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Cellulose Conversion with Tungstated-Alumina-Based Catalysts: Influence of the Presence of Platinum and Mechanistic Studies

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The performances of platinum supported on tungstated alumina (Pt/AlW) in the hydrothermal conversion of cellulose at 190 °C under H_2 pressure were evaluated and compared to that of Pt-free tungstated alumina (AlW). We show that the presence of Pt significantly increased the extent of conversion and led to a different product distribution with the formation of acetol and propylene glycol as the main products and a global yield of up to 40%. Based on previous reports, we propose the formation of pyruvaldehyde on the Lewis acid sites of the tungstated alumina as a key intermediate. Pyruvaldehyde can then be transformed to acetol and propylene glycol or lactic acid depending on the presence or absence of supported Pt.

Introduction

Cellulose is considered as a promising renewable resource to produce fuels and chemicals.[1–3] The chemical valorisation of cellulose is a great challenge as this bio-polymer is very resistant to chemical transformations under conventional conditions. The number of studies on the conversion of cellulose into valuable molecules has grown spectacularly over the past few years. Different reaction media and conditions have been reported for the conversion of cellulose, which includes hydrolysis in water by liquid mineral acids or enzymes or alternatively in non-conventional media such as ionic liquids and super-critical solvents.[4–7]

The use of heterogeneous catalysts under hydrothermal conditions has been reported recently and is the subject of intensive research.[8–10] Various catalytic systems with specific properties have been applied to produce different products. The simple hydrolysis of cellulose in water into glucose has been reported at mild temperatures with mono-functional solid-acid catalysts such as sulfonated C,[11,12] sulfonated silica/C nanocomposites[13] or with catalytic systems based on Ru supported on mesoporous C.[14] Alkane diols such as propylene and ethylene glycols can be obtained under H_2 with the use of metal-oxide-supported Ni catalysts,[15] C-supported Ru associated with tungstic acid[16] or tungsten carbide catalysts.[17,18] Pioneering work on the conversion of cellulose into sugar alcohols (sorbitol, mannitol) was reported by Fukuoka and Dhepe.[19] They evidenced the efficiency of the bi-functional catalyst Pt/γ-Al_2O_3, which is able to convert cellulose into sugar alcohols at 190 °C under H_2 with a yield of 31%. Since then, various catalytic systems have been reported. Principally, they are formed of C-supported Ru associated with mineral acids,[20] soluble[21,22] or insoluble[23] hetero-poly acids or formed from Ru directly supported on heteropoly acids.[24] Other systems such as Pt[25] or Ni phosphides[26] supported on C and mineral acids associated with Ru in zeolites[27] are also known. The use of 2-propanol as a hydrogen source has also been reported.[28] These new systems allow the decrease of the reaction temperature (160–190 °C) while increasing the yields of the sugar alcohols (40–80%). However, in some cases a cellulose ball-milling pre-treatment was applied to increase the reactivity.

In a recent study, we compared the efficiency of solid Lewis and Brønsted acids on the conversion of cellulose in water. We showed that the solid Lewis acids tungstated zirconia (ZrW) and especially tungstated alumina (AlW) are remarkable catalysts that promote cellulose conversion under hydrothermal conditions to yield lactic acid as the main product with yields up to 27% when using AlW.[29,30] To the best of our knowledge, this was the first example of high yields of lactic acid obtained directly from cellulose by using solid catalysts.

Herein, we report the influence of Pt supported on the solid Lewis acid AlW on cellulose conversion and product distribution. We also propose a general reaction scheme that leads to various products depending on the presence or absence of Pt and hydrogen on the Lewis acid catalyst.

Results and Discussion

Cellulose conversion

For comparison, in addition to AlW, we studied the performances of other catalysts with regard to the acidic nature of the

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Table 1. Main features of the different catalysts used in this study.

Catalyst	A_{BET} [$m^2 g^{-1}$]	Composition [wt %]	$d_{particle}$[a] [nm]	Acid-site density[b] [μmol g^{-1}]	Lewis-acid-site proportion[c] [%]
AlW	294	W: 18.8	–	652	100
Pt/AlW	235	Pt: 2.0	1.1	722	100
Pt/γ-Al_2O_3	208	Pt: 2.5	1.1	425	85
Pt/SiO_2	297	Pt: 1.8	4.6	54	–

[a] Mean diameter of the metal particles was determined by using TEM. [b] Determined by NH_3 adsorption monitored by using thermogravimetric analysis (TGA). [c] Determined by performing pyridine adsorption–desorption experiments.

support to evidence a possible peculiarity of the Pt/AlW system. Silica was chosen because of its neutral character, and γ-Al_2O_3 was included because of its previously reported efficiency as a support for cellulose conversion.[19] The main characteristics of all these catalysts are presented in Table 1. The surface areas of the different supports evaluated in this reaction are in the same range (200–300 $m^2 g^{-1}$). TEM measurements (not shown here) demonstrate that on silica, the Pt particle size is approximately 4.6 nm, whereas much smaller particles were obtained on AlW and γ-Al_2O_3 supports (1.1 nm). Solely AlW and Pt/AlW catalysts possess 100 % Lewis acid sites with a density of up to 700 μmol g^{-1}.

The influence of the supports and the supported metallic catalyst on the hydrothermal conversion of cellulose was studied to determine the role of the metal on cellulose reactivity (Table 2). The reaction was carried out under a H_2 atmosphere for all the materials tested. The results show that the conversions significantly increased in the presence of Pt on the solids, except for the neutral silica support. With γ-Al_2O_3 and AlW, the cellulose conversion increased by 21 and 15 percentage points, respectively. The highest cellulose conversion was obtained in the presence of Pt/AlW (70 %).

Table 2. Cellulose conversion in the presence of the different catalysts.[a]

Catalyst	Differential cellulose conversion owed to the metallic phase [pp][b]	Cellulose conversion [%]
none	–	31
SiO_2		39
Pt/SiO_2	−11	28
γ-Al_2O_3		41
Pt/γ-Al_2O_3	+21	62
AlW		55
Pt/AlW	+15	70
none		31

[a] Cellulose (1.6 g), catalyst (0.68 g), H_2O (65 mL), P_{H_2} = 5 MPa, 190 °C, 24 h. [b] pp = percentage points.

Cellulose conversions over time for AlW, Pt/AlW and without catalyst are presented in Figure 1, and similar profiles are seen in these three cases. Nevertheless, the conversion increase was slightly faster with AlW and even more with Pt/AlW to give rise to a considerably higher conversion after 30 h of reaction.

Clearly, the presence of a Pt phase on AlW had a strong influence on the final cellulose conversion with a more rapid conversion principally after prolonged reaction times. This confirms the important role played by Pt in the cellulose dissolution process as already reported for Pt/γ-Al_2O_3, but the explanation of this phenomenon is still a matter of debate. According to Fukuoka and Dhepe, the acidic function of alumina promotes cellulose hydrolysis and the H_2/Pt system enhances the solid catalyst acidity through H_2 splitting on the metal, which leads to a higher conversion.[19] In one of our previous studies, we re-investigated the catalytic properties of Pt/γ-Al_2O_3 and proposed that fast hydride transfer promoted by the H_2/Pt system contributed to the acceleration of cellulose conversion.[31] In a previous study, we observed enhanced cellulose solubilisation when solid Lewis acids were used. We proposed that Lewis centres might coordinate the soluble oligomers that issue from the cellulose hydrolysis initiated by the hot-water medium and that the cooperation between the Brønsted acidity of the hot water and the Lewis centres explains this enhancement.[29] All these explanations might still hold true in the presence of Pt/AlW. A recent report highlighted the importance of the Pt precursor on the Pt/γ-Al_2O_3 system. It was proposed that the use of H_2PtCl_6 could shift the dissociation equilibrium of water to enhance the hydrothermal conversion of cellulose by increasing the acidity of the aqueous reaction medium.[32] Iglesia et al. proposed that if Pt was supported on ZrW (Pt/ZrW), the hydrogen activated by the supported Pt participates in the formation of protonic sites on the surface of the material.[33,34] As it is a similar catalyst, this may be also true for Pt/AlW, which partly explains the faster and higher cellulose conversion obtained by increasing the proton density in the reaction medium. In the case of SiO_2 and Pt/SiO_2, the conversions were in the same range as those observed without a catalyst. This can be explained by the very low acidity of the support for which the

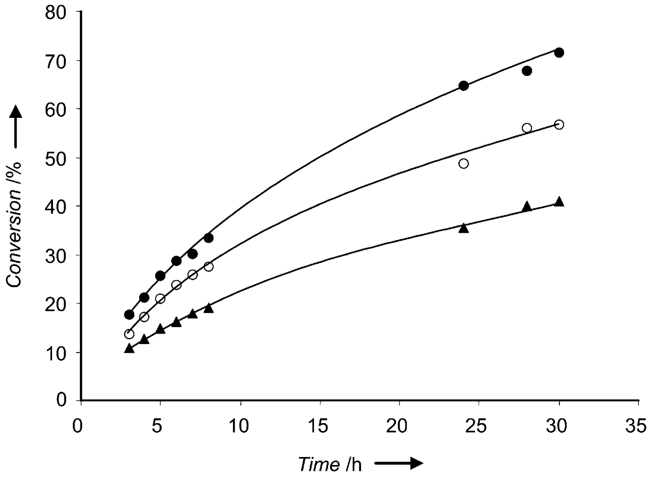


Figure 1. Cellulose conversion without (▲) and with the catalysts Pt/AlW (●) and AlW (○) as a function of time.

above propositions on the presence of Pt should not be valid, which leads to no value-added catalyst.

Product selectivity

The product yields obtained with each system under a H_2 atmosphere are presented in Figure 2. In some cases, the results obtained are as expected and in agreement with that already reported. For example, in the absence of Pt, AlW had a completely different behaviour to SiO_2 and γ-Al_2O_3. Indeed, although SiO_2 and γ-Al_2O_3 formed lactic acid and acetol in similar yields, with AlW, acetol was absent and lactic acid was predominant.[29]

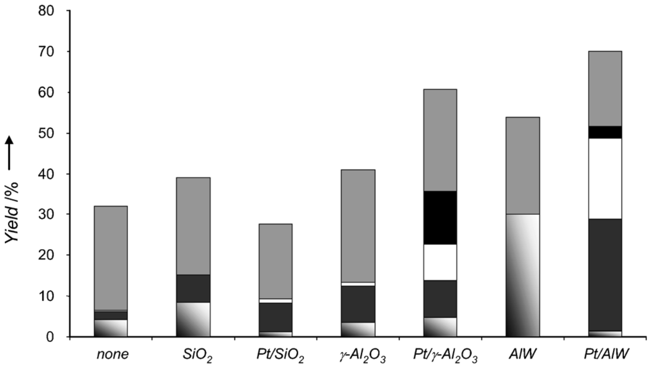


Figure 2. Product yields [black: sorbitol; white: propylene glycol; dark grey; acetol; shaded from grey to white: lactic acid; light grey; others (glucose, levulinic acid, formic acid, acetic acid, unidentified)] of the hydrothermal cellulose conversion with the various catalysts. Conditions: 190 °C, 5 MPa H_2, 24 h.

Next, the presence of a metallic phase on the supports influenced the distribution of the products and this different behaviour depends dramatically on the nature of the support. With Pt/SiO_2, we can see that the yield of lactic acid decreased significantly, whereas that of acetol remained unchanged. With Pt/γ-Al_2O_3, the yield of acetol and lactic acid remained similar; however, sorbitol produced by the hydrogenation of glucose emerged as the main product (14 %).[19] Other C_3 products (propylene glycol) were also observed. The main difference is that, in the presence of Pt/AlW, acetol (28 %) and propylene glycol (20 %) were formed predominantly at the expense of lactic acid, which was obtained in a very low yield. Importantly, sorbitol was also obtained but in a low amount, which confirms the significantly different behaviour of γ-Al_2O_3 and AlW.

The difference in selectivities obtained for these products showed the importance of the nature of the acid sites. If we consider the acidic features of Pt-based catalysts (Table 1), it appears that the cellulose conversion into acetol and propylene glycol is enhanced both by a high number of acid sites and Lewis acidity. As this paper was in preparation, the performances of catalytic systems composed of AlW and Ru/C for the formation of propylene glycol along with ethylene glycol and sorbitol under a H_2 atmosphere were reported, and the influence of the amount of supported W species on the selectivities was highlighted.[35]

Finally, the global yield of the other products (glucose, organic acids, un-identified, etc) is always in the 20–25 % range independent of the catalytic system. Although their global selectivity is predominant with SiO_2 and γ-Al_2O_3, the presence of the solid AlW decreased this selectivity in favour of lactic acid or acetol and propylene glycol. Therefore, the presence of pure Lewis acid AlW leads to more selective transformations. This tendency was already reported with the support alone,[29] and we demonstrate in this paper that it is also true in the presence of supported Pt.

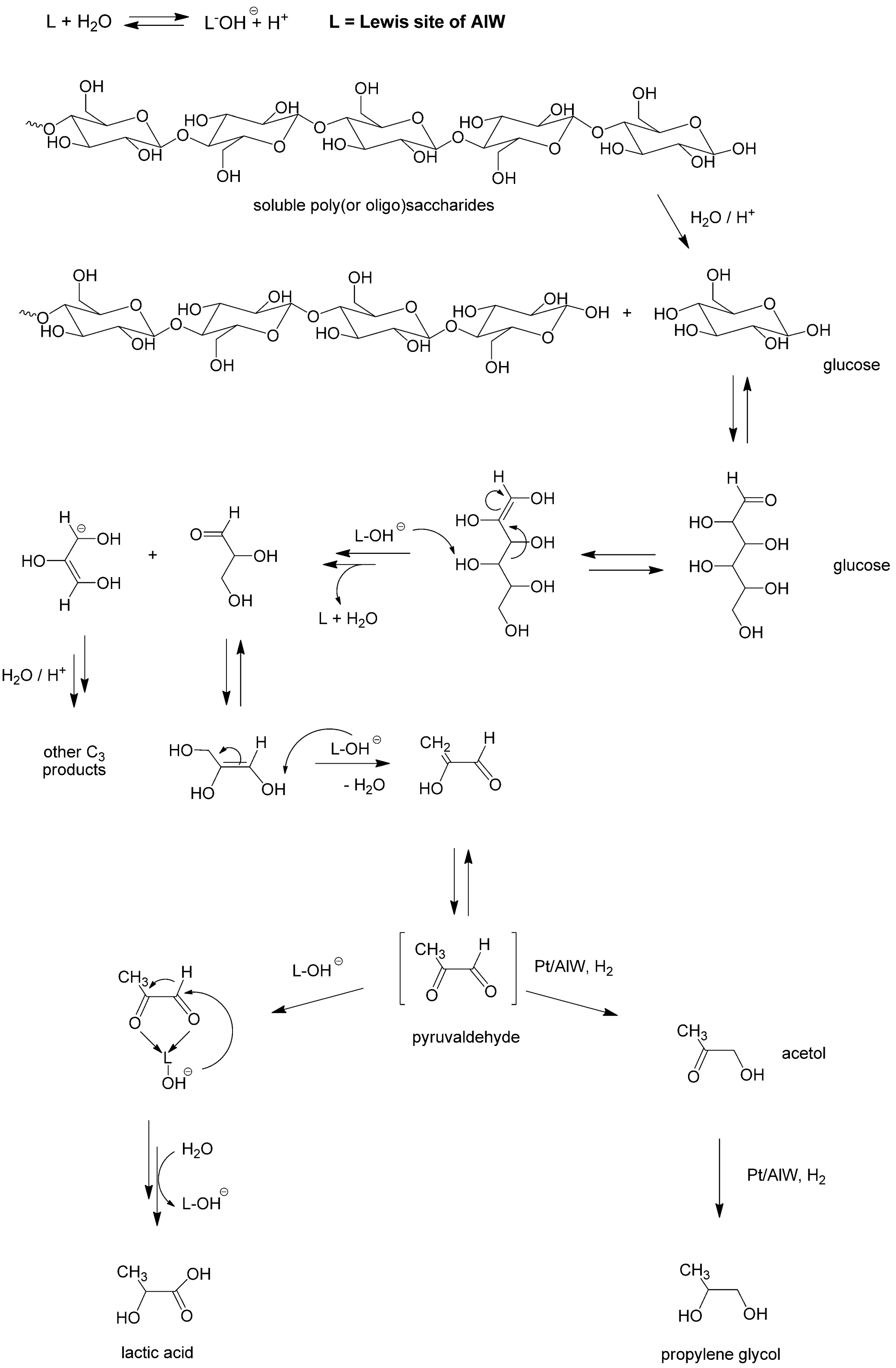
Mechanistic studies

If cellulose was treated under H_2 in the presence of the Lewis acid AlW, the formation of lactic acid was predominant, whereas the additional presence of Pt led to a mixture of acetol and propylene glycol. Here, we aim to propose a mechanistic view to explain both the higher extent of cellulose dissolution in the presence of AlW and the formation of the main products depending on the conditions (Scheme 1).

First, the solid Lewis acid (L) suspended in water can form supported negatively charged hydroxide species (L–OH^-). This also forms protons, which increases the H^+ density and could explain partly the conversion increase to produce glucose through the hydrolysis of the polysaccharides solubilised by water auto-protolysis.[29,31] Ellis and Wilson demonstrated that the reaction of glucose in aqueous NaOH formed pyruvaldehyde through cleavage and dehydration as the main steps; both reactions were catalysed by the OH^- species.[36] If we consider in our case that the surface species L–OH^- also possesses basic sites, we can suppose this transformation to be possible, which releases pyruvaldehyde into the medium. Therefore, the L–OH^- species would also be an active site of this overall transformation. Pyruvaldehyde has also been identified as an intermediate product in a recent report on glucose reactivity in sub-critical water.[37] Here, we can explain again the importance of the support: if Pt/γ-Al_2O_3 was used, these types of sites probably would not have been formed (or in a lower amount) and glucose would not have been transformed into sorbitol by fast hydrogenation (see above); this transformation was not predominant with the AlW support.

Then, we expect the formed pyruvaldehyde to be very reactive under our conditions, and it would be subject to various transformations depending on the catalyst. In the absence of Pt, it will finally yield lactic acid through coordination of the carbonyl groups on the Lewis sites of the catalyst similar to that proposed by Vogel et al.[38] In the presence of supported Pt, pyruvaldehyde leads to acetol through the hydrogenation of the aldehyde function and acetol is transformed into propylene glycol by the reduction of the remaining carbonyl function.

These hypotheses were confirmed by separate experiments. Pyruvaldehyde was treated under H_2 with AlW (100 °C, 2 h) or Pt/AlW (190 °C, 8 h). In the first case, lactic acid was obtained selectively with 53 % yield and 66 % conversion. In the second



Scheme 1. Proposed mechanism for the formation of lactic acid, acetol and propylene glycol from cellulose with AlW or Pt/AlW catalysts under H_2.

case, propylene glycol was obtained with 80% yield along with lactic acid (4% yield) for full conversion. Moreover, it seems that these transformations are faster when pyruvaldehyde is used as the reactant than if cellulose is present

Figure 3 represents the evolution of the selectivity as a function of the cellulose conversion for AlW and Pt/AlW.

The final main products were formed, even at low conversions, during the first minutes of the reaction. This would

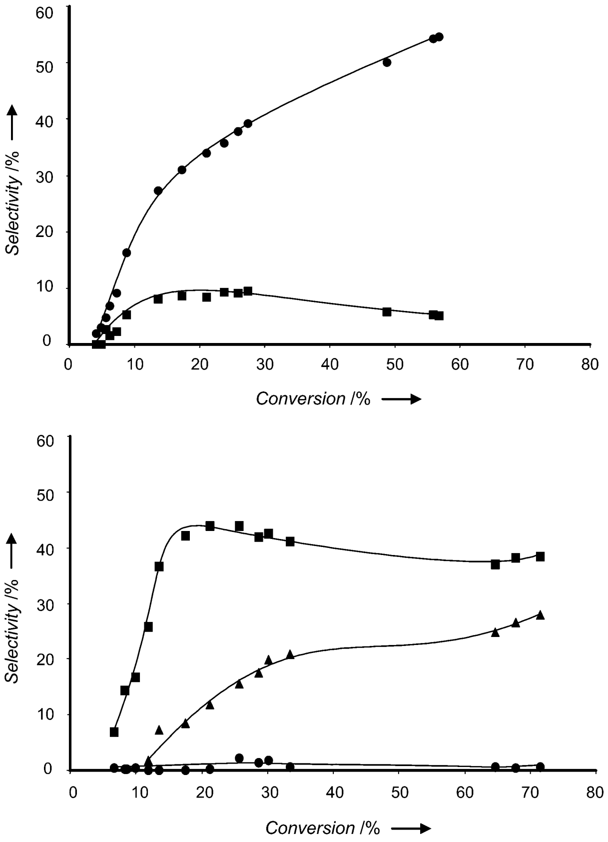
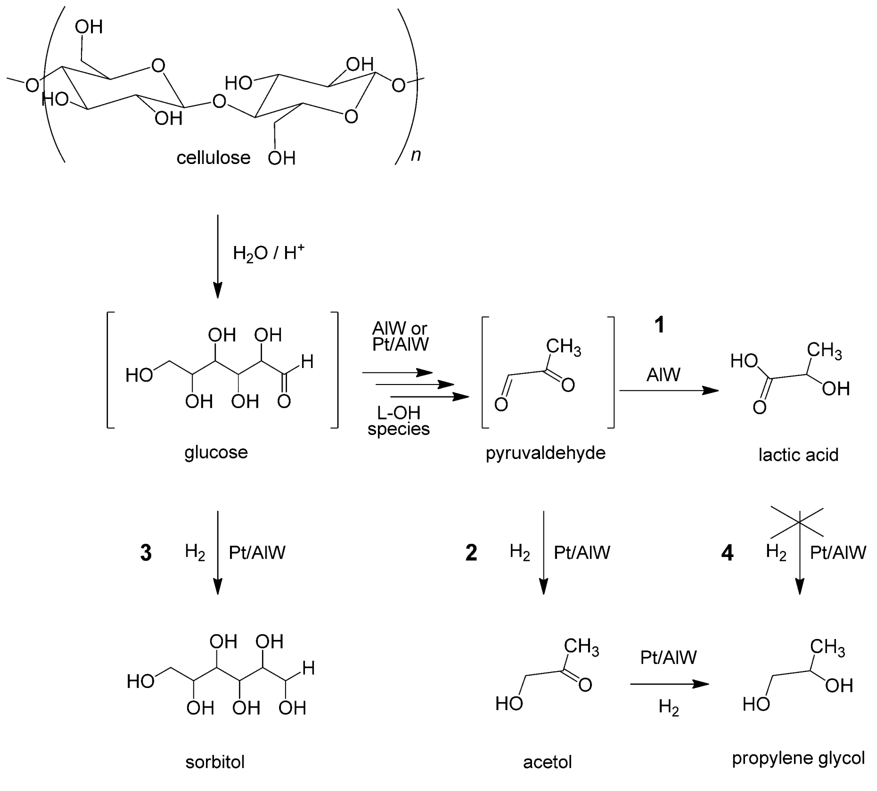


Figure 3. Evolution of the selectivities (● lactic acid; ■ acetol; ▲ propylene glycol) as a function of cellulose conversion with AlW (top) and Pt/AlW (bottom).

agree with the high disappearance rate of the first intermediates (glucose, pyruvaldehyde). In the presence of AlW, the selectivity in lactic acid was quite low at the beginning of the reaction but increased rapidly and continuously, which showed that lactic acid accumulated with reaction time and was an end-product for the transformation of cellulose with AlW. Acetol was also detected and its selectivity was constantly low, which indicates that its formation was never dominant here.

In the presence of Pt/AlW, we can see that the formation of acetol was predominant at low conversion and attained its maximum selectivity after 4 h (corresponding to 20% conversion). A decrease of the selectivity of acetol then occurred along with an increase in the formation rate of propylene glycol, which was absent at the lowest conversions. These data indicate clearly that propylene glycol was formed from acetol by the H_2/Pt/AlW system. This was confirmed independently by treating acetol with Pt/AlW under 5 MPa of H_2 for 24 h, which resulted in complete conversion with full selectivity into propylene glycol.

To summarise (Scheme 2), it appears that from the glucose intermediate, in the presence of AlW alone, route 1 is favoured with the largely predominant formation of lactic acid from the proposed key intermediate pyruvaldehyde. In the presence of Pt/AlW, this route is less favoured and the selectivity shifts towards the faster formation of acetol and propylene glycol (route 2). The selectivity balance between acetol and propylene glycol could be tuned by adapting the reaction time, and we will probably obtain a much higher selectivity into propylene glycol after prolonged reaction times. Route 3, which yields sorbitol from glucose, is also observed but is not a major route. Certainly the cleavage of glucose by proton transfer is faster than its hydrogenation. Route 4, which gives rise to propylene glycol from lactic acid, is less probable as the reduction of carboxylic acids requires different conditions than those used here. We confirmed this by performing a separate experiment, which showed that no propylene glycol was observed if an aqueous lactic acid solution was treated in the presence of Pt/AlW under H_2 at 190 °C.



Scheme 2. Possible transformations of glucose with AlW or Pt/AlW catalysts.

Catalyst stability and recycling

We studied the stability of the catalysts first by determination the extent of leaching (Table 3) through elemental analysis of the recovered solutions. Pt/AlW and Pt/γ-Al_2O_3 are quite stable, with leaching of less than 0.05 % of initial Pt and 0.8 % of initial W. The participation of these solubilised species on cellulose conversion is negligible. Indeed, if a solution recovered after the first reaction was treated in the presence of fresh cellulose, a conversion similar to that obtained in the absence of any catalyst was obtained.

Table 3. Stability of the different catalysts.

Catalyst	Metal dissolution [%][a]	
	Pt	other
Pt/SiO_2	0.25	Si: 6
Pt/γ-Al_2O_3	<0.05	
Pt/AlW	<0.05	W: 0.8

[a] In reference to the initial amount of metal in the catalyst.

Pt/SiO_2 emerges as an unstable catalyst under hydrothermal conditions. This probably explains its poor activity for cellulose transformation, which is similar to that obtained without any catalyst (Table 2, Figure 2).

After reaction, the catalysts were collected by filtration and washed extensively before analysis. The XRD pattern of used Pt/AlW was similar to that of the fresh material, except for the presence of residual adsorbed cellulose. The signals attributed to the support are not altered and no signal that corresponds to Pt is observed, which indicates that the particles were still well dispersed (Figure 4). This also indicates that re-precipitation of leached AlW should be marginal.

TEM measurements (not shown here) indicated that the mean particle size of Pt increased from 1.1 to 2.1 nm after reaction.

Finally, we performed a recycling experiment with Pt/AlW (Figure 5). To minimise catalyst modification before recycling, we treated the recovered solid, which consisted of the catalyst and the un-reacted cellulose, at 300 °C for 2 h under a H_2 flow to reduce the metallic sites. A catalytic test with fresh cellulose was performed in the presence of this solid phase. We obtained a slightly lower conversion with the used catalyst, which can probably be explained by the weak sintering of the metallic catalyst after the first run and/or by the presence of the residual initial cellulose, which could prevent the full recyclability of the catalyst. However, the respective yields of acetol and propylene glycol were maintained, which shows the potential recyclability of the Pt/AlW catalyst.

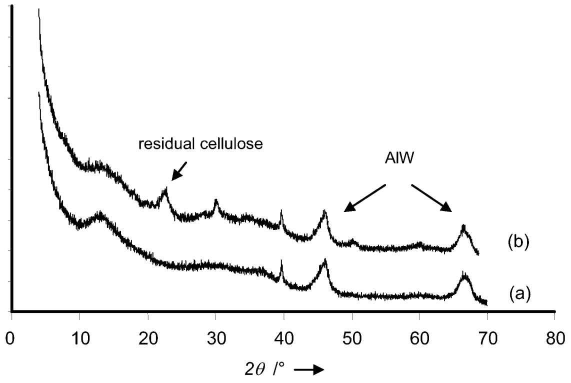


Figure 4. XRD spectra of Pt/AlW (a) before and (b) after reaction.

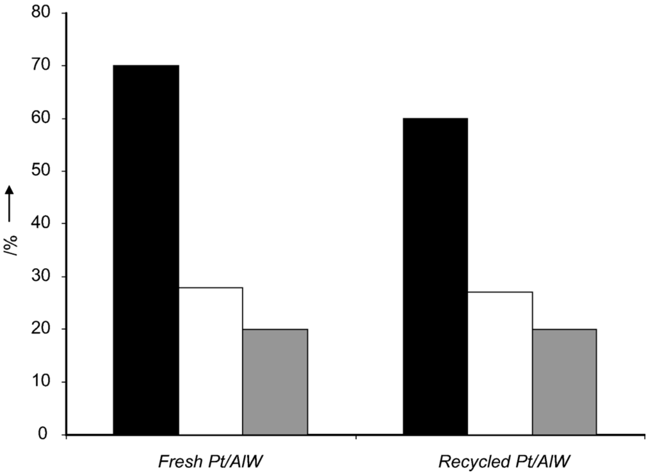


Figure 5. Recycling experiment with Pt/AlW (black: conversion; white: acetol yield; grey: propylene glycol yield). Conditions: cellulose (1.6 g), catalyst (0.65 g), water (65 mL), 5 MPa H_2, 190 °C, 24 h.

Conclusions

In this study, we compared the reactivity of AlW and Pt/AlW for the conversion of cellulose under hydrothermal conditions under H_2 pressure. We showed that the presence of Pt on AlW significantly increases the conversion and changes the product distribution of the reaction. Based on literature data, we propose that the presence of Lewis acid sites in the water medium would lead to pyruvaldehyde as key intermediate, which would react differently depending on the catalyst. With AlW, pyruvaldehyde would be mainly transformed into lactic acid, whereas the presence of supported Pt on AlW would lead to acetol and propylene glycol through hydrogenation of pyruvaldehyde by the metallic phase. Pt/AlW has been shown to be an efficient and recyclable catalyst for the formation of these two important C_3 molecules, and an interesting global yield of 40 % was obtained, which corresponds to a 60 % global selectivity after 24 h.

Experimental Section

Materials

Microcrystalline cellulose purchased from Sigma–Aldrich was used as received (estimated polymerisation degree 250, crystallinity index 70 %, and particle size 20 µm, estimated 4 wt % water). AlW[29] and Pt/γ-Al_2O_3[31] were prepared as reported previously. Pt/SiO_2 and Pt/AlW were prepared by incipient wetness impregnation of SiO_2 (Alfa Aesar, 300 $m^2 g^{-1}$) by $Pt(NH_3)_4Cl_2$, and of AlW by H_2PtCl_6 (8 wt% in H_2O). Calcination (air, 500 °C, 2 h) and reduction (H_2, 300 °C, 2 h) gave rise to catalysts with 2 wt% Pt.

Cellulose transformation

The reactions were performed in a 100 mL Parr Hastelloy autoclave equipped with a Rushton turbide. The autoclave was filled with cellulose (1.6 g), catalyst (0.68 g) and de-ionised water (65 mL). Pt-containing catalysts were reduced ex situ (H_2, 300 °C, 2 h). The autoclave was flushed three times with H_2 at room temperature and then heated to 190 °C (5 °C min^{-1}). The pressure was adjusted to 5 MPa using H_2, and these conditions were maintained for 24 h. The reaction was stopped by cooling with an ice bath. The pressurised gas was evacuated, and the reaction mixture filtered for separate analyses of the liquid and the residual solid.

The monitoring of the conversion over short reaction times (3–10 h) was performed according to the following procedure. The autoclave was equipped with a 20 mL stainless steel dropping funnel, which can be pressurised. The autoclave was filled with the catalyst (0.68 g) and de-ionised water (50 mL). A suspension of cellulose (1.6 g) in de-ionised water (15 mL) was introduced into the dropping funnel connected to the autoclave. The autoclave was flushed three times with H_2 and heated to 190 °C. The cellulose suspension was introduced into the hot autoclave, and the pressure was adjusted to 5 MPa of H_2. This experimental set-up prevents possible cellulose reactivity during the heating period. Aliquots of the reaction mixture were collected over time.

For catalyst leaching and recycling studies, the solid phase that consisted of the catalyst and the un-reacted cellulose was collected by filtration and washed with water. The amounts of metallic species in the liquid phase were determined by elemental analysis. A treatment at 300 °C for 2 h under H_2 flow was applied to the recovered solid before re-use.

Analytical methods

The textural and acidity features of the solids were determined as previously reported.[29]

The liquid phase was analysed by using an Agilent HPLC system with an RI detector (ICE COREGEL 107H column, 0.00 L% H_2SO_4, 0.5 mL min^{-1}, 80 °C). The liquid phase was also analysed by using a Shimadzu TOC-V_{SCH} total organic carbon (TOC) analyser (720 °C, Pt/Al_2O_3 catalyst, IR detector).

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

$$\text{conversion } [\%] = \text{solubilisation } [\%] = 100\,\% \times \frac{\text{mg}_{\text{C}_{\text{liquid phase}}}}{\text{mg}_{\text{C}_{\text{initial cellulose}}}}$$

The C 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 cellulose, corrected by the number of C atoms:

$$\text{yield}_i \; [\text{C}\,\%] = 100\,\% \times \frac{n_{\text{C}_i}}{6} \times \frac{n_i}{n_{\text{glucosyl units}}}$$

in which n_{C_i} is the number of C atoms in product *i*, n_i is the number of mols of product *i* determined by HPLC analysis and $n_{\text{glucosyl units}}$ is the initial number of moles of glucosyl units in the cellulose sample ($m_{\text{cellulose}}$/162).

TEM and XRD measurements were performed by using a JEOL 2010LaB6 microscope and a Bruker D8 Advance A25 diffractometer, respectively.

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Keywords: heterogeneous catalysis · hydrothermal synthesis · lewis acids · platinum · tungsten

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