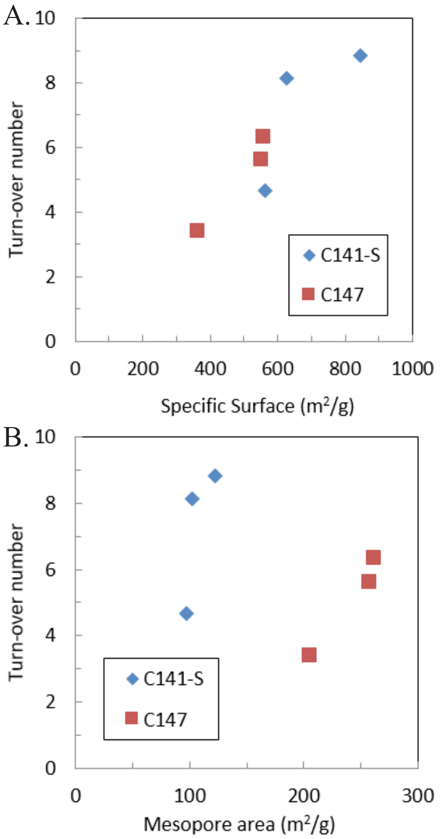

Figure 5. Influence of specific surface and mesopore area on turn-over number.

Adsorption onto the catalyst surface is the first step of hydrolysis reactions over solid acids. A strong adsorption between adsorbate and the catalyst has already been related to an easier hydrolysis step, requiring weaker acid sites (Yabushita, 2016). The kinect diameter of cellobiose is 8.9Å (Chen et al., 2015). Previous work has shown that adsorption of cellobiose occurs primarily in micropores (pore diameter lower than 20A). Moreover, cellobiose adsorption occurs preferentially on hydrophobic surfaces, via CH-Pi hydrogen bonds (Yabushita, 2016).

It should be noted that the average pore diameter of carbons C-141-S is around 20Å, while for carbons C-147 the value observed is 33Å. In addition, carbon C-141-S has a lower amount of non-sulfonic acid sites (main oxygenated acid sites) and total oxygen content, presenting a more hydrophobic surface. Both characteristics can increase adsorption capacity and are desired to maximize the activity of sulfonic sites.

In this way, the adsorption of cellobiose in micropores present in C-141-S stabilized the molecule, due to van der Waals forces, making the hydrolysis reaction more likely to occur. On the other hand, the concept of accessibility has to be taken into consideration. Mesopores facilitate the diffusion of cellobiose to micropores, giving access to acidic sites located inside such pores, thereby enhancing the overall rate. Therefore, both are important in the determination of the reaction rate.

In conclusion, the existence of mesopores is important to give access to the acid sites located in micropores. However, the micropore area and surface polarity should play a key role. So the combination of a massive micropore surface area with an adequate presence of mesopores, presenting a low polarity surface seems to be the conditions needed to improve the activity of sulfonic sites.

CONCLUSIONS

Acidic sulfonated carbons may be prepared via treatment with sulfuric acid. However, such treatment modifies textural properties of the parent carbons. Indeed, typical microporous carbons become mesoporous upon acid treatment. Also, acid treatment changes the surface pH of carbons. Even carbons presenting basic surfaces become rather acidic after treatment with sulfuric acid. This acidity occurs because new sulfonic groups are generated on the surface upon treatment.

Furthermore, the generation of sulfonic groups is inversely proportional to the temperature of treatment. Indeed, less sulfur is incorporated on the surface as the sulfonation temperature increases.

Regarding the catalytic properties of sulfonated carbons, they are excellent catalysts for acid-catalyzed reactions, such as the hydrolysis of cellobiose. Carbons sulfonated at 120ºC were the most active catalysts for the hydrolysis of cellobiose. Higher sulfonation temperatures brought about lower activities.

Carbon mesoporosity seems to play an important role in the reaction studied. However the combination of a huge micropore area with an adequate mesopore presence seems to be of great importance. Sulfonic groups generated upon sulfuric acid treatment are the active sites for the hydrolysis reaction, the conversion into glucose being proportional to the density of such sites. Nevertheless, accessibility to such sites also plays an important role in the reaction rate. As a matter of fact, the concept of accessibility is becoming increasingly important in Catalysis, mainly when voluminous molecules are concerned. The diffusion of such molecules into the catalyst pores is somewhat hindered; hence, the presence of mesopores associated with micropores may facilitate the diffusion of such molecules. This concept is being commercially applied to FCC catalysts and is also useful for biomass conversion, since reactions involving biomass products usually concern voluminous molecules.

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REFERENCES

Almeida, J.M.A.R., Da Via, L., Demma Cara, P., Carvalho, Y., Romano, P.N., Peña, J.A.O., Smith, L., Sousa-Aguiar, E.F., and Lopez-Sanchez, J.A.; Screening of mono- and bi-functional catalysts for the one-pot conversion of cellobiose into sorbitol. Catalysis Today, 279, 187-193 (2016). https://doi.org/10.1016/j.cattod.2016.06.017

Carvalho, Y., Almeida, J. M. A. R., Romano, P. N., Farrance, K., Demma Carà, P., Pereira, N., Lopez-Sanchez, J. A., and Sousa-Aguiar, E. F., Nanosilicalites as Support for β-Glucosidases Covalent Immobilization. Applied Biochemistry and Biotechnology, 1, 1-11 (2017). https://doi.org/10.1007/s12010-017-2422-7

Cavalcante, C. L., Silva, N. M., Souza-Aguiar, E. F., and Sobrinho, E. V.; Diffusion of Paraffins in Dealuminated Y Mesoporous Molecular Sieve. Adsorption, 9(3), 205-212 (2003). https://doi.org/10.1023/A:1024793615830

Chen, G.; Wang, X.; Jiang Y.; Mu, X.; and Liu, H.; Insights into deactivation mechanism of sulfonated carbonaceous solid acids probed by cellulose hydrolysis. Catalysis Today, 319, 25-30 (2018). https://doi.org/10.1016/j.cattod.2018.03.069

Chen, J., Lu, F., and Xu, J., Formation of uniform hollow nanocages with heteroatom-doped MCM-41 structures, RSC Adv., 5(7), 5068-5071 (2015). https://doi.org/10.1039/C4RA13959C

Fraga, A., Quitete, C., Ximenes, V., Sousa-Aguiar, E.F., Fonseca, I., and Rego, A.M., Biomass derived solid acids as effective hydrolysis catalysts, Journal of Molecular Catalysis A: Chemical, 422, 248-257 (2016). https://doi.org/10.1016/j.molcata.2015.12.005

Hara, M. Biodiesel Production by Amorphous Carbon Bearing SO3H, COOH and Phenolic OH Groups, a Solid Brønsted Acid Catalyst. Topics in Catalysis, 53(11–12), 805–810 (2010). https://doi.org/10.1007/s11244-010-9458-z

Kitano, M., Yamaguchi, D., Suganuma, S., Nakajima, K., Kato, H., Hayashi, S., and Hara, M., Adsorption-Enhanced Hydrolysis of β-1,4-Glucan on Graphene-Based Amorphous Carbon Bearing SO3H, COOH, and OH Groups. Langmuir, 25(9), 5068–5075(2009). https://doi.org/10.1021/la8040506

Kobayashi, H., Komanoya, T., and Guha, S.K., Conversion of cellulose into renewable chemicals by supported metal catalysis. Applied Catalysis A–General, 409, 13-20 (2011). https://doi.org/10.1016/j.apcata.2011.10.014

Onda, A., Ochia, T., and Yanagisawa, K., Selective hydrolysis of cellulose into glucose over solid acid catalysts. Green Chem., 10, 1033–1037(2008). https://doi.org/10.1039/b808471h

Romano, P, N., Almeida, J. M. A. R., Carvalho, Y., Priecel, P., Sousa-Aguiar, E.F, and Lopez-Sanchez, J. A. Microwave-Assisted Selective Hydrogenation of Furfural to Furfuryl Alcohol Employing a Green and Noble Metal-Free Copper Catalyst. ChemSusChem, 9, 3387-3392 (2016). https://doi.org/10.1002/cssc.201601398

Sing, K.S., Everett, D.H., Haul, R.A., Moscou, L., Pierotti, R.A., Rouquérol, J., and Siemieniewska, T., Reporting physisorption data for gas/solid systems, Pure Appl. Chem. 57(4), 603-619 (1985).

Sousa-Aguiar, E. F., Almeida, J. M. A. R, Romano, P. N., Fernandes, R. P., and Carvalho, Y., Green Chemistry: The Evolution of a Concept. Química Nova, 37(7), 1257-1261 (2014a). https://doi.org/10.5935/0100-4042.20140212

Sousa-Aguiar, E. F.; Murta-Valle, M. L.; Silva, M. P.; and Silva, D. F. Influence of the external surface area of RE-containing Y zeolites on the cracking of 1,3,5 TIPB. Zeolites, 15, 620-623 (1995). https://doi.org/10.1016/0144-2449(95)00069-I

Sousa-Aguiar, E. F.; Murta-Valle, M. L.; E. V. Sobrinho; and Cardoso, D., Cracking of 1,3,5TIPB over deeply dealuminated Y zeolites. Studies in Surface Science and Catalysis , 97, 417-423 (1995b). https://doi.org/10.1016/S0167-2991(06)81916-6

Sousa-Aguiar, E.F., Appel, L.G., Zonetti, P.C., Fraga, A.C., Bicudo, A. A., and Fonseca, I., Some important catalytic challenges in the bioethanol integrated biorefinery. Catalysis Today, 234, 13-23 (2014b). https://doi.org/10.1016/j.cattod.2014.02.016

Suganuma, S., Nakajima, K., Kitano, M., Yamaguchi, D., Kato, H., Hayashi, S., and Hara, M., Hydrolysis of Cellulose by Amorphous Carbon Bearing SO3H, COOH, and OH Groups. J. Am. Chem. Soc., 130 (38), 12787–12793(2008). https://doi.org/10.1021/ja803983h

Van Pelt, A.H., Acid-Modified Activated Carbon Stability and Application in Biomass Hydrolysis, Thesis, Georgia Institute of Technology, 2012.

Yabushita, M., A Study on Catalytic Conversion of Non-Food Biomass into Chemicals: Fusion of Chemical Sciences and Engineering, Biomass into Chemicals, Springer Theses, 2016. https://doi.org/10.1007/978-981-10-0332-5

Yamaguchi, D, Watanabe, K., and Fukumi, S., Hydrolysis of Cellulose by a Mesoporous Carbon-Fe2(SO4)3/γ-Fe2O3 Nanoparticle-Based Solid Acid Catalyst. Sci Rep., 6, 20327(2016). https://doi.org/10.1038/srep20327

Yamaguchi, D., Kitano, M., Suganuma, S., Nakajima, K., Kato, H., and Hara, M., Hydrolysis of Cellulose by a Solid Acid Catalyst under Optimal Reaction Conditions. J. Phys. Chem. C, 113(8), 3181-3188(2009). https://doi.org/10.1021/jp808676d

Zhou, C., Xia, X., Lin, C., Tonga, D., and Beltramini, J., Catalytic conversion of lignocellulosic biomass to fine chemicals and fuels. Chem. Soc. Rev., 40, 5588-5617(2011). https://doi.org/10.1039/c1cs15124j

Zhu, P., Dai, H., Lei H., Xu, X., Le-ming, C., Qin-hui, W., and Shi, Z., Aluminum extraction from coal ash by a two-step acid leaching method. Journal of Zhejiang University-SCIENCE A. 16(2), 161–169(2015). https://doi.org/10.1631/jzus.A1400195