

Non-catalyzed and Pt/ γ -Al₂O₃-catalyzed hydrothermal cellulose dissolution–conversion: influence of the reaction parameters and analysis of the unreacted cellulose

Véronique Jollet,^a Flora Chambon,^a Franck Rataboul,^{*a} Amandine Cabiac,^b Catherine Pinel,^a Emmanuelle Guillon^b and Nadine Essayem^{*a}

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Hydrothermal dissolution and/or conversion of cellulose Avicel® occurred at 190 °C under 5 MPa of H₂ in the absence of catalyst. This reaction is temperature and time dependent. A dissolution–conversion ratio of 35% was obtained after 24 h of reaction and glucose and HMF were detected as monomeric products in a global yield of less than 5%, indicating that the majority of the products are composed of soluble oligo- and polysaccharides. The unreacted cellulose was analyzed using XRD, ¹³C solid state NMR, TGA-DTA and SEM and compared to the initial cellulose. We showed that although morphology changes occurred during the reaction, no modification of the crystallinity was observed and that hydrothermal treatment did not affect a specific part of the cellulose polymer. The presence of Pt/ γ -Al₂O₃ increased the initial rate of dissolution–conversion significantly as well as the distribution of the monomeric products. Pt and H₂ atmosphere were seen to increase the dissolution–conversion ratio however their role has not been yet well established.

Introduction

The transformation of cellulose into valuable organic chemicals has recently received a great deal of attention. Indeed, as a widely available polysaccharide, it is regarded as a promising resource for the production of bio-products (glucose and derivatives) or bio-fuels to replace edible resources.^{1–3} However, cellulose is very resistant to chemical transformations due to its specific structure based on a dense hydrogen-bond network. This bio-polymer is almost insoluble in common solvents. These are the main drawbacks that have hampered its use for the above applications. Indeed, since these transformations need the presence of a catalyst, a cellulose solution rather than a suspension would allow a better contact of the reactant with the catalyst (especially if the catalyst is a solid) and therefore induce a greater efficiency.

The resistance of cellulose to hydrolysis is well known. However, cellulose can be hydrolyzed in pure water with attack by electrophilic hydrogen atoms on the glycosidic bonds, but this is a very slow reaction at ambient temperature and pressure. The rate of hydrolysis can be increased by the use of elevated temperatures and pressures (e.g. in supercritical water) or by acid catalysis. The acid hydrolysis of cellulose proceeds *via* the protonation of the polysaccharide, which slowly breaks down to give a cyclic carbenium ion. After rapid addition of water, free sugars (glucose) are liberated (Scheme 1).⁴

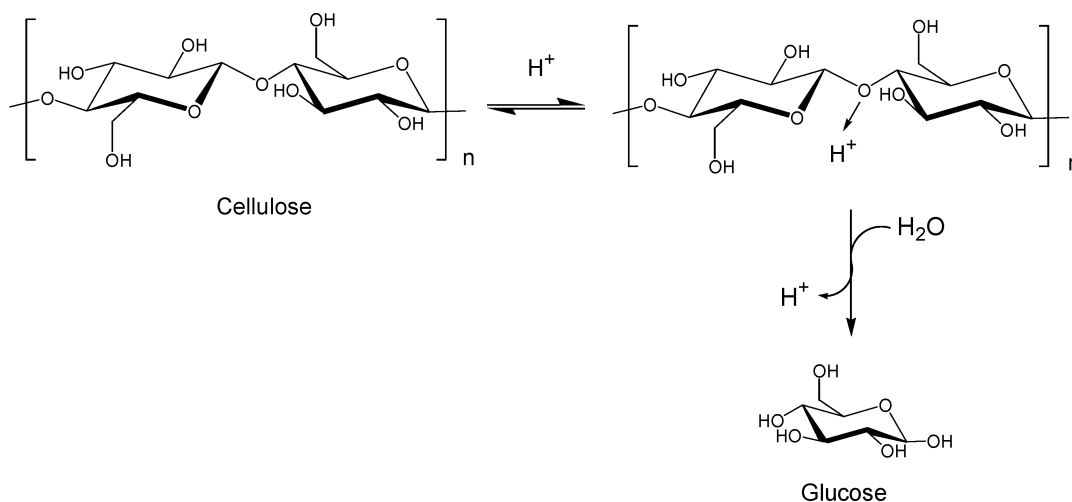
The homogeneous acid-catalyzed hydrolysis of lignocellulosic biomass into wood alcohol has been known since before the First World War. Production units were even built at that time^{5–8} but the development of this technology was limited due to the abundance of accessible cheap oil.

Hydrolysis of cellulose into sugars can be catalyzed by a variety of mineral acids such as H₂SO₄, HCl, HF and HNO₃. Because diluted H₂SO₄ is inexpensive, this method remains the most often used in research pilots or in the few processes at industrial scale.⁵ The method using liquid acids is quite efficient at producing glucose but liquid acids cause corrosion and waste elimination remains problematic. Moreover, if acid hydrolysis conditions are severe (high temperature or concentration), a large fraction of sugars are degraded to undesirable products and tars. Later, enzymatic catalysis was introduced with very selective cellulases for glucose production.⁸ However, these enzymes remain expensive and still have a rather low activity. To try to overcome these drawbacks, other methods have been proposed such as non-catalyzed hydrolysis in supercritical water^{9,10} and the use of heterogeneous catalysis under hydrothermal conditions. In this last field, several studies have been reported during the past few years dealing with the use of metallic and/or acid solid catalysts. Three different approaches have been considered with respect to the nature of the solid catalyst used to dissolve and/or convert (“dissolution–conversion”) cellulose in aqueous media: i) the use of a bi-functional metal–acid catalyst under H₂ atmosphere; ii) the use of a mono-functional solid acid catalyst; iii) the use of mono-functional metallic catalysts. First, Fukuoka and Dhepe reported the direct formation of sugar alcohols (sorbitol and mannitol) in water from cellulose in 31% yield, with bi-functional catalysts such as Pt/ γ -Al₂O₃

^aUniversité de Lyon 1, IRCELYON, Institut de recherches sur la catalyse et l'environnement de Lyon, CNRS, UMR 5256, 2 avenue Albert Einstein, F-69626 Villeurbanne, France.

E-mail: nadine.essayem@ircelyon.univ-lyon1.fr

^bIFP-Lyon, BP 3, F-69360 Solaize, France



Scheme 1 Acid catalyzed hydrolysis of cellulose.

(190 °C, 5 MPa H₂, 24 h).¹¹ In this case Pt/γ-Al₂O₃ may act as a bi-functional catalyst because two functions are present within the same material: the support and the supported metal both play an active role in the reaction. The acidic function of alumina is supposed to promote the hydrolysis of the cellulose into glucose and the supported Pt promotes the hydrogenation of glucose into sorbitol. The use of pure metallic catalysts was investigated by Luo *et al.* in 2007.¹² They reported the treatment of cellulose in hot water in the presence of Ru/C catalysts giving 39% alcohol sugars for 85% conversion (245 °C, 6 MPa H₂, 30 min). Very recently, Ji *et al.* reported the hydrogenolysis of cellulose using supported nickel-promoted tungsten carbides Ni-W₂C/C for the production of ethylene glycol in 60% yield with 100% conversion (250 °C, 6 MPa H₂, 30 min).¹³ In 2008, the conversion of cellulose by means of metal-free solid acids was reported by several teams. Onda *et al.* reported the selective hydrolysis of cellulose into glucose with sulfonated activated carbon (150 °C, 24 h) with yield of 40% for 42% conversion.¹⁴ Suganuma *et al.* described the hydrolysis of cellulose into glucose in 4% yield only (for 65% conversion), using sulfonated amorphous carbon materials but under milder conditions (100 °C, 3 h).¹⁵ Takagaki *et al.* reported the use of transition metal oxides such as HNbMoO₆ for hydrolysis into glucose with a poor yield of 1% (130 °C, 12 h).¹⁶

In the field of biomass transformation, the work reported above is of fundamental importance. Indeed, a novel method of biomass dissolution–conversion is emerging, quite different from biomass pyrolysis since significant lower temperature and pressure levels are involved, together with solid catalysts. However, in the majority of these reports, the results obtained from blank reactions were never deeply analyzed or even mentioned. Moreover, except for Luo *et al.*,¹² the analysis of the solid residue obtained in the case of incomplete cellulose conversion was not reported. The information that could be obtained from these points may be of great importance in order to understand the reactivity of the substrate in the reaction media.

Regarding the work of Fukuoka *et al.*,¹¹ the authors reported the use of bi-functional catalysts under H₂ pressure for the direct

transformation of cellulose into sugar alcohols. The optimised conditions were a temperature of 190 °C, a pressure of 5 MPa and a reaction time of 24 h. The most efficient catalyst was Pt/γ-Al₂O₃. The authors suggested that the acid sites for the hydrolysis of cellulose were generated by a dissociative adsorption of H₂ on the Pt particles followed by a spill over onto the surface of the support, in addition to the intrinsic acid sites of the latter. In this study, the influence of various supports and metals on the yield of sugar alcohols has been well established. However, there is no mention of either the cellulose conversion or the influence of the reaction parameters in the absence of catalyst.

Here we report our results concerning the conversion of cellulose, first in the absence of catalyst, under hydrothermal conditions (150–190 °C) close to those used in the recent investigations reported above. Then, the promoting effect of Pt/γ-Al₂O₃ was investigated. Moreover, a systematic analysis of the solid residue (un-dissolved cellulose) was performed using, X-ray diffraction and ¹³C solid-state NMR spectroscopy, thermo-gravimetric analysis (DTA-TGA) and scanning electron microscopy (SEM).

Experimental

Microcrystalline Avicel® cellulose (degree of polymerisation = 250, mean particle size = 20 μm) was purchased from Aldrich and used as received. Mesoporous γ-Al₂O₃ (BET surface = 208 m² g⁻¹) is commercially available from Axens. Pt/γ-Al₂O₃ (2.5 wt%) was prepared at IFP-Lyon by impregnation of the alumina with H₂PtCl₆ followed by calcination at 520 °C (2 h) (Pt dispersion = 81%, Cl content = 1.77 wt%). The BET surface area of Pt/γ-Al₂O₃ equals 208 m² g⁻¹. The catalyst total acidity and strength distribution was determined by calorimetry of NH₃ adsorption as described elsewhere.¹⁷ Before NH₃ adsorption, the catalyst was reduced at 350 °C in the presence of 13 kPa of H₂, then evacuated at 350 °C for one hour. The calorimetric investigation showed the presence of acid sites of weak strength with a heat of ammonia adsorption of 100–130 kJ mol⁻¹. The total acid sites density equals 130 × 10⁻⁶ mol g⁻¹.

Before use in the catalytic test, the catalyst was reduced under H₂ flow at 350 °C for 3 h. Reactions were performed

in a 150 mL autoclave equipped with graphitized Teflon vessel and a vigorous mechanical agitation system. The autoclave was filled with a suspension of cellulose (0.800 g, 5 mmol equiv. of $C_6H_{10}O_5$ units) in de-ionized water (100 mL), 0.340 g of catalyst (when used) and flushed three times with He at room temperature before introduction of H_2 . The autoclave was then heated up to the desired temperature at $5\text{ }^\circ\text{C min}^{-1}$, the pressure was adjusted to 5 MPa with H_2 and the reaction was run for the specified time. The reaction was stopped by cooling the autoclave using an ice bath. The pressurized gas phase was evacuated, the reaction mixture was collected and the residual solid filtered from the liquid phase over Millipore® Teflon filters (0.45 μm), and dried for 24 h at ambient temperature before weighing. The liquid phase was analysed using a HPLC system equipped with a CarboSep 87C column (300 mm \times 7.2 mm, 80 $^\circ\text{C}$) and a RID detector using water as eluent (0.5 mL min^{-1}). The liquid phase was also analyzed on a Shimadzu TOC-V_{SCH} Total Organic Carbon (TOC) analyzer (720 $^\circ\text{C}$, Pt/ γ - Al_2O_3 catalyst, IR detector). The un-converted solid cellulose was analyzed by TGA-DTA (Setaram A92-12), by XRD (Bruker D5005 X-ray diffractogram), by ^{13}C CP-MAS NMR (Avance DSX400 Bruker spectrometer: 25 $^\circ\text{C}$, 10 kHz, 4 mm probe, NS = 10240, D1 = 4 s, reference TMS) and by SEM (FEI ESE-XL30 microscope).

The degree of crystallinity was calculated using the Diffrac-Plus software as the peak intensities ratio of the crystalline area and total area as indicated in Fig. 1.

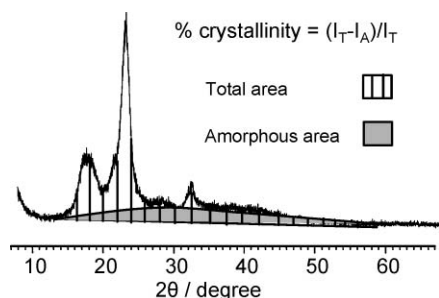


Fig. 1 Degree of crystallinity of cellulose deduced from XRD pattern.

Solubilisation percentages were calculated as the ratio between the total mass of carbon equivalent (mequC) in the filtrate obtained from TOC analysis and the initial mequC calculated as follows: (mass of dry cellulose) \times 12 \times 6/162 (162 = M of $C_6H_{10}O_5$).

Product yields were calculated as the ratio between the number of moles of the product obtained from HPLC to the initial number of moles of $C_6H_{10}O_5$ units (mass of cellulose introduced/M). When a solid catalyst was used, the catalyst mass was subtracted from the mass of remaining solid to get the amount of un-converted cellulose. Indeed, no dissolution of the catalyst (Pt/ γ - Al_2O_3) was observed as indicated by chemical analysis of Pt and Al in the filtrate obtained after 24 h of reaction at 190 $^\circ\text{C}$ under 5 MPa of H_2 (0.340 g of 2.5 wt% Pt/ γ - Al_2O_3 , 100 mL: Pt: $< 0.1\text{ mg L}^{-1}$; $< 0.1\text{ wt}\%$ solubilisation; Al: 0.7 mg L^{-1} ; $0.05\text{ wt}\%$ solubilisation).

Carbon balances were calculated as the ratios of the sum of total mequC obtained from TOC analysis and the mequC in

the remaining solid to the initial mequC in the fresh cellulose sample.

Results and discussion

Our goal was to study the non-catalyzed cellulose dissolution–conversion under the most usual conditions reported in the recent literature and, to investigate the extent of the promotion effect of Pt/ γ - Al_2O_3 on cellulose conversion under these conditions.

Cellulose dissolution–conversion under hydrothermal conditions in the absence of solid catalyst

First, we evaluated the influence of the temperature on the dissolution–conversion of cellulose in the absence of catalyst. Fig. 2 shows that only 2% of cellulose can be dissolved or converted at 150 $^\circ\text{C}$ after hydrothermal treatment for 24 h. This is consistent with the resistance of cellulose to water dissolution under soft conditions.⁴ However, at higher temperatures, significant cellulose dissolution was observed: 11% of the cellulose dissolved at 175 $^\circ\text{C}$ and 35% dissolved at 190 $^\circ\text{C}$, after 24 h of reaction under 5 MPa of H_2 . These results were not expected starting from crystallized cellulose. Indeed, cellulose hydrolysis is generally reported under more severe temperature conditions, *i.e.* under sub or supercritical water conditions.⁹ To our surprise, this extent of non-catalyzed cellulose dissolution–conversion under relatively mild hydrothermal conditions (175–190 $^\circ\text{C}$) was not really reported in the recent publications dedicated to cellulose conversion by means of solid catalysts.

Second we evaluated the influence of the atmosphere. We performed the reaction with cellulose in water at 190 $^\circ\text{C}$ in the absence of pressurized hydrogen. Note that the autogeneous pressure at this temperature was 1 MPa. We observed a solubilisation ratio of 40% after 24 hours (Entry 4, Table 1). This result shows that in the absence of catalyst and for the same reaction time, the solubilisation ratio seems to be only temperature dependent.

Then, we evaluated the influence of the residence time, at 190 $^\circ\text{C}$ under 5 MPa of H_2 . Fig. 3a shows that the cellulose dissolution–conversion increased with time until reaching a plateau at 60% dissolution after 100 hours of reaction. In the absence of catalyst, the liquid reaction mixture analysis showed a yield of 2% glucose and 3% 5-hydroxymethylfurfural (5-HMF, a dehydration product of glucose) (Entry 1, Table 1). This monomer distribution did not change significantly with the residence time (Entry 3, Table 1). This indicates that the observed phenomenon is rather limited to the dissolution–conversion of the cellulose into soluble polymers or oligomers under these conditions and that higher residence time does not favour the further transformation of soluble polymers into monosaccharides and other derivatives as could be expected. However, for the longest residence time, we cannot exclude the possible side oligomerisation of monomer derivatives such as 5-HMF since only mono and disaccharides are identified by the HPLC method we used. Higher soluble oligo and polysaccharides or other polymers are only detected by TOC analysis. Advanced mass spectrometry techniques are in progress to check if the nature of the soluble polymers is residence time dependent.

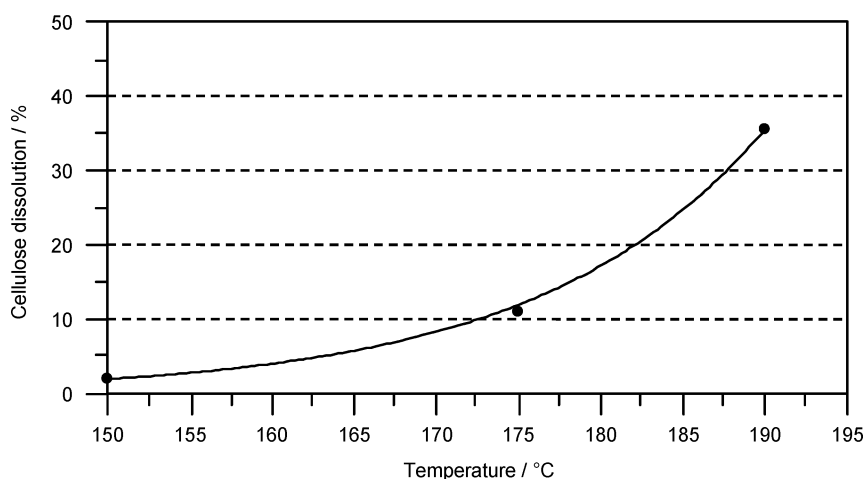


Fig. 2 Dissolution of cellulose as a function of temperature. Conditions: 800 mg cellulose, 100 mL H₂O, 5 MPa H₂, 24 h.

Table 1 Dissolution of cellulose under various conditions^a

Entry	Cellulose	Atmosphere	Reaction time (h)	Catalyst	Solubilisation (%)	Carbon balance (%)	Products yields (%)
1	Fresh	H ₂	24	—	35	90	Glucose 2% 5-HMF 3%
2	Re-used	H ₂	24	—	38	75	Glucose 4% 5-HMF 6%
3	Fresh	H ₂	100	—	60	77	Glucose 1% 5-HMF 1%
4 ^b	Fresh	He	24	—	40	92	Glucose 1% 5-HMF 4.8%
5	Fresh, diluted	H ₂	100	—	60	92	Glucose 1.5% 5-HMF 4.5%
6	Fresh, conc.	H ₂	100	—	35	90	Glucose 2%
7	Fresh	H ₂	24	γ-Al ₂ O ₃	41	84	Glucose 3% 5-HMF < 1%
8	Fresh	H ₂	24	Pt/γ-Al ₂ O ₃	60	89	Glucose < 1% Sorbitol 15%
9	Fresh	H ₂	100	Pt/γ-Al ₂ O ₃	69	97	Glucose < 1% Sorbitol 11%
10 ^c	Fresh	H ₂	24	Pt/γ-Al ₂ O ₃	7	94	Glucose < 1% 5-HMF 0%
11	Fresh	He	24	Pt/γ-Al ₂ O ₃	38	65	Glucose < 1% 5-HMF 0%

^a Common conditions: 5 MPa, 190 °C. ^b 1 MPa bar of autogeneous pressure. ^c 150 °C.

To determine if the dissolution–conversion phenomenon occurred on a specific part of the cellulose material (amorphous or crystalline part), un-dissolved cellulose was used as reactant (*i.e.* charged in pure water for a second hydrothermal treatment, in the same conditions). Again, 38% of the re-used solid cellulose was dissolved after 24 h, a similar percentage of dissolution as for the fresh cellulose (35%) (Entry 2, Table 1). This may indicate that the recovered cellulose does not correspond to a less reactive part of the material, and that the cellulose dissolution–conversion occurred homogeneously onto the polymer. Therefore, it appears possible that the observed 60% solubility after 100 h (corresponding to 480 mg of cellulose dissolved) correspond to the maximum solubility of the cellulose under our concentration conditions (*i.e.* saturation of the solution with soluble polymeric species). This would

mean that with a lower concentration of cellulose a higher percentage of dissolution should be obtained. Using half of the initial cellulose concentration, 400 mg in 100 mL of water instead of 800 mg, the percentage solubility also reached 60% after 100 h (corresponding to 240 mg of cellulose dissolved) (Entry 5, Table 1). Moreover, using twice the amount of cellulose, 1600 mg in 100 mL, 35% solubility was obtained after 100 h, corresponding to 560 mg of dissolved cellulose (Entry 6, Table 1). This ruled out the possibility of saturation of the solution since increasing the amount of cellulose in the reactor increased the amount of cellulose dissolved.

Glucose and 5-HMF yields are known to be formed *via* acid hydrolysis of cellulose and acid catalyzed dehydration of hexoses. Accordingly, we propose that, in the absence of a metal catalyst, the global process is governed by protonic catalysis, as suggested

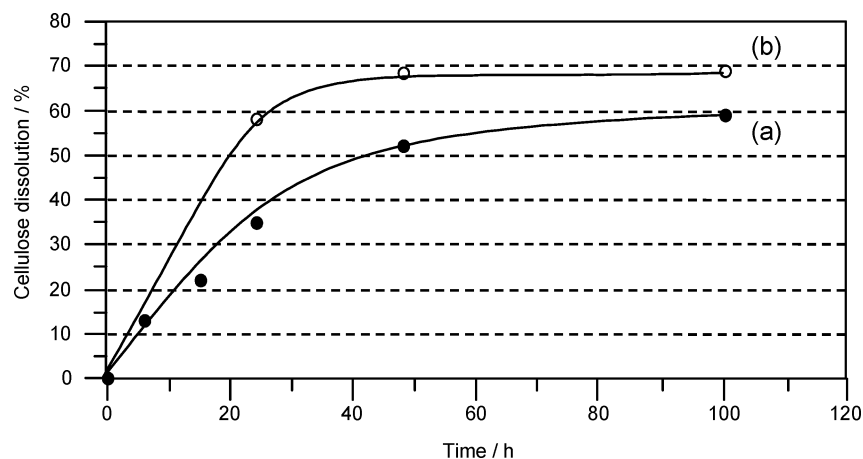


Fig. 3 Dissolution of cellulose as a function of time: (a) in the absence of catalyst, (b) in the presence of Pt/ γ -Al₂O₃. Conditions: 800 mg cellulose, (340 mg catalyst), 100 mL H₂O, 5 MPa H₂, 190 °C.

in the case of sub and supercritical water media. The pool of H₃O⁺ is most likely produced by water auto-protolysis, favoured by the temperature increase.

Our results simply evidence the dependence of the dissolution–conversion of cellulose on the severity of the main parameters for hydrothermal treatment (temperature and residence time) although relatively mild conditions were involved (temperature range of 175–190 °C). These observations are in agreement with a recent investigation of starch hydrothermal degradation.¹⁸

Cellulose dissolution–conversion under hydrothermal conditions in the presence of 2.5 wt% Pt/ γ -Al₂O₃

We also studied the dissolution–conversion of cellulose in the presence of heterogeneous Pt/ γ -Al₂O₃ over 24, 48 and 100 h of reaction (Fig. 3b). We note that the “initial rate” (0–24 h) of cellulose dissolution–conversion is significantly increased in the presence of Pt/ γ -Al₂O₃. In the absence of solid catalyst, the “initial rate” of cellulose dissolution–conversion equals 0.72 meq G.U. h⁻¹ (G.U. for glycosyl unit = C₆H₁₀O₅ entities) versus 1.25 meq G.U. h⁻¹ in the presence of Pt/ γ -Al₂O₃. Most likely, distinct mechanisms are involved as suggested by the different nature of the species produced (Entries 1, 3, 8 and 9, Table 1). A yield of 15% sorbitol was obtained after 24 h, in agreement with the results reported by Fukuoka *et al.* (Entry 8, Table 1).¹¹ After 100 h of reaction, this yield was 11% (Entry 9, Table 1).

The influence of the atmospheric composition was investigated. Hydrogen was replaced by 5 MPa of He. Here, the percentage of cellulose dissolution was lowered from 60% to 38% (Entry 11, Table 1). H₂ atmosphere combined with a metallic center was seen to increase the cellulose dissolution. The roles of H₂ and Pt in this process are not straightforward. (Note that due to the large excess of H₂ (300 mmol vs 5 mmol of reactant), its consumption during the reaction was not monitored.)

The first remark concerns the higher overall activity for monomer formation and the higher yield of sorbitol obtained over Pt-containing γ -Al₂O₃ compared to the yield of glucose (2–3%) obtained in the absence of a solid catalyst or even over Pt-free γ -Al₂O₃ (Entry 7, Table 1). This may indicate

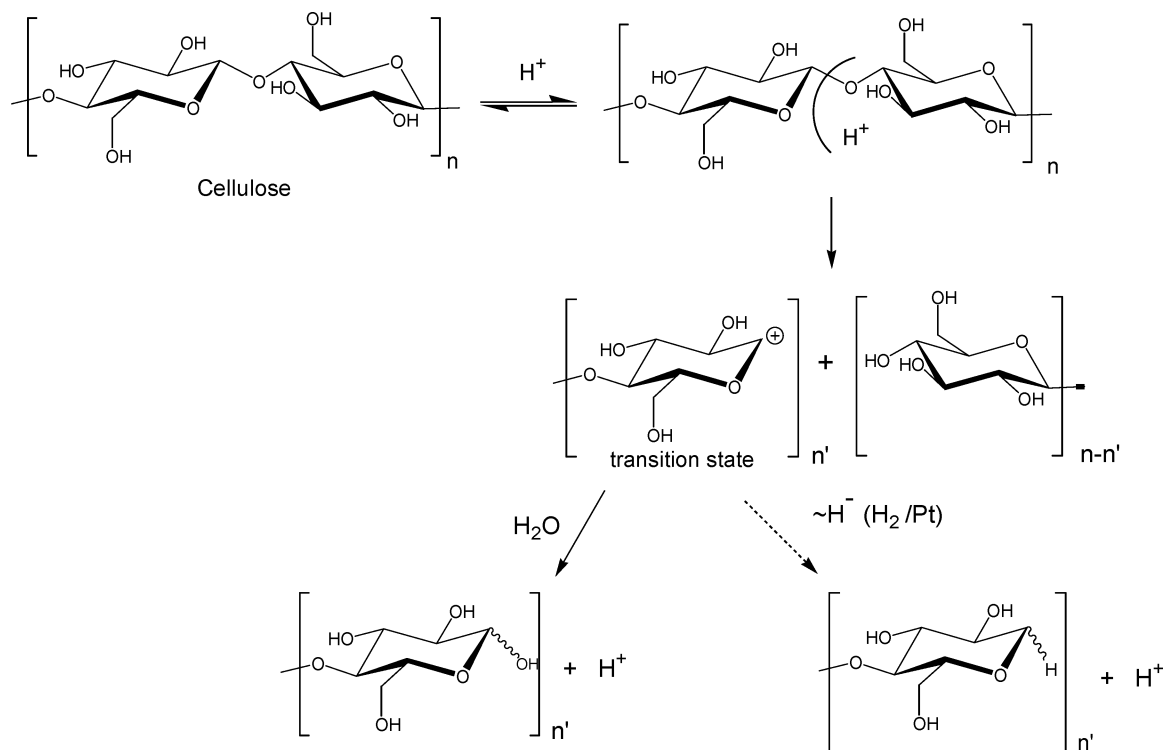
that the metallic function is not restricted to the successive hydrogenation of the monosaccharide to the corresponding sugar alcohol (sorbitol) and also plays a role in the dissolution–conversion reaction. In the presence of hydrogen, the metallic function may directly affect the initial activation step of the cellulose by increasing the pool of H⁺ formed by heterolytic H₂ dissociation as proposed by Fukuoka *et al.*¹¹ The metallic centres in the presence of H₂ may intervene in the carbocationic chain mechanism initiated by the glycosidic bond cleavage with H₃O⁺. The cyclic carbenium ions, once formed, might react with H₂O or they may be involved in a hydride transfer step promoted by H₂/Pt, which results in H⁺ release to the media (Scheme 2). The above proposition is based on literature data only. Indeed, earlier work reports the possibility of such a heterolytic H₂ activation with supported and non-supported Pd catalysts. It was shown that the polarisation Pd^{δ+}–H^{δ-} or Pd^{δ-}–H^{δ+} depends on the polarity of the substrate.^{19–21} In our case, a carbocationic substrate would favour Pt^{δ+}–H^{δ-} species promoting the hydride transfer step.

The second remark concerns the yield of sorbitol which did not increase and even slightly decreased when the cellulose dissolution was kept constant for a longer residence time. One could suggest that the successive transformations of soluble polysaccharides into monosaccharides and their derivatives remain of limited importance under these conditions of temperature and pressure, over Pt/ γ -Al₂O₃ in the presence of H₂. Moreover, the possibility of catalyst deactivation after 48 hours cannot be excluded.

Finally, one can note the absence of cellulose dissolution–conversion at 150 °C over Pt containing γ -Al₂O₃ in the presence of H₂ (Entry 10, Table 1), which may reflect the very high activation energy needed for that reaction, and confirms the low acid strength of the aqueous media at 150 °C to promote cellulose protonation at such a low temperature.

Characterization of the solid cellulose recovered after non-catalyzed hydrothermal treatment for 24 h at 190 °C

Crystallinity modification. The degree of crystallinity of cellulose can be determined by X-ray diffraction.²² This method is mainly used for the determination of crystallinity changes in



Scheme 2 Hydrothermal depolymerisation of cellulose in the presence of H_2 and $Pt/\gamma-Al_2O_3$: a possible pathway.

cellulose dissolution or cellulose surface chemical modification.^{23–27} However, few reports concern the partial hydrolysis of cellulose. As an example, Luo *et al.* reported that after partial hydrolysis in hot water (250 °C), no change in the degree of crystallinity was detected even at very high conversion.¹²

Fig. 4 shows the XRD patterns obtained from cellulose before reaction and after 24 h of reaction at 190 °C under 5 MPa of H_2 , in the absence of catalyst. We can see that the hydrothermal treatment did not affect the crystallinity index of the material. Calculations gave a crystallinity index of 71% and 69% before and after reaction, respectively.

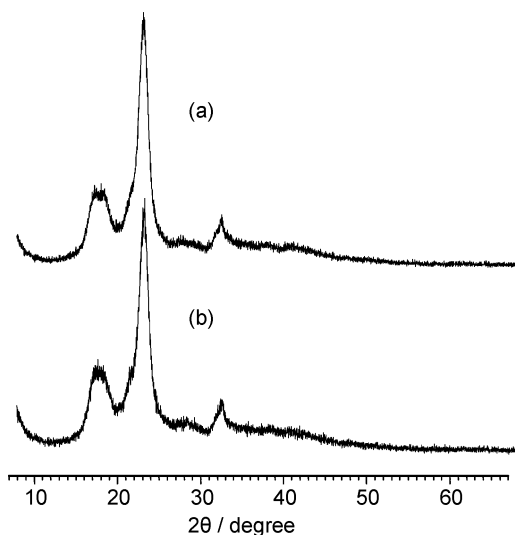


Fig. 4 XRD spectra of cellulose: (a) before reaction, (b) after hydrothermal treatment of 24 h at 190 °C under 5 MPa H_2 .

The degree of crystallinity of cellulose can also be determined using ^{13}C solid-state NMR spectroscopy. A typical spectrum of cellulose displays 6 signals from 105 to 64.0 ppm.²⁸ The signals around 89.0 and 84.0 ppm are attributed to the C4 carbon of glycosyl units present in the crystalline and amorphous regions, respectively. Some earlier works have shown contradictory results on the determination of the crystallinity change using this technique. While some studies clearly indicated a change in the degree of crystallinity during the course of partial acidic hydrolysis^{29,30} or dissolution in ionic liquids²⁸ others showed the absence of any effect.³¹ Fig. 5 shows the solid-state ^{13}C CP-MAS NMR spectra obtained from cellulose before reaction and after 24 h of reaction at 190 °C under 5 MPa of H_2 . Almost identical spectra were obtained. The ratio of intensities of the signals at 86.6 and 82.2 ppm are very close (1.39 and 1.32, respectively), again showing no significant change in the crystallinity index.

From XRD and NMR analysis, we can say that the crystallinity index of the un-dissolved cellulose was not modified by hydrothermal treatment for 24 h at 190 °C. Therefore, this indicates clearly that the dissolution–conversion of the cellulose did not specifically affect the amorphous part of the polymer as one could expect. This is in line with our experimental results reported above, which have shown that the cellulose recovered after hydrothermal treatment did not correspond to the more resistant part of the substrate to water.

Morphology modification. To get information on a possible morphology evolution, we performed SEM analysis of the samples before and after reaction. The pictures in Fig. 6 indicate that the average particle size increased from 20–30 μm (particle size of Avicel®) before reaction to 150–200 μm after 100 h of

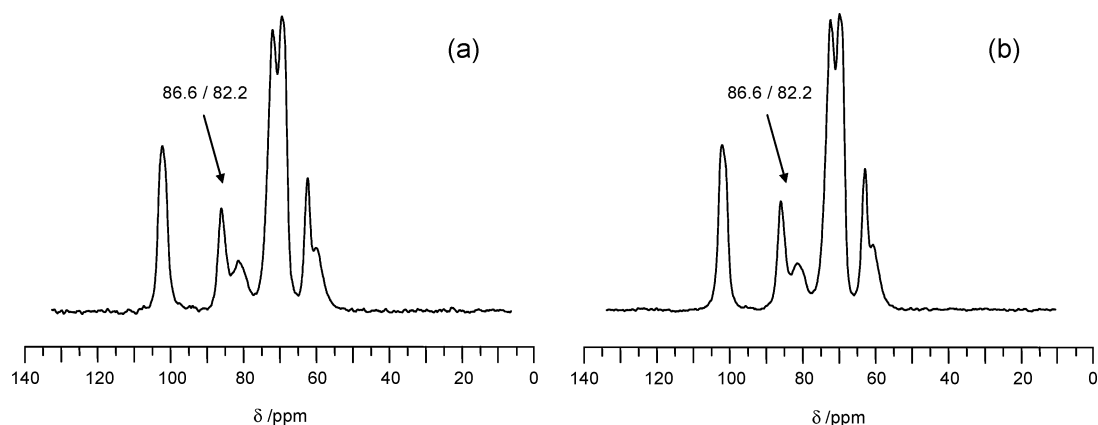


Fig. 5 Solid-state ^{13}C CP-MAS NMR spectra of cellulose: (a) before reaction, (b) after hydrothermal treatment for 24 h at 190 °C under 5 MPa H_2 .

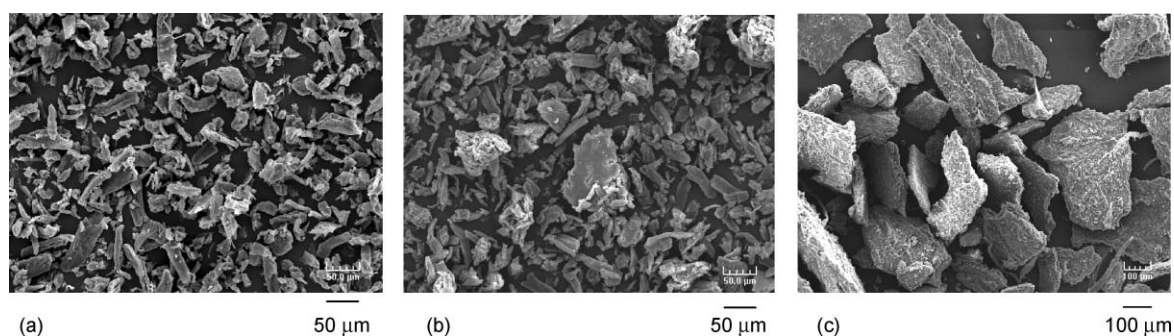


Fig. 6 SEM analysis of cellulose: (a) before reaction, (b) after 24 h of reaction, (c) after 100 h of reaction at 190 °C under 5 MPa H_2 .

reaction, with the appearance of 50 μm particles after 24 h of reaction. Therefore a change in the morphology of the cellulose particles occurred during the reaction. The reaction led to the formation of bigger particles. Most likely these larger particles may correspond to agglomerations of the primary cellulose crystals since the crystallinity index did not change. Such a change in the morphology but not in the structure was observed previously by Zhao *et al.* during the acid hydrolysis of cotton linters.³¹ It is worthy of note that the non-round shape of these particles suggests the absence of the formation of humins,³⁰ the insoluble dark-brown substance usually formed during acid decomposition of glucose and polysaccharides.

We also performed thermo-gravimetric analysis^{31,32} under air flow to determine the behaviour of the cellulose before and after reaction as a function of hydrothermal temperature and duration. The TG curves are displayed in Fig. 7 (temperature dependence) and in Fig. 8 (time dependence). All curves show two mass losses at 340 °C and at 460 °C which occur together with intense exothermic phenomena. The combustion is completed in all cases at 500 °C. Interestingly, the relative intensity of these two weight losses changes depending on the reaction temperature or the reaction time, showing a relative decrease of the low temperature degradation phenomenon with the severity of the hydrothermal treatment (temperature or residence time). Even if the interpretation of these two distinct oxidations is not direct, we can underline the clear relation between their relative evolution and the percentage of cellulose dissolution–conversion. Accordingly, one can note that the TG curves of the cellulose

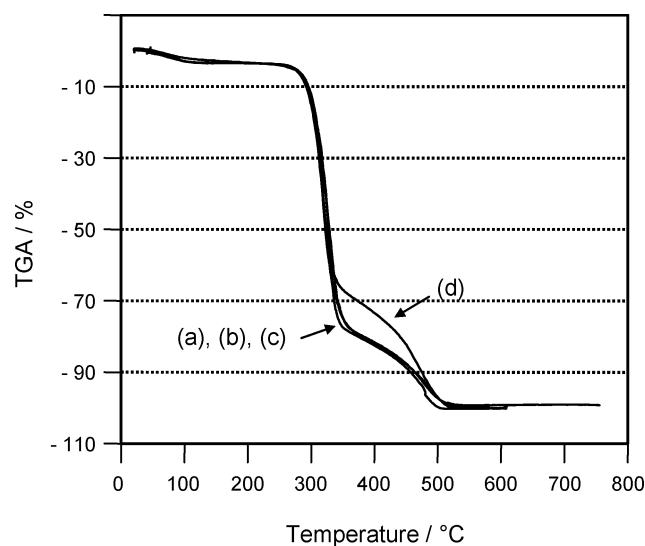


Fig. 7 TGA analysis of fresh and recovered cellulose after 24 h of hydrothermal treatment at different temperatures. (a) Fresh, (b) 150 °C, (c) 175 °C, (d) 190 °C.

treated at 150 °C are similar to those of the fresh cellulose, in full agreement with the lack of dissolution–conversion at this temperature. This implies that a higher temperature is needed for the full oxidation of the cellulose remaining after a more severe treatment.

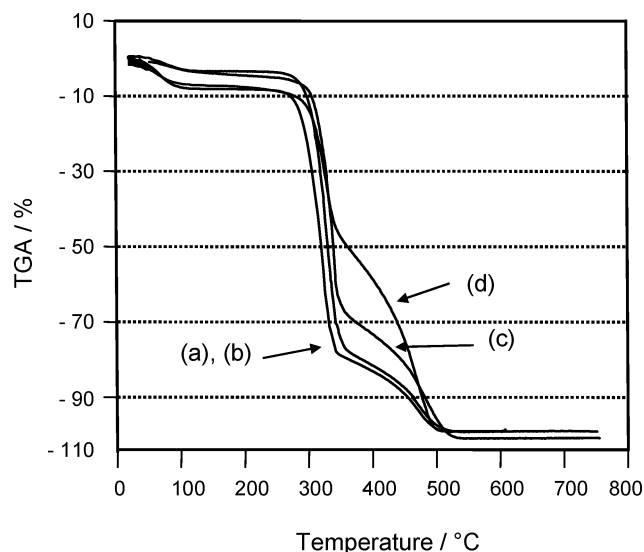


Fig. 8 TGA analysis of fresh and recovered cellulose after hydrothermal treatment at 190 °C for increasing duration (a) Fresh, (b) 3 h, (c) 24 h, (d) 100 h.

Nevertheless, an explanation may be proposed to tentatively rationalize all the previous observations together with earlier published studies. Moissev *et al.*³² have proposed that the transformation of cellulose may involve different glycosidic bonds with different reactivities, depending on their location within the polymer, *i.e.* internal or terminal bonds. It is reasonable to think that the glycosidic bonds located at the surface of the cellulose crystals or at the agglomeration of crystalline (or amorphous) cellulose as well as those located at the ending of the linear polymer may present a higher reactivity simply due to an easier accessibility. Therefore, TG curves might reveal the contribution of internal and external glycosyl units with different reactivity with respect to oxidation, which seems to fit well with the cellulose dissolution–conversion behaviour in hydrothermal conditions. The decreasing reactivity of the residual cellulose is also in agreement with the formation of larger particles, which present a reduced proportion of superficial glycosidic bonds.

Conclusion

We showed that dissolution–conversion of cellulose occurred at 190 °C under 5 MPa of H₂ to an extent of 35% of the introduced amount after 24 hours even in the absence of catalyst. This temperature is needed to obtain significant dissolution and a yield of 2% glucose can be obtained. Analysis of the residue indicated that the reaction did not occur specifically on the amorphous or on the crystalline parts of the polymer. XRD and ¹³C solid-state NMR showed that the crystallinity of the introduced cellulose and of the recovered cellulose kept constant. SEM analyses showed a change in the morphology when the reaction was pursued over 100 hours. The presence of bigger particles, more difficult to degrade, may arise from the agglomeration of primary cellulose particles. TGA analyses of the fresh and non-solubilized cellulose evidenced two distinct oxidation phenomena. They are tentatively ascribed to oxidation of internal and external glycosyl units. The contribution of external glycosyl units which are dominant in the fresh cellulose was seen

to be strongly dependent on the severity of the hydrothermal treatment. Finally, the presence of Pt/ γ -Al₂O₃ increased the initial rate of dissolution–conversion significantly as well as the total yields of monomer sugars, especially sorbitol, formed during this treatment. Platinum associated with hydrogen is proposed to intervene not only in the hydrogenation of glucose into sorbitol but most likely in one of the elementary steps such as H⁺ generation *via* H₂ heterolytic dissociation and/or hydride transfer steps.

As a general comment, we may say that the system H₂O/Pt/ γ -Al₂O₃ presents some indisputable advantages compared to the use of acid solutions to promote cellulose depolymerization: the problem of acid waste elimination is avoided, together with the corrosion problems associated with the use of liquid acids.

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