Catalysis Today 179 (2012) 178–184

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Direct conversion of cellulose to glucose and valuable intermediates in mild reaction conditions over solid acid catalysts

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ARTICLE INFO

Article history:
Received 13 June 2011
Received in revised form 14 July 2011
Accepted 15 July 2011
Available online 20 August 2011

Keywords:
Cellulose
Solid acid catalysts
Zeolites
Glucose, HMF

ABSTRACT

The direct hydrolysis of cellulose to glucose, HMF and other soluble by-products at 190 °C in water solution using zeolites (H-BEA, H-MOR), sulphated zirconia supported over mesoporous silica (SBA-15), Amberlyst® 15, heteropolyacids and $AlCl_3 \cdot 6H_2O$ as acid catalysts was studied using a high cellulose to catalyst ratio (10), not-pretreated (neither mechanically nor chemically) cellulose and a static (not mixed) autoclave. Under these conditions, not usually considered, but relevant for industrial applications, micro and mesoporous solid acid catalysts are active in the direct hydrolysis of cellulose to glucose, HMF and other soluble by-products. The reactivity in crystalline cellulose conversion is determined on one side from the need to realize an efficient solid–solid interaction between the external surface of the catalyst and the crystalline cellulose, and on the other side on the need to limit the secondary reactions of the formed products. Microporous materials, due to the presence of shape-selectivity effects limiting the polymerization of glucose to humic-type species show the highest formation of glucose and HMF with respect to the sulphated zirconia supported over mesoporous silica (SBA-15) and homogeneous heteropoly acids.

1. Introduction

The conversion of cellulosic biomass to valuable chemicals is currently one of the main interest of worldwide R&D to foster a bio-based economy [1]. In fact, the exploitation of ligno-cellulosic material in 2nd generation processes is crucial to avoid the competition with an increasing food demand and the social aspects related to this. To achieve this aim it is necessary to find effective methodologies to selectively de-structure the ligno-cellulose maintaining chemical integrity of the components (hexoses and pentoses from cellulose and hemi-cellulose). In fact, these platform molecules can be used in a variety of applications, from chemicals to materials and energy, thus making effective the possibility of developing bio-refineries [2,3].

Considerable efforts have been devoted up to now to the depolimerization of cellulose. In fact the tight packing of cellulose chains in microfibrils protects the β-1,4-glycosidic linkages between the glucose units, making the cellulose hard to attack and deconstruct. Harsh hydrolysis conditions very often preceded by a pretreatment (e.g. partial chemical degradation or physical degradation such as ball milling) are thus required [4]. Hydrolysis with mineral acids, such as H_2SO_4 [5], HCl [6] and HF [7] is still the main established route to treat cellulose and it is currently the reference point of most pilot-plant scale technologies but problems such as the generation of acid-waste, the need to purify downstream products from acidic solutions and the corrosion hazards (with consequent significant long-term plant stress) make this technology hard to manage [8].

The use of enzymes has been on the spotlight since decades [9]. Bacteria and fungi like *Trichoderma viride*, *Trichoderma reesei* and *Sporotrichum pulverulentum* can produce a high level of extra-cellular cellulase able to hydrolyze the cellulose to glucose. The treatment with enzymes takes place in mild conditions but on the other hand it shows limits in terms of cost of the enzymes, the long times required due to the hard accessibility to crystalline structures (when a pretreatment to break the hydrogen linkage between the chains is not used) and the poor efficiency in a fast adaptation to different raw materials feeds.

Hydrothermal treatment is one of the more effective methods to convert cellulosic biomass to its degradations products, because water under high temperature and pressure shows peculiar properties. One of the main hydrothermal technologies is based on the use of supercritical water (temperature higher than 374 °C and pressure above 22 MPa) [10]. Using this method cellulose is quantitatively hydrolyzed to oligosaccharides and then to glucose in very short reaction times (less than 20 s). Drawbacks like a proper control of the reaction kinetics, implying a decrease in selectivity and yield due to further uncontrolled decomposition and dehydration of the

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doi:10.1016/j.cattod.2011.07.018

products (glucose and oligomers), the harsh working conditions and difficulties in scale-up limit the industrial use of supercritical water.

A new way to effectively exploit biomass and avoid drawbacks related to previously discussed technologies could be the use of solid acid catalysts. This new route could, for example, easily overcome above-mentioned problems such as the use of low environment friendly chemicals and products purification. Several papers have reported the use of different solid acid catalysts to convert cellulose [11], but it must be anticipated that often the amount of catalyst is so high (equal or superior to cellulose itself) and therefore the exploitation of the results is difficult. A recent paper reports the high efficiency of a magnetic solid acid catalyst based on SBA-15 and its easy separation from solid cellulosic residues [12]. Although this approach facilitates the catalyst separation and recovery, still processes based on a very high catalysts\cellulose ratio are not feasible for economic costs.

Leading work by Schüth and co-workers [13] has underlined the efficient synergy between ionic liquids and a common acidic solid catalyst (Amberlyst®15) under mild conditions to hydrolyze cellulose to mono- and oligosaccharides. This is likely due both to the affinity of chloride-containing ionic liquids to hydrogen bonding of hydroxyl functions in cellulose chains and intrinsic Amberlyst®15 Brönsted acid properties in solvent media. According to the authors themselves, the cost-efficient removal of solubilized products remains a main concern and this aspects together with the relatively high cost of ionic liquids could be disadvantageous on a future plant up-scaling. In addition, using real ligno-cellulose materials the inorganic elements present in them tend to accumulate in the ionic liquid and often a fast decrease of the performances is observed. It was also reported the depolymerization of cellulose into polyols on noble [14] and transition metals [15] on carbon supports by combination of hydrolysis in hot water and hydrogenation under compressed hydrogen gas. This catalytic process presents some disadvantages such as the need of noble metals and hydrogen as well as the limited utilization of polyols with respect to glucose.

Very limited attention has been given to the use of solid acid catalysis for the depolymerization of cellulose in water under realistic conditions for the possible exploitation, i.e. temperatures below about 200 °C (to avoid secondary transformation of the produced sugars), reasonable high cellulose to catalyst ratio and avoiding the use of energy-intensive pretreatments methods for cellulose, such as long-time ball-milling typically used in most of the literature works [11]. In this paper we report the direct catalytic conversion of cellulose to glucose and 5-hydroxymethylfurfural (HMF) over microporous and mesoporous solid acid catalysts in water under mild conditions. No physical or chemical pretreatments have been used to increase the non crystalline cellulose fraction and the separation of products and catalysts has been readily carried out by filtration.

2. Experimental

2.1. Reactants

Commercially available microcrystalline cellulose powder by Fluka was used for the degradation tests. H-form zeolite materials, as H-mordenite (H-MOR) by ALSI-Penta Zeolithe GmbH, H-BEA by Zeolyst International were obtained from the corresponding ammonic forms by thermal activation at 723 K for 12 h. Amberlyst®15, Aluminum Chloride hexahydrate, 99%, Phosphotungstic acid hydrate (PTAH) and Phosphomolybdic acid hydrate (PMAH) were from Sigma–Aldrich.

The reactants used for the preparation of SBA-15 based catalysts were tetraethyl orthosilicate (TEOS, 99.999% Aldrich) as silica source, Pluronic P123 triblock polymer (PEO–PPO–PEO, Aldrich) as directing agent and Zirconium(IV) oxychloride octahydrate ($\geq$99.5% (Sigma–Aldrich)) as zirconia source.

2.2. Catalysts preparation

Mesoporous SBA-15 was prepared according to literature and the detailed procedure described elsewhere [16]. ZrO_2 was dispersed on the SBA-15 support by an urea hydrolysis method using zirconium oxychloride ($ZrOCl_2{\cdot}8H_2O$) as zirconia source [17]. The theoretical zirconia loading was 30 wt%. The mixture was refluxed at 90 °C for 5 h (pH about 8), and the resulting gel was filtered and washed with distilled water until removal of chloride ions. After centrifugation, the ZrO_2-SBA-15 gel was dried and calcined at 550 °C for 6 h. This sample is indicated hereinafter as Z-SBA-15. Z-SBA-15 was sulphated using H_2SO_4 1 N (15 ml/g) at room temperature, dried and calcined at 550 °C for 3 h. This catalysts is indicated hereinafter as SZ-SBA-15.

2.3. Catalysts characterization

Powder X-ray diffraction (XRD) data were recorded using a Phillips PW 1710 diffractometer with CuK_α radiation. The samples were scanned in the range of 2θ from 1 to 8° in steps of 0.005° with a count time of 1 s at each point.

Surface area and porosity properties of samples were evaluated by N_2 adsorption/desorption isotherms carried out at 77 K on a Micromeritics ASAP 2020 sorption analyzer. The specific surface area was determined by applying the BET equation to the isotherm. Mesopore size distribution was calculated using the adsorption branch of the nitrogen adsorption isotherm and the Barrett–Joyner–Halenda (BJH) equation. The average pore diameter and the cumulative volume were obtained from the distribution curve of the mesopore sizes.

The morphology and habit of the crystalline phase of the samples were examined by scanning electron microscopy (SEM, JEOL JSTM 330 A). The chemical composition of the crystals was determined by Energy Dispersive X-ray analysis (EDX).

The concentration of acid sites on the catalysts was determined by titration method with NaOH in aqueous solution.

2.4. Catalytic experiments

For catalytic tests a Parr stainless steel Teflon-lined pressure vessel under air was used. In a typical run, 2 g of cellulose, 200 mg of catalyst and 55 ml of water were introduced in the reactor. The catalytic hydrolysis was carried out using three different cellulose/catalysts ratios (10, 5, 1). The temperature was 190 °C and the reaction mixture was stirred vigorously for the reaction time chosen (commonly up to 5 h). Tests were also done without stirring. After the reaction, the catalyst and the unreacted cellulose were removed by filtration. The filtered solution was analyzed by a DIONEX Ion Chromatograph coupled with an amperometric detector ED-40 for glucose determination and by a Dionex HPLC-UV Vis for HMF identification and quantification. Total water soluble organic compounds in the resultant solutions were determined by a Total Organic Analyzer (TOC) from Shimadzu.

Calculations were made analytically by TOC results as follows:

$$\text{Reacted cellulose}\quad(\text{mol}) = \frac{\text{TOC}\,(\text{mg/l})/1000\,(\text{mg/g})}{\text{Carbon Atomic Weight}} \times (\text{Reaction Volume})$$

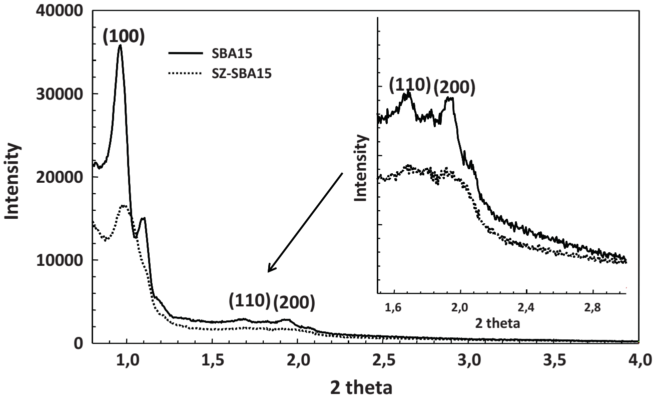

Fig. 1. Low-angle X-ray scattering of SBA-15 based catalysts: SBA-15 and SZ-SBA-15.

$$\text{Charged cellulose (mol)} = \frac{\text{Charged cellulose, g}}{\text{Gluscose Molecular Weight}} \times 6$$

$$\text{Cellulose Conversion (\%)} = \frac{\text{Reacted cellulose modules}}{\text{Charged cellulose moles}} \times 100$$

The selectivity to water soluble organic compound (WSOCs) was calculated similarly as reported by Onda et al. [11] on the base of TOC results as follows:

$$\text{WSOCs selectivity (\%)} = \frac{\text{mol of water soluble organic carbon}}{\text{Reacted cellulose moles}} \times 100\%$$

The selectivity to glucose, HMF and by-products was calculated according to the following equations:

$$\text{Glucose selectivity (\%)} = \frac{\text{Glucose moles} \times 6}{\text{Reacted cellulose moles}} \times 100\%$$

$$\text{HMF selectivity (\%)} = \frac{\text{HMF moles} \times 6}{\text{Reacted cellulose moles}} \times 100\%$$

$$\begin{aligned}\text{By-product selectivity (\%)} &= \text{WSOCs selectivity (\%)} \\ &\quad - \text{glucose selectivity (\%)} \\ &\quad - \text{HMF selectivity (\%)}\end{aligned}$$

The so calculated value of cellulose conversion well fit with the correspondent value we got by calculating it (as commonly reported in literature) as a weight difference, between the amount of charged cellulose and that recovered after filtration [14]. We decided to calculate cellulose conversion by TOC in order to avoid a significant source of error due to the adhering humic solids to the vessel walls [18].

3. Results and discussion

3.1. Low-angle X-ray diffraction

Three characteristic diffraction peaks of SBA-15 structure, (1 0 0), (1 1 0) and (2 0 0) at ca. $2\theta = 0.95$, 1.6, 1.95, respectively, which are characteristic of P6mm hexagonal mesoporous materials, were observed in the low-angle X-ray patterns (Fig. 1). The XRD pattern of SZ-SBA-15 is qualitatively similar to that of SBA-15, but a weakening and broadening of the (1 0 0), (1 1 0) and (2 0 0) reflections is observed which also shift to slightly higher angles. This indicates a lower degree of order in SZ-SBA-15 with respect to SBA-15 as well as a slightly different 2D packing, as usually observed when an oxide is loaded onto mesoporous silica [19].

Table 1
Surface area and acidity properties of some of tested catalysts.

Catalyst	Si/Al ratio	BET surface area (m^2/g)	Acid sites (meq/g)
SZ-SBA-15	>1000	426	–
H-MOR	7	374	1.3
H-BEA	13	536	1.1
Amberlyst® 15	nd	45	1.9

At higher angles, no further diffraction lines were detected, indicating that crystalline ZrO_2 is not present, confirming that the preparation leads to a high dispersion of zirconia on the mesoporous silica support.

3.2. Porosity characterization

Nitrogen adsorption analysis was made on the prepared samples and the main results are summarized in Table 1. For SBA-15 based catalyst, the isotherms of nitrogen adsorption show the typical IV-type profile, according to the IUPAC classification, consisting in a step condensation behavior due to mesopores.

3.3. Electron microscopy characterization

SEM micrographs of SBA-15 based materials show the typical SBA-15 wheat-like morphology with a crystal size in the range of 1–2 μm. A well homogeneous distribution of zirconia, without detection of Zr-rich areas, was evidenced by EDX measurements (Fig. 2).

The homogeneity of the distribution of zirconium and its influence on the well-ordered hexagonal array of mesopores typical of SBA-15 were also analyzed by transmission electron microscopy (TEM). No evidences were observed of the presence of zirconia crystallites on the outer surface of the mesoporous silica, confirming thus that XRD and SEM indications that zirconia is mainly located within the mesoporous silica channels as an XRD-amorphous phase, probably homogeneously distributed on the inner walls of the channels, in agreement with textural data. TEM of the parent SBA-15 shows an homogeneous ordering of channels and it evidences that the diameter of the channels is about 6.4 nm, with a wall thickness of about 3 nm.

3.4. Catalytic activity

The catalytic performances of acidic zeolites (H-MOR and H-BEA), and of sulphated ZrO_2 supported on SBA-15 were studied in the reaction of hydrolysis of cellulose to glucose and other valuable components. The selection of these catalysts was based on the possibility to have different Brönsted and Lewis acidities, and different possible modalities of interaction with the cellulose. The latter cannot clearly diffuse inside the zeolitic structure and the activity is thus related essentially to external reactivity, but which depend on the physical contact between the micro/mesoporous material and the crystalline (insoluble) cellulose. However, glucose and small linear oligomers can diffuse inside the zeolite channels and give secondary reactions. Due to the low surface area of zirconia, it was supported on the mesoporous SBA-15, which itself, due to the low acidity, was not active in the reaction.

The catalytic activity of these catalysts was compared with those of the commercial resin Amberlyst® 15 and of water soluble acids such as heteropolyacids (PTAH and PMAH). $AlCl_3{\cdot}6H_2O$ was also tested to have a homogeneous Lewis acid catalyst. As reported in

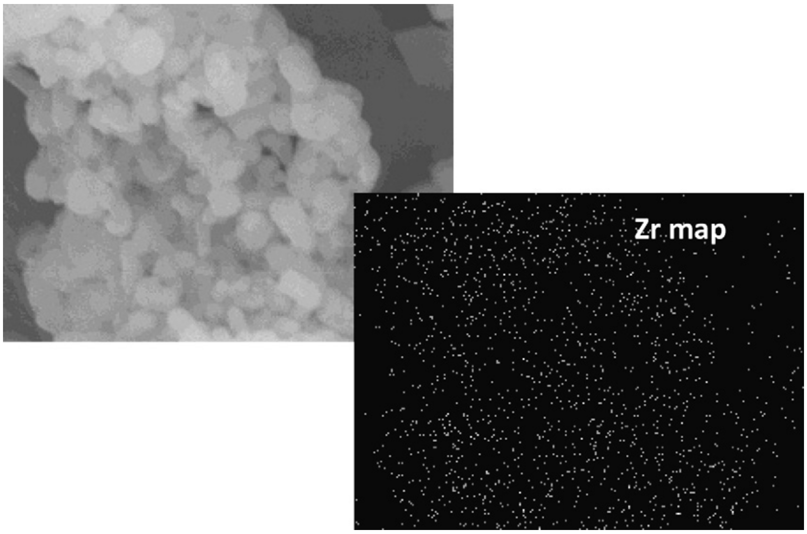

Fig. 2. EDAX mapping of Zr distribution for SZ-SBA-15 catalyst.

Section 2, mild conditions were chosen for the study of the catalytic activity of the above cited catalysts.

We have investigated these materials in the 140–190 °C temperature range, but we limit here discussion to the reaction temperature of 190 °C (about 10 atm of autogenic pressure). At this temperature, a significant conversion of the not-pretreated cellulose could be reached in a reaction time of few hours. In principle, this reaction time could be a valid compromise between too short reaction times, typical of water supercritical treatments (hardly feasible from industrial point of view) and too long reaction times usually required by enzymatic treatments. Operating at temperatures below 200 °C can limit secondary reaction of thermal degradation/polymerization [20] leading to insoluble and products hard to convert. Note, that the cellulose/catalyst ratio used in these tests is significantly higher than that often reported in literature. At temperatures below 190 °C, i.e. about 160 °C, the conversion of cellulose drops significantly.

A second aspect to remark regards the use of a static autoclave under autogenic air pressure. Avoiding the use of stirring is important from the practical perspective to limit the operative costs, and favor the solid–solid contact between the catalyst and cellulose.

In these conditions, and due to the presence of a reaction largely determined from the solid–solid contact between the catalyst and cellulose, the dependence from classical reaction parameters is different from the usual. In fact, the interaction between cellulose chain and catalyst surface is essentially due to van der Waals forces. This type of interaction is favored when sedimentation, due to natural difference of densities of the two different solid phases, occurs. Stirring would affect negatively this interaction. Indeed, when catalytic tests are performed under stirring we do not record a decrease of performances because very likely, beyond solid phases contact, other factors play a relevant role.

For example, a critical parameter cited in the introduction is the cellulose to catalyst ratio. As shown in Fig. 3a for the case of H-BEA catalyst, there is not a relevant decrease in the catalytic performances when the cellulose to catalyst ratio is increased of a factor 10, but there is a significant decrease of selectivity to glucose, particularly at the shorter times. Increasing the reaction time, determines an increase of the productivity, but also a lowering of the selectivity to glucose, due to secondary reactions of glucose conversion (Fig. 3b).

The low dependence of the productivity from the cellulose to catalyst ratio, but significant dependence of the selectivity, can be explained in terms of solid–solid interaction and static conditions. Already for the cellulose/H-BEA ratio of 10 there is an optimal contact between the catalyst and cellulose. A further increase in the amount of catalyst does not lead to a relevant improvement in the contact area, being essentially the additional zeolite covering the first zeolite layer in contact with the cellulose fibers. However, the glucose units, formed from the selective hydrolysis of the β-1,4-glycosidic linkages, may further react with the zeolite, being soluble and thus able to interact with the whole zeolite crystals.

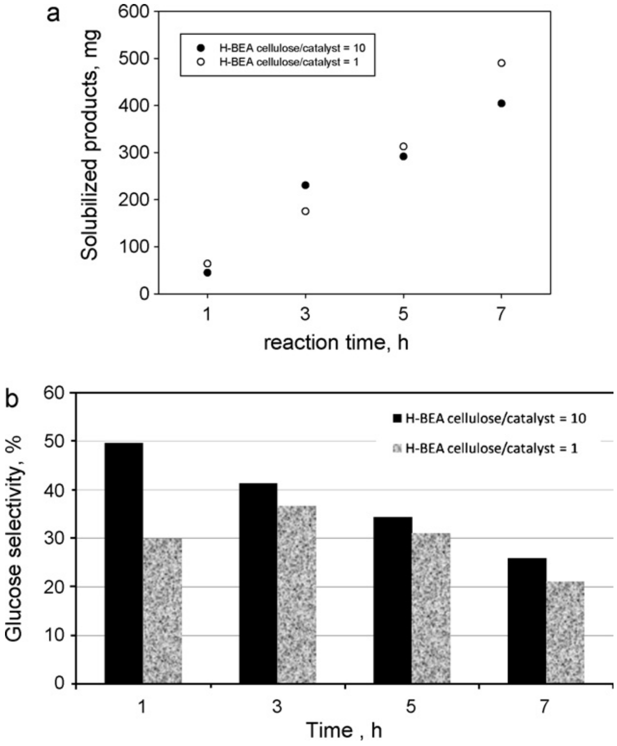

Fig. 3. Effect of different cellulose:catalyst ratios on the catalytic performances of H-BEA catalyst (a) and on the glucose selectivity (b) (reaction time 7 h, temperature 190 °C, autogenic pressure, cellulose/catalyst 10 and 1).

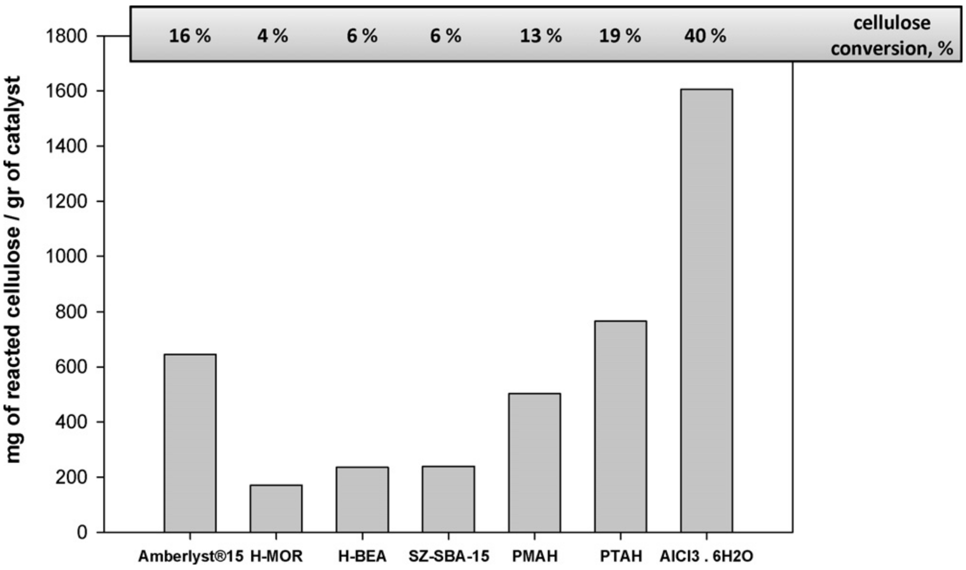

Fig. 4. Cellulose hydrolysis over various acid catalysts at 190 °C. Reaction conditions: 2 g cellulose, 0.2 g catalyst, distilled water 55 ml, 5 h. Catalysts: Amberlyst® 15, $AlCl_3{\cdot}6H_2O$, Phosphotungstic acid hydrate (PTAH), Phosphomolybdic acid hydrate (PMAH), sulphated zirconia SBA-15 (SZ-SBA-15), H-BEA and H-Mordenite (H-MOR).

These data thus evidence that the solid–solid interaction is the first factor and good interactions may be obtained even for high cellulose to catalyst ratios, while the excess of zeolite may catalyze further transformations of the glucose units formed from the acid-hydrolysis of the β-1,4-glycosidic linkages. Being this interaction depending on many factors, but primarily from the chemical and van der Waals interactions between the cellulose and the catalyst, and the external surface area of the catalyst particles and their morphology, the optimal cellulose to catalyst ratio changes from catalyst to catalysts. On the average, we observed that a ratio 10 between cellulose and catalyst and reaction times between 1 and 2 h (for a reaction temperature of 190 °C) are optimal to maximize the formation of glucose, while lower ratios or longer times enhance secondary reactions of small linear oligomers and glucose, such as dehydration of glucose to HMF whose formation increases with time of reaction.

The comparison of activity of different catalysts is summarized in Figs. 4 and 5. All of the catalysts are active in the hydrolysis of cellulose to glucose, HMF and other soluble products at 190 °C without any pretreatment. The catalytic behavior of H-MOR and H-BEA is quite similar to that of the reference catalyst Amberlyst® 15, in terms of products distribution but different in terms of activity, giving for both zeolite forms a value of reacted cellulose for grams of catalyst that is roughly half of Amberlyst® 15. This is likely due to the different acidity properties and textural properties (Table 1). This trend agrees with the results of Onda et al. [11] that reported Amberlyst® 15 as the solid acid showing the highest yield of glucose in cellulose hydrolysis and better than a series of zeolites. However, Onda et al. [11] used milled cellulose, showing the importance of pretreatment which not only open the fibrils, but creates surface defects on cellulose fibrils which could significant alter the interaction with the catalyst.

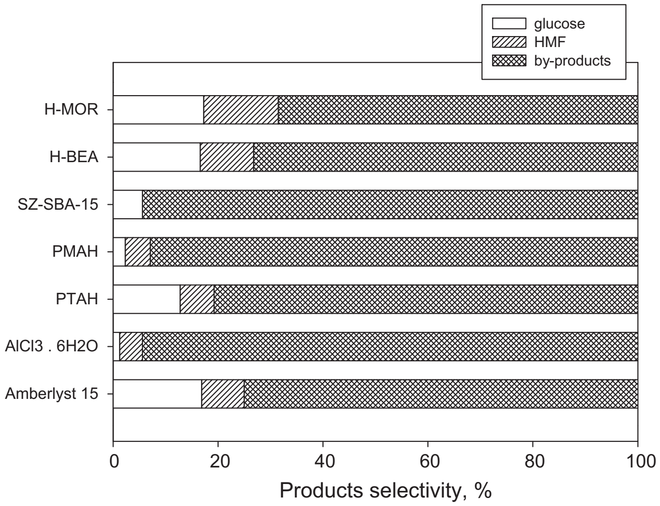

Fig. 5. Selectivity data for glucose, HMF and byproducts on different acid catalysts (reaction conditions see Fig. 4).

H-MOR followed by H-BEA gives the highest selectivity to HMF, the latter deriving from glucose dehydration. For these catalysts there is a correlation between number of acid sites and dehydration activity (formation of HMF). In fact for H-BEA catalyst with a lower amount of acidic sites (1.1 H^+ meq/g) we observe a minor HMF selectivity but when the amount of acidic sites is increased, like in the case of H-MOR (1.3 H^+ meq/g) the selectivity to HMF increases of 40%, reaching an overall 14%. If we consider a more acidic catalyst, like Amberlyst® 15, a direct correlation to HMF does not seems straightforward because the excess of acidity leads to side reaction products (humics) hard to quantify for a reliable correlation.

Even with large channels as those available in SBA-15 mesoporous materials, the internal accessibility is limited. In SZ-SBA15 sulphated zirconia acidic sites are mainly located inside the channels of the mesoporous support, as evidenced by TEM results, but the bulky oligomers can hardly diffuse inside them. This catalyst shows low formation of glucose, no HMF and large amounts of soluble oligomers. We supported the sulphated zirconia over the SBA-15 in order to increase the potential surface area and have a potentially bifunctional catalyst which combines Brönsted and Lewis acidity. Degirmenci et al. [21] reported recently that zirconia modified SBA-15 becomes a very active catalyst for the selective hydrolysis of cellobiose to glucose after sulphation. The strong Brönsted acidity created from sulphation of supported zirconia was able to broken the β-1,4-glycosidic bonds in cellobiose, a model reaction for the depolymerization of cellulose. However, with crystalline cellulose, we observed poor performances, reasonably due to the low degree on solid–solid interaction between the catalyst and the crystalline cellulose.

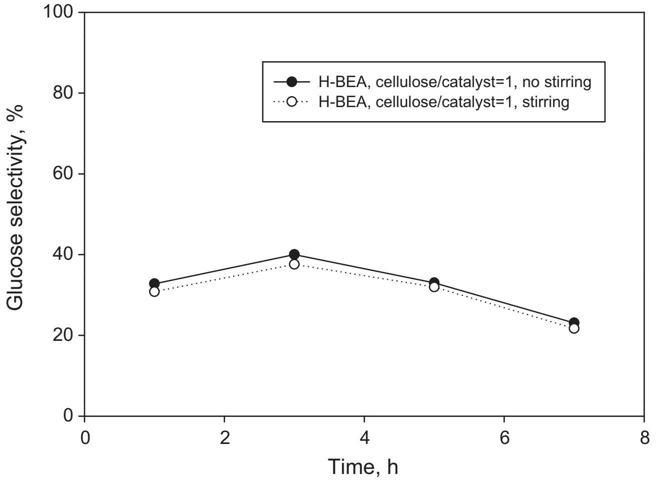

Fig. 6. Comparison of activity for H-BEA in catalytic tests performed with and without stirring (reaction conditions see Fig. 4).

Comparing the activity of the above cited catalysts with the one of the acids in homogeneous phase, like heteropolyacids, as PTAH and PMAH, and $AlCl_3 \cdot 6H_2O$ we can observe a more efficient hydrolysis of cellulose to depolymerization by-products (in the case of $AlCl_3 \cdot 6H_2O$ nearly 1.5 g for gram of catalyst), but a lower selectivity to glucose and HMF. Shimizu et al. [22] reported recently that heteropolyacids ($H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$) and their salts with metal cations act as effective homogeneous catalysts for selective hydrolysis of cellobiose and cellulose (ball-milled for 48 h) to glucose in an aqueous phase. The activity was correlated with the presence of strong Brönsted acidity, but the presence of strong Lewis acid sites increased the activity.

In our case, we also observed high activity, but low formation of glucose in the case of $AlCl_3 \cdot 6H_2O$ and phosphotungstic acid (PTAH), while better yields of glucose in the case of phosphomolybdic acid (PMAH). HMF formation is comparable in the three cases. PMAH is a weaker acid than PTAH [23]. This different behavior could be explained considering that differently from the solid acids, glucose, when formed from cellulose hydrolysis, may further reacts to give *humics* species, e.g. polymerize again. Lower acidity of PMAH with respect to PTAH limits this secondary reactions, and for this reason the formation of glucose is higher. In addition the study of the catalytic activity of $AlCl_3 \cdot 6H_2O$ over longer reaction time (24 h) showed no presence of glucose and HMF but only the presence of depolimerization by-products hard to identify and a negligible increase in cellulose conversion with respect to the 5 h test.

This condition is far less present when solid species are employed as catalysts. In this case, most of the acid sites are present inside the channels, where glucose may diffuse, but secondary polymerization is inhibited from shape-selectivity effects. This is probably the reason why the sulphated zirconia supported over SBA-15 gives a poor glucose yield. The larger channels in SBA-15 (around 6 nm) with respect to zeolites (H-BEA and H-MOR) do not limit these secondary reactions on glucose leading to humic-type products.

The reactivity of micro- and meso-porous materials in crystalline cellulose conversion is thus determined on one side from the need to realize an efficient solid–solid interaction between the external surface of the catalyst and the crystalline cellulose, and on the other side on the need to limit the secondary reactions of the formed products. Further confirmation of this hypothesis is given by the comparison of the activity of H-BEA in catalytic tests performed with and without stirring (Fig. 6). The results evidence that stirring is not essential for an efficient reaction with respect to static conditions, as expected when solid–solid interaction is the dominant factor for reactivity.

According to some recent literature [24] the use of ultrasounds could improve the efficiency of cellulose treating. In order to prove the result of synergy between ultrasound and acidity of catalyst we pretreated commercial microcrystalline cellulose by ultrasounds for 1 h at 20.2 kHz. After this, the sample was collected, the usual quantity of catalyst added and a proper amount of water was added to obtain a total volume of 55 ml. Activated BEA zeolite was chosen as catalyst and employed in three different cellulose/catalyst ratios ranging from 10, the highest commonly used in our tests to a less than 1. Obtained results showed that the contribution of ultrasounds to the depolymerization rate is not much relevant both from the cellulose conversion point of view and glucose selectivity while it seems to better affect HMF selectivity. This is probably due to the fact that earlier depolymerization products anyway need a minimum amount of solvent to migrate in. Ultrasound treatment makes cellulose chains blown up with water not allowing products to pass efficiently in the reaction solvent.

4. Conclusions

The use of solid acid catalysts to hydrolyze cellulose selectively into glucose in water solution is presented as an environmentally friendly and industrially attracting chemical process [11,25–29]. This approach certainly overcomes many potential problems of other routes such as the large volume of salts produced using homogenous acids (sulphuric acid, for example), the energy-intense pretreatment (for example, by steam explosion) necessary for enzymatic conversion, the environmental impact and costs for separation for organo-solvents or ionic liquids. However, we remarked in the introduction that often experiments were made using conditions quite far from those necessary for the possible industrial exploitation of the results. In particular, we remarked the need to use high cellulose to catalyst ratios, avoid stirring in autoclave and energy-intensive pretreatment of cellulose, such as ball-milling. The aim of this work was thus to evaluate some solid acid catalysts under these conditions, in order check the applicability and some limiting factors of the use of solid acid catalysts for crystalline cellulose depolymerization in water solution. The choice of the catalysts was based on literature indications which pointed the interest on zeolites, sulphated zirconia supported over mesoporous silica (SBA-15), Amberlyst®15 and heteropolyacids. Quite interesting results have been also reported recently on carbon-based catalysts [25–27], but we have not included these materials in the investigation. Although the comparison was made in a broader temperature range, we have limited here data to the reaction temperature of 190 °C as compromise to have reasonably short reaction time (5 h or less) and a mild temperature preventing uncontrolled and significant conversion of glucose to humic-type of species.

Under these conditions and the aspects remarked above, micro and mesoporous solid acid catalysts are active in the direct hydrolysis of cellulose to glucose, HMF and other soluble by-products. The choice of an higher-than-common cellulose catalyst ratio (10) proved to be anyway efficient in converting crystalline not pretreated (mechanically or chemically) cellulose. The hydrolysis of cellulose on zeolytic based catalysts occurs similarly to Amberlyst®15, that is nowadays one of the reference acidic material. According to our catalytic results obtained with H-MOR and H-BEA, to deconstruct selectively cellulose to glucose and HMF, first a proper contact between cellulose chains and surface acidity of zeolysts is needed, after the diffusion of these depolymerization products inside pores of the catalyst leads to formation of glucose from oligomers and its subsequent dehydration to HMF. Inside pores acidity play a minor role for activity, but a more relevant role regarding the selectivity, affecting secondary reactions on glucose.

This is further confirmed by the catalytic tests in homogeneous phase made with heteropolyacids, such as PTAH and PMAH, and $AlCl_3{\cdot}6H_2O$ whose catalytic tests give a selectivity to by-product higher than glucose and HMF. At least at the temperature investigated, the performances of these catalysts are determined from the secondary conversion of glucose to humic-type species. A decrease in the acidity limits these reactions, favoring the glucose formation. Anyway the highest cellulose conversion obtained using $AlCl_3{\cdot}6H_2O$ represents an interesting finding because this reaction system was operated under mild conditions using essentially a catalytic amount of the aluminum chloride and no pretreatment was required.

In conclusion, the reactivity of micro- and meso-porous materials in crystalline cellulose conversion is determined on one side from the need to realize an efficient solid–solid interaction between the external surface of the catalyst and the crystalline cellulose, and on the other side on the need to limit the secondary reactions of the formed products. Microporous materials, due to the presence of shape-selectivity effects limiting the polymerization of glucose to humic-type species show the highest formation of glucose and HMF with respect to the sulphated zirconia supported over mesoporous silica (SBA-15) and homogeneous heteropoly acids.

Acknowledgements

This work was realized in the frame of the activities of the PRIN08 project “Catalytic upgrading of the fraction C5 in ligno-cellulosic biorefineries” and of the Cost Action CM0903 (UBIOCHEM).

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