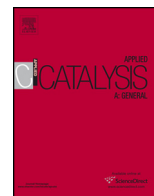




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# Conversion of cellulose to 2,5-hexanedione using tungstated zirconia in hydrogen atmosphere

Flora Chambon<sup>a,\*</sup>, Franck Rataboul<sup>a</sup>, Catherine Pinel<sup>a</sup>, Amandine Cabiac<sup>b</sup>,  
Emmanuelle Guillon<sup>b</sup>, Nadine Essayem<sup>a,\*</sup>

<sup>a</sup> Institut de Recherche sur la Catalyse et l'Environnement de Lyon, IRCELYON, Université Lyon 1, CNRS, UMR5256, 2 avenue Albert Einstein, F-69626 Villeurbanne, France

<sup>b</sup> IFP Energies nouvelles – Lyon Establishment, BP 3, F-69360 Solaize, France

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### ABSTRACT

2,5 Hexanedione is produced from cellulose using ZrW in the presence of hydrogen while lactic acid is the main product in helium atmosphere. FTIR and kinetics studies strengthened the proposed mechanism which involves important elementary steps, namely hydroxyls abstractions and hydride transfers promoted by the Lewis acid sites of ZrW. Moreover the important increase in cellulose conversion in the presence of ZrW in hydrogen atmosphere was explained by the likely formation of additional Brønsted acid sites formed by hydrogen interacting with ZrW which catalyze the protolysis of the glycosidic bonds in cooperation with the pool of hydroxonium ions provided by the self-protolysis of water at 190 °C.

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## 1. Introduction

For environmental and sustainable development concerns, researchers are doing a spectacular efforts in using renewable resources for the production of biofuels and platform chemicals, especially the lignocellulosic one due to its large availability and non-edibility. Cellulose, the main component of the lignocellulose is a biopolymer composed of glucose units linked by  $\beta$ -1,4-glycosidic bonds which constitutes a material of choice since it is seen as a glucose reserve. Intermolecular and intramolecular hydrogen bonds existing in the crystalline network of the cellulose confer to it a high resistance to chemical conversion in conventional solvents [1]. However, it is known that hydrolysis of cellulose into sugars can be catalyzed by strong mineral Brønsted acids such as  $H_2SO_4$ , HCl and HF. Because mineral acids are inexpensive, this method remains the most often used in research pilot development or in the few processes at industrial scale [2]. This method using liquid acids produces glucose but causes corrosion and waste elimination remains problematic. Moreover, if acid hydrolysis conditions are severe (high temperature and/or concentration), a large

fraction of sugars is degraded to undesired oligomers and tars. Later, enzymatic catalysis has been introduced with very selective cellulases for glucose production. However, these enzymes remain expensive and have still a rather low activity [2]. Recently, to try to overcome these drawbacks, other methods using heterogeneous catalysis in hydrothermal conditions appeared as an important breakthrough. From the pioneering works of Fukuoka in 2007, we can distinguish three main routes of cellulose transformation based on the nature of the bioproducts derived from glucose: hydrogenation, hydrogenolysis, or dehydration [3]. The first one is based on noble metals such as Ru/C [4] or Pt/ $Al_2O_3$  [3] and leads to the formation of sorbitol and hexitols directly from cellulose. The second route produces shorter polyols in hydrogenolysis conditions, typically using transition metal catalysts and higher temperatures, i.e. ethylene glycol formation over Ni/WC at 245 °C [5]. The third one concerns the use of Brønsted acid catalysts such as sulfonated carbon [6–8] under milder temperature conditions to give glucose and its derivatives formed via Brønsted acid catalyzed mechanism: 5-HMF and levulinic acid.

Beside these three main ways of cellulose transformation, a fourth one can be considered, using Lewis acids as catalysts to produce lactic acid in aqueous media [9] or lactate in alcoholic media [10]. In a previous study, we have shown that solid Lewis acids, such as tungstated alumina and tungstated zirconia, promote selectively

\* Corresponding authors. Tel.: +33 4 72445315.  
E-mail address: [nadine.essayem@ircelyon.univ-lyon1.fr](mailto:nadine.essayem@ircelyon.univ-lyon1.fr) (N. Essayem).

the cellulose depolymerization in lactic acid in water. We proposed that the solid Lewis acid sites intervene in cooperation with the pool of hydroxonium ions provided by the water self-protolysis at 190 °C to selectively depolymerize crystalline cellulose into lactic acid [9]. The Lewis sites are proposed to promote C–C and C–O scissions via coordination of the hydroxyl groups of the soluble polysaccharides with the Lewis centres.

The present paper reports the influence of H<sub>2</sub>/He atmosphere on cellulose conversion using tungstated zirconia as catalyst in hot liquid water (190 °C). Indeed, since noble metal free ZrW solids were previously reported to interact positively with molecular hydrogen in an acidic demanding reaction like alkane isomerizations in gas phase [11], we wanted to check if such interaction might occur in the aqueous medium and influence the cellulose conversion.

## 2. Experimental

### 2.1. Tungstated zirconia synthesis

Tungstated zirconia was prepared by anionic exchange between a tungstic acid (Aldrich) solution in hydrogen peroxide (Aldrich, H<sub>2</sub>O<sub>2</sub> 30%) and zirconium hydroxide according to a patented method [12]. Zirconium hydroxide was prepared by precipitation at pH 9 with a zirconyl chloride solution (ZrOCl<sub>2</sub>·8H<sub>2</sub>O, Aldrich) and ammonia solution 1.8 M. After agitation of the suspension for 20 min, the mixture was centrifuged and the precipitate washed several times with deionized water to remove chloride ions. The solid was then dried at 110 °C for 24 h. Then, 10 g of zirconium hydroxide were exchanged with the tungstic acid solution (0.25 M) in hydrogen peroxide (30%, 150 mL) for 15 min. The exchanged solid was filtered and dried at 80 °C for 24 h. Finally, the solid was calcined at 700 °C under air flow for 3 h [12]. The XRD pattern of ZrW shows the exclusive formation of the tetragonal ZrO<sub>2</sub> phase as expected from the optimized method of preparation via anionic exchange [13]. The W loading and the BET surface area equal 11.8 wt% and 219 m<sup>2</sup> g<sup>-1</sup> respectively.

### 2.2. In situ FTIR studies

FTIR spectra of self-supported pellets of ZrW were recorded with a Bruker Vector 22 spectrometer in the absorption mode with a resolution of 2 cm<sup>-1</sup>. The samples were placed in an IR cell equipped with CaF<sub>2</sub> windows and treated in situ. The wafer of ZrW samples was first pretreated at 400 °C under flowing oxygen for 2 h. Pyridine vapor pressure was introduced in the cell for 15 min at ambient temperature and the ZrW pellet was desorbed at 150 °C for 1 h in order to remove the physisorbed pyridine species. Then 100 Torr of hydrogen were introduced in the cell at ambient temperature, and the ZrW pellet, previously saturated with pyridine, was treated at increasing temperature in H<sub>2</sub> atmosphere. Finally, hydrogen was vacuum treated at ambient temperature, in order to compare the pyridine spectra before and after hydrogen treatment.

### 2.3. Classical batch experiments

Untreated microcrystalline cellulose was purchased from Sigma–Aldrich and used as received (degree of polymerization = 250, crystalline index 70%, particles size 20 μm).

Reactions were performed in a 100 mL Parr Hastelloy autoclave equipped with a Rushton turbide. The autoclave was filled with cellulose (1.60 g), catalyst (0.68 g) and de-ionized water (65 mL). The autoclave was flushed three times with He at room temperature, and then was heated at 190 °C (5 °C/min). The pressure was adjusted to 5 MPa with He or H<sub>2</sub> for 24 h. The reaction was stopped by cooling the autoclave with an ice bath. The pressurized gas was

evacuated, the reaction mixture was filtered and the liquid phase and the residual solid were collected.

### 2.4. Kinetic experiments

The Parr Hastelloy autoclave was connected to a 20 mL stainless steel sampling vessel, pressurized with He or H<sub>2</sub> at 5 MPa. Typically, the autoclave was filled with catalyst (0.68 g) and de-ionized water (48 mL). A suspension of cellulose (0.8 g) in de-ionized water (18 g) was introduced into the pressurized sampling vessel connected to the autoclave. The autoclave is flushed three times with He and then heated up to 190 °C. When the temperature is reached, the cellulose suspension in the sampling vessel is introduced into the autoclave under 5 MPa of He or H<sub>2</sub>. This is the time zero of the reaction.

### 2.5. Analytical methods

The liquid phase was analyzed by a HPLC system with an ICE COREGEL 107H column (300 mm × 7.8 mm, 80 °C) and a Refractive Index detector using acidified water as eluent (0.5 mL/min, 0.01% mol H<sub>2</sub>SO<sub>4</sub>). The liquid phase was also analyzed on a Shimadzu TOC-V<sub>SCH</sub> Total Organic Carbon (TOC) analyzer (720 °C, Pt/Al<sub>2</sub>O<sub>3</sub> catalyst, IR detector).

The solubilization percentage, also defined as the conversion percentage, was calculated as the ratio of the total mass of carbon in the liquid phase obtained from TOC analysis and the initial mass of carbon in the charged cellulose:

$$\begin{aligned} \text{Conv}(\%) &= \text{Solubilisation}(\%) \\ &= 100 * (\text{mgC}_{\text{liquid phase}} / \text{mgC}_{\text{initial cellulose}}) \end{aligned}$$

The carbon yields of the products detected by HPLC were calculated as the molar ratio of the product *i* and the initial glucosyl units present in the initial cellulose, corrected by the number of carbon atoms:

$$\text{Yield}_i(\%) = 100 * (nC_i/6) * (n_i/n_{\text{glucosyl units}})$$

*nC<sub>i</sub>*: number of carbon atoms in the product,  
*n<sub>i</sub>*: number of moles of the product *i* determined by the HPLC analysis,  
*n<sub>glucosyl units</sub>*: initial number of moles of glucosyl units in the cellulose sample = *m<sub>cellulose</sub>*/162.

The yield of soluble oligosaccharides and polymers (SOP) was deduced from the difference between the conversion and sum of the yields of products analyzed by HPLC:

$$\text{Yield}_{\text{SOP}}(\%) = \text{conv}(\%) - \sum \text{Yield}_i(\%)$$

## 3. Results and discussion

### 3.1. Influence of hydrogen or helium atmosphere on the cellulose conversion over ZrW

The results of cellulose conversion at 190 °C for 24 h under hydrogen or helium atmosphere in the presence or absence of ZrW catalyst are summarized in Table 1. Blank experiments, done without solid catalyst and under H<sub>2</sub> or He, give same results and lead to cellulose conversions of 31–32% without any selective formation of products. When the reaction was performed using ZrW, under He atmosphere, a lactic acid yield of 18.5% was obtained with a cellulose conversion of 35%. Beside, under hydrogen, in the presence of ZrW, the cellulose conversion was raised to 65%, with yields

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