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A small change in the surface polarity of cellulose causes a significant improvement in its conversion to glucose and subsequent catalytic oxidation

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ABSTRACT

Three different amino acids were adsorbed onto the surface of microcrystalline cellulose, which caused changes in the polarity and roughness at the cellulose surface. The adsorptions partially modified the hydrogen bonding network of the cellulose structure, leading to more reactive cellulose residues that were facilely oxidised to gluconic acid by oxygen in the presence of gold zeolite supported catalysts. The conversion of cellulose and the selectivity for gluconic acid was controlled by the identity and amount of amino acid adsorbed onto the cellulose and the extra-framework cation in the zeolite support.

1. Introduction

Cellulose is the largest organic raw material in the world, but many cellulosic products are at present not renewable. Therefore, efforts have been made to convert cellulosic materials into valuable chemicals and renewable fuels [1,2]. The molecular structure of cellulose strongly inhibits its depolymerisation. Cellulose chains are built up from linearly connected anhydroglucopyranose units that are covalently bonded through acetal functions [3,4]. Because of the abundance of hydroxyl groups and oxygen atoms, cellulose is able to form an extensive network of intra- and intermolecular hydrogen bonds, which confers remarkable chemical stability and makes the direct utilisation of cellulose a challenge. One of the promising methods to convert cellulose is heterogeneous catalysis. In this context, acid catalysis has been used to depolymerise cellulose, producing glucose monomers that were converted into bioethanol [5,6] or ethylene glycol [7–9]. Some other efforts for high-temperature pyrolysis or gasification of cellulose to bio-oils have also been reported [10], but the optimisation of these processes remains incomplete.

The transformation of cellulose under mild conditions into glucose or other molecules that can in turn be converted to chemicals is quite desirable. Therefore, many studies have been focused on the development of an efficient heterogeneous catalyst for the depolymerisation of polysaccharides containing β-1,4-glycosidic linkages [11,12]. Cellobiose, which is a D-glucose dimer connected by a β-1,4-glycosidic bond, has been used as a simple model of cellulose [13]. Of course, there are significant differences between cellobiose and cellulose, but it was assumed that the catalytic conversion of cellobiose may provide helpful insights for the development of efficient routes of cellulose degradation. Thus, some works have reported heterogeneous catalytic conversions of cellobiose by hydrolysis or hydrogenation in an acidic aqueous medium [14,15]. Recently, the oxidative conversion of cellobiose to gluconic acid in the presence of oxygen catalysed by gold nanoparticles loaded on several supports was reported [16,17]. The best results were obtained with a catalyst based on gold nanoparticles in an acidic support. However, the works where cellulose was used instead cellobiose are scarce [18]. This work intends to perturb the hydrogen bonds network of microcrystalline cellulose and then catalytically oxidise the material to gluconic acid in the presence of gold

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Table 1
Elemental analysis of the grafted and ungrafted samples of cellulose.

Code sample	Amount (wt%) of chemical elements			Amount (wt%) of amino acid
	C	O	N	
MC	47.40	52.60	–	–
Ala-MC	47.17	52.32	0.51	3.1
Pro-MC	47.54	52.16	0.30	2.2
PhAla-MC	48.17	51.50	0.33	3.7
Ala-MC-L	47.16	52.57	0.27	1.3
Ala-MC-H	47.79	51.39	0.82	5.0
Ala-MC-VH	47.58	51.17	1.25	7.4
PhAla-MC-L	48.41	51.38	0.21	2.4
PhAla-MC-H	48.48	51.01	0.51	5.6
PhAla-MC-VH	48.56	50.72	0.72	8.2

nanoparticles supported on the acid zeolite HY. It was earlier [19,20] reported that it is possible the substitution of hydroxyl groups in cellulose with small biological molecules, such as amino acids. The grafting of cellulose was accompanied, in general, by the carbamate functionalisation at cellulose surface. To perturb the cellulose surface and pretend to increase its reactivity, in this work amino acids (alanine, proline, and phenyl alanine) were adsorbed onto the cellulose surface, weakening the hydrogen-bond network. The surface polarity of the cellulosic materials was characterised by the adsorption of 3-(4-amino-3-methylphenyl)-7-phenylbenzo-1,2b:4,5b′-difuran-2,6-dione, a solvatochromic molecule [21]. This is a suitable probe because the interaction of the surface environment with a solvatochromic dye is influenced by various interactions, such as acid–base, dipole–dipole and induced dipole–dipole interactions as well as London dispersion forces.

2. Experimental procedures

2.1. Materials

Proline, phenyl alanine, alanine, microcrystalline cellulose and all solvents were acquired from Sigma–Aldrich (USA).

Microcrystalline cellulose (MC) was hydrothermally treated with an amino acid (alanine, phenyl alanine or proline). Typically, 10 g MC was suspended in 100 mL aqueous solution containing 1 g ^{13}C-enriched amino acid. The suspension was stirred for 1 h and then refluxed. After 10 min of refluxing, the pH was adjusted to 5 by adding concentrated HCl. Refluxing was continued for 5 h, and the solid was then separated by centrifugation and washed repeatedly until the wash water pH became neutral. The MC functionalised with alanine was named Ala-MC. The samples functionalised with phenyl alanine and proline were labelled PhAla-MC and Pro-MC, respectively, and these compounds were prepared in a similar manner as Ala-MC.

In order to elucidate the effect of the amount of a same amino acid adsorbed on the cellulose surface, two other series of samples were prepared. The first one was prepared in a similar manner as Ala-MC but the amount of alanine was varied, basically a sample with a lower and two with a higher amount of alanine than in Ala-MC were prepared. Sample with the lowest amount of amino acid was named Ala-MC-L and two with higher amount were labelled Ala-MC-H (H for high) and Ala-MC-VH (VH means very high), Table 1. The chemical analysis of the series where the amount of phenyl alanine was varied is also reported in Table 1.

Catalyst Au-HY was prepared from zeolite NH_4Y (Si/Al ratio of 5.1), which was heated at 400 °C for 6 h to obtain the corresponding protonated HY zeolite. The HY zeolite was suspended in a solution of colloidal Au (5 nm) purchased from Sigma–Aldrich (USA). After 3 h, the solid was separated by centrifugation, repeatedly washed until the wash water was colourless, dried at 50 °C and reduced at 400 °C under hydrogen flow (10 mL/min) for 4 h. The amount of gold in the catalyst was determined by atomic absorption spectroscopy as 0.8 wt%. This catalyst was named Au-HY. Two other gold-faujasite catalysts were prepared in a similar manner except that the compensating cation was changed using sodium and barium faujasite supports to form Au-NaY and Au-BaY, with a gold loading of 0.93 and 0.97 wt%, respectively.

2.2. Characterisation

The cellulose samples were characterised by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), small angle X-ray scattering (SAXS), and infrared (FTIR) and ^{13}C nuclear magnetic resonance (MAS NMR) spectroscopy. Changes in polarity at the cellulose surface were characterised by the adsorption of 3-(4-amino-3-methylphenyl)-7-phenylbenzo-1,2b:4,5b′-difuran-2,6-dione dye [22,23] followed by UV–vis spectroscopy.

Catalyst AuY was characterised by XRD, ^{27}Al and ^{29}Si MAS NMR and transmission electron microscopy (TEM).

The chemical analysis was obtained using XPS. The analysis was carried out using a VG Microtech ESCA2000 Multilab UHV system, with a Mg Kα X-ray source (1253.6 eV) and a CLAM4 MCD analyser. The base pressure during the analysis was 1.37×10^{-8} Pa. The peak positions were referenced to the C 1s hydrocarbon groups in 284.50 eV central peak position. The XPS spectra were fitted with the program SDP v 4.1 [24].

The XRD patterns were acquired using a diffractometer (D8 Advance-Bruker) coupled to a copper anode X-ray tube. Kα radiation (40 kV and 30 mA), wavelength of 1.315 Å, was selected with a diffracted beam monochromator. The presence of different crystalline phases was confirmed by fitting the diffraction pattern with the corresponding Joint Committee Powder Diffraction Standards (JCPDS).

A Kratky camera coupled to a copper anode tube was used to measure the SAXS curves. The distance between the sample and the linear proportional counter was 25 cm, and a Ni filter selected for the Cu Kα radiation. To perform the measurements, the sample was introduced into a capillary tube. Intensity $I(h)$ was measured for 9 min to obtain statistical significance. The SAXS data were processed with the ITP program [25–27], where the angular parameter (h) is defined as $h = 4\pi \sin\theta/\lambda$, where θ and λ are the X-ray scattering angle and wavelength, respectively. The obtained data can be described by $I(q) = \Sigma_i I_i(0) \exp[-(R_{gi}q)^2/3]$, where $I_i(0)$ denotes the scattering intensity at $q = 0$ of the scattering centre i with the radius of gyration R_{gi} [26]. The fractal dimension of the scattering objects was evaluated from the slope of the curve $\log I(h)$ versus $\log(h)$ according to the Porod law [28,29].

Mid-infrared (FTIR) spectra were acquired at room temperature using a Perkin Elmer Series spectrophotometer (Model 6X) operated in the ATR-FTIR mode. The spectra were recorded over the 400–4000 cm^{-1} spectral window by averaging 32 scans at a maximum resolution of 4 cm^{-1}.

^{13}C CP MAS NMR spectra were obtained at a frequency of 100.58 MHz using a 4 mm cross-polarisation (CP) MAS probe spinning at a rate of 5 kHz. Typical ^{13}C CP MAS NMR conditions for ^{1}H–^{13}C polarisation experiment used a $\pi/2$ pulse of 4 μs, contact time of 1 ms and delay time of 5 s. Chemical shifts were referenced to a solid shift at 38.2 ppm relative to TMS.

The morphology of the samples was studied with a SEM Jeol 7600 scanning electron microscope.

The UV–vis absorption maximums of the aminobenzofurandione dye adsorbed on the cellulosic materials were recorded in the reflectance mode using a UV–vis spectrometer (Perkin-Elmer Lambda 40). A solution of the solvatochromic probe in 1,2-dichloroethane was added to the cellulose materials. The amount of dye was 0.1 mg per gram of sample.