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Valorization of cellulose over metal supported mesoporous materials

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ABSTRACT

Hydrolytic hydrogenation of bleached birch (betula) kraft pulp from a Finnish pulp mill into sugars and sugar alcohols was carried out in liquid phase in a batch mode under 20 bar of hydrogen at 458 K over metal supported mesoporous materials. Proton form of MCM-48 mesoporous material along with Pt on this support and Ru on carbon was tested. The conversion of cellulose and xylans present in the pulp varied depending on type of active sites, their number and metal. The yields of the main products, e.g. sugars, sugar alcohols and furfurals (xylose, glucose, xylitol, sorbitol, furfural, furfuryl alcohol and 5-hydroxymethyl furfural), varied depending on active sites, acidity, presence of metal and structure of the mesoporous material.

1. Introduction

The route towards the application of sustainable principles in economies and societies involves the development and utilization of processes converting biomass into valuable chemicals. Being the most abundant organic compound in the world, valorization of cellulose will most certainly play one of the main roles in the utilization of the renewables. The processes upgrading the bio-polymer should, however, be green in the sense that they should not produce detrimental waste, involve harmful solvents and consume large amounts of energy. Advanced development of the processes converting the renewables into fuels and chemicals needs to be done, where the role of heterogeneous catalysis will be very important. Lignocellulosic biomass is an excellent raw material for these processes since the utilization of the biomass does not compete with the food production.

Catalytic upgrading of cellulose into sugars and sugar alcohols has gained a lot of interest in the recent years and several research groups have reported the valorization of cellulose into chemicals in aqueous media through hydrolytic hydrogenation [1,2]. This process is attractive since it converts cellulose into sugars and sugar alcohols in a one step procedure using water as a solvent at elevated temperatures and in the presence of hydrogen.

Fukuoka and Dhepe and Deng et al. have reported the application of supported metal catalysts for biomass conversion under hydrogenolysis conditions [1,3–6]. In particular supported Pt and Ru catalysts show high activity for the conversion of cellulose into sugar alcohols at elevated temperatures in hydrogen atmosphere. Various transition metals were impregnated on solid supports and used for cellulose conversion into sugar alcohols such as sorbitol and mannitol. Sorbitol used as a sweetener in diet foods and pharmaceutical tablets because of its low caloric value, is industrially produced through hydrogenation of glucose over Raney Ni catalyst [7]. Furthermore, it is a potential raw material for the synthesis of a variety of value-added chemicals such as isosorbide, 1,4-sorbitan, glycols, glycerol, lactic acid and L-sorbose [8].

In the conversion of cellulose over various supported Ru catalysts Deng et al. reported that Ru on carbon nano tubes (CNT) was the most effective in transforming cellulose into sorbitol [4]. The influence of Ru loading on catalytic activity on the Ru/CNT catalyst was investigated and the highest yield was obtained with a metal loading of 1.0 wt% of Ru and the yield decreased with lower and higher Ru loading.

Dhepe and Fukuoka compared the catalytic performances of Pt catalysts loaded on different supports in the conversion of cellulose and did not find any particular relationship between the activity and the acidity of the support [1]. It was concluded, therefore, that there might exist other factors in determining the catalytic performances in addition to the acidity. Regarding the reaction temperature Fukuoka and Dhepe observed that the optimum temperature for the formation of sorbitol from cellulose over Pt/γ-Al_2O_3 was 463 K [5].

Mesoporous materials are interesting catalysts in the sense that they have large pore structures allowing big molecules to enter the cavities. MCM-48 has a large pore diameter (27.8 Å) and a three dimensional system advantageous for molecular diffusion [9].

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In this work we report the transformation of cellulose into sugars and sugar alcohols over Pt modified mesoporous materials and for comparison Ru on carbon. The catalytic performance with respect to catalyst structure and acidity was investigated.

2. Experimental

2.1. Catalyst synthesis and characterization

2.1.1. Synthesis of H-MCM-48

Synthesis of Al-MCM-48 was carried out using the method described by Pu et al. [9] with some modifications. NaOH and cetyl trimethyl ammonium chloride (CTMACl) were added to distilled water. Aluminium isopropoxide (AIP) was added to the solution and stirred for 15 min to allow the hydrolysis of AIP. Finally tetraethyl orthosilicate (TEOS) was added and stirred in an open vessel at room temperature for 1 h to achieve complete hydrolysis of TEOS. The pH of the mixture was measured. The gel was transferred into a 300 ml autoclave, thereafter the synthesis was carried out at 373 K for 75 h. Na-MCM-48 was ion-exchanged with an ammonium chloride solution for 48 h, washed with distilled water, dried and calcined to obtain H-MCM-48.

2.1.2. Synthesis of Pt-H-MCM-48

2 wt% Pt-MCM-48 catalyst was prepared by evaporation impregnation method using aqueous solution of hexachloroplatinic acid. The catalyst was dried at 373 K and calcined at 623 K after the impregnation. The metal modified catalyst was activated at 625 K for 2 h under flowing hydrogen gas prior to testing.

2.1.3. Ruthenium on carbon

5 wt% ruthenium on carbon catalyst was purchased from Tate & Lyle and activated at 625 K for 2 h under flowing hydrogen gas before the catalytic testing.

2.1.4. Catalyst characterization

The specific surface area of fresh catalysts was measured by the nitrogen adsorption method (Sorptometer 1900, Carlo Erba Instruments). The catalysts were outgassed at 423 K prior to the measurement and the BET equation was used to calculate the specific surface area.

The acidity of the synthesized mesoporous materials was measured by infrared spectroscopy (ATI Mattson Infinity spectrometer) by using pyridine (≥99.5%, a.r.) as a probe molecule for qualitative and quantitative determination of both Brønsted and Lewis acid sites. The FTIR spectrometer was equipped with an *in situ* cell containing ZnSe windows. The samples were pressed into thin self-supported discs (weight 15–20 mg and radius 0.65 cm). Pyridine was first adsorbed for 30 min at 373 K and then desorbed by evacuation at different temperatures (523, 623 and 723 K) to obtain a distribution of acid site strengths. All spectra were recorded at 373 K with a spectral resolution equal to 2 cm^{-1}. Spectral bands at 1545 and 1450 cm^{-1} were used to identify the Brønsted (BAS) and Lewis acid sites (LAS). The amounts of BAS and LAS were calculated from the intensities of corresponding spectral bands using the molar extinction coefficients reported by Emeis [10].

The Pt dispersion was determined from the amount of chemisorbed CO by a pulse method. The experiments were carried out using a Micromeritics TPD/TPR 2910 AutoChem instrument. The sample (~0.170 mg) was inserted into a quartz U-tube and was reduced with H_2 stream (AGA, 99.999%, 20 ml/min). A ramp rate of 5 K/min was applied and the temperature was linearly raised to the final temperature 623 K, thereafter it was held for 120 min. The sample was then cooled to 313 K under flowing He (AGA, 99.999%) and the experiment started once the baseline was stable. CO (AGA, 10% in He) was introduced and the pulses were repeated until complete saturation.

The metal loading was determined by ICP-OES. Approximately 0.1 g of sample was inserted into a teflon bomb, 4 ml HF, 1 ml of HCl and 0.5 ml of HNO_3 were added. The zeolite was dissolved in microwave oven, and diluted with deionized water to decrease the HF concentration.

X-ray powder diffractiometer (Philips PW 1820) was applied to study the structure and phase purity of MCM-48 mesoporous material, whereas scanning electron microscope (Leica) was used to investigate the morphology of the material.

2.2. Pulp characterization

The degree of polymerization of the pulp was determined by viscosity measurement in cupriethylenediamine solution [11] upon which the degree of polymerization could be calculated [12]. For determining if some free monosaccarides were present in the pulp, 64 mg of the dry pulp was put in a tube along with 10 ml of deionized water. The suspension was stirred and left over night, after which the water was filtered and analyzed with HPLC and silylation GC–MS. The hemicelluloses were determined by acid methanolysis and GC [13]. The pulp was freeze dried and about 7 mg was submitted to acid methanolysis with 2 mol/L HCl in anhydrous methanol. The methanolysis degrades non-cellulosic polysaccharides into their monomeric sugar units. After 5 h at 373 K the samples were neutralized with pyridine, and sorbitol was added as internal standard. Part of the clear sample was transferred to a new flask and dried, silylated and analyzed by GC.

2.3. Catalytic experiments

The catalytic experiments were performed in a 300 ml Parr autoclave connected to a prereactor with a volume of 200 ml. The autoclave was provided with a 1 μm filtered sampling outlet, which prevented the catalyst particles to pass through it. The temperature was measured with a thermocouple and controlled automatically (Brooks Instrument). 0.32 g of bleached birch (betula) kraft pulp from a Finnish pulp mill was dissolved in 50 ml of deionized water along with 0.15 g of catalyst with a particle size between 150 and 250 μm. In order to get a narrow particle size range for the zeolite catalyst, pellets of the zeolites powder were first pressed and thereafter crushed and sieved. 20 bar of hydrogen pressure was applied and the solution was heated to 458 K. The stirring rate was 1145 rpm to eliminate external diffusion. When the reactor had reached its set temperature, stirring was applied and this was considered as initial reaction time. Liquid samples were taken at different times and analyzed with an HPLC equipped with an HPX-87C as well as a HPX-87H column.

2.4. Product analysis

2.4.1. Silylation-GC–MS

500 μl of the liquid samples were transferred to a test tube and dried in a water bath operating at 313 K under nitrogen flow. A blank sample containing only distilled water was dried as a reference. The dried samples were silylated by addition of 100 μl of pyridine (Fluka, >99%), 200 μl of hexametyldisilazane (Fluka, >98%), and 100 μl of chloromethylsilane (Fluka, >98%). The samples were stirred and left overnight. Thereafter, the samples were transferred into small ampulles and analyzed with GC–MS. The GC–MS was equipped with an HP-1 column (25 m × 0.2 mm × 0.11 μm) and the following temperature program was used: dwelling at 333 K for 0.25 min and heating to 573 K with the heating rate 6 K/min.

Table 1
Acid sites of the catalyst used.

Catalyst	Brønsted acid sites (μmol/g)			Lewis acid sites (μmol/g)		
	523 K	623 K	723 K	523 K	623 K	723 K
H-MCM-48-F1	59	18	2	63	25	7
Pt-MCM-48-IMP	39	6	5	62	6	3
Ru/C	–	–	–	–	–	–

Table 2
Surface area, metal loading and dispersion of Pt of the tested catalysts.

Catalyst	Surface area (m^2/g), BET	Metal loading (wt%)	Metal dispersion (%)	Metal particle diameter (nm)
MCM-48	719	–	–	–
Pt-MCM-48	410	1.6	35	3
Ru/C	690	5.0	40	3

2.4.2. GC–MS-Solid phase micro extraction

The volatile compounds were analyzed with GC–MS and headspace solid phase micro extraction (HS-SPME). An aliquot of the solution (2 ml) containing the reaction products was transferred into a small (4 ml) flask equipped with a rubber cap. The sample flask was heated to 320 K. The needle with the fibre was penetrated through the cap into the bottle and the fibre was exposed to the headspace of the sample for 30 min. The fibres used for extraction were of the type carboxen/polymethylsiloxane (CAR/PDMS) coated with a 2 cm to 75 μm film and divinylbenzene/carboxen/PDMS (DVB/CAR/PDMS) coated with a 2 cm 50/30 μm thick film. Both fibres were purchased from Supelco (Bellefonte, PA, USA). The holder used for manual injection was also obtained from the same supplier. The components were enriched on the surface and as equilibrium was reached between the headspace and the fibre, the syringe was injected into the GC–MS for analysis. The inlet chamber was set to 543 K, at which temperature the absorbed and adsorbed analytes were thermally desorbed into the hot injector of the gas chromatograph. The desorption time was 10 min which was sufficient to ensure total desorption, moreover no memory effect was observed as the same fibre was inserted for a second time. The GC–MS was equipped with a capillary column (DB-Petro 50 m × 0.2 mm × 0.5 μm). The following temperature program was used: dwelling for 10 min at 313 K, heating 0.9 K/min to 348 K followed by heating 1.1 K/min to 393 K, heating 10 K/min to 473 K and dwelling at 473 K for 20 min.

2.4.3. HPLC

The products and the conversion of the birch pulp were analyzed quantitatively with HPLC with two different columns. The samples taken from the reaction were analyzed with an Aminex HPX-87C as well as a Aminex HPX-87H column. The HPX-87C column was connected to a refractive index (RI) detector where diluted calcium sulphate solution ($CaSO_4$, 1.2 mM) was used as a mobile phase. The flow was 0.4 ml/min and the temperature was set to 353 K. Low concentrated sulphuric acid (0.005 M) was used as a mobile phase in the Aminex cation H+ column, the flow was 0.5 ml/min and the temperature was set to 338 K. The samples were injected into the HPLC's directly after the experiments without any pretreatment other than filtering to prevent solid particles from entering the columns. Several different concentrations of different standards were made and analyzed with HPLC. The standards were purchased from Aldrich or Fluka and had a purity of ≥99%. The HPLC was calibrated with the different standards which made it possible to calculate the molar ratios (equal molar yields) of the achieved products.

For determining the total amount of dissolved cellulose, i.e. liquid products, the total organic compound (TOC) was determined. The pH was also measured after the reaction was stopped.

3. Results

3.1. Catalyst characterization results

3.1.1. Acidity

H-MCM-48 exhibited almost the same amount of Brønsted as Lewis acid sites (Table 1). With introduction of Pt into the structure the Brønsted acidity decreased considerably, while no considerable change was seen in the Lewis acidity.

3.1.2. Surface area

The surface area and metal loading are shown in Table 2. There was a decrease in surface area since the introduced Pt partially blocked the pores. The dispersion of the metal was 35% corresponding to the metal particle size of 3 nm.

3.2. Pulp characterization results

The degree of polymerization was determined to 1900. No products were detected in the water phase from the pulp–water suspension, indicating that no free monosaccharides were present in the raw material. The main monosaccharide detected from the analysis of the hemicelluloses was xylose, originating from xylans present in the pulp.

3.3. Product characterization results

3.3.1. Total organic carbon (TOC) and pH

The total amount of carbon was measured in the liquid after the reaction time of 24 h and the results are shown in Table 3. The results are displayed as percent of carbon dissolved in the liquid after 24 h in proportion to the total amount of carbon of the cellulose input, converted into glucose. The highest value was obtained with Pt-MCM-48 catalyst indicating that this material was the most efficient in converting the non-soluble cellulose into water soluble products. The low value for Ru/C indicates that this catalyst not was very efficient in breaking the bonds of the cellulose. The organic compound that was not detectable with TOC refers not only to the unreacted cellulose but also the tar that was formed on the reactor wall. Throughout the experiment there where some tar formation of the reactor walls which increased with reaction time. There were some differences in the measured pH

Table 3
TOC and pH measured on the liquid at the end of the experiment.

Catalyst	TOC, (%)	pH
H-MCM-48	55	3.4
Pt-MCM-48	67	4.0
Ru/C	15	5.5

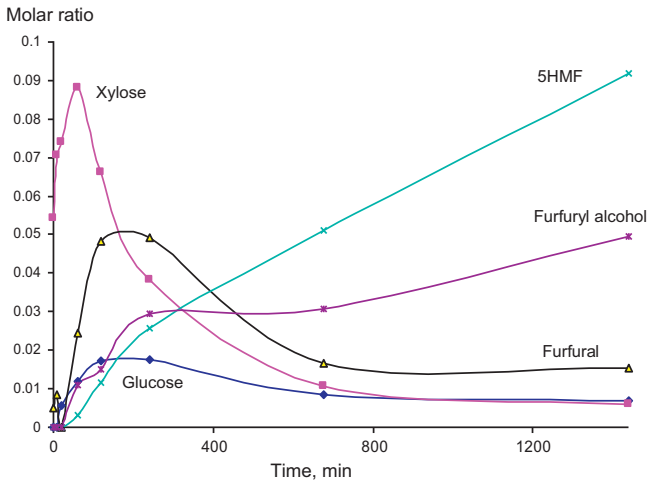


Fig. 1. Products formed over H-MCM-48.

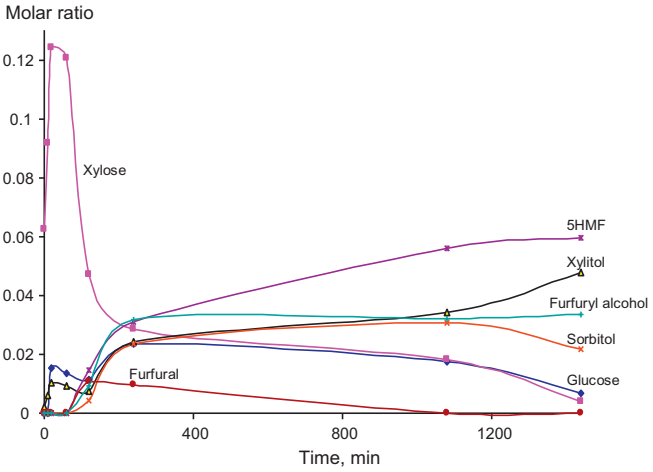


Fig. 2. Products formed over Pt-MCM-48.

of the samples, which decreased in the order Ru/C > Pt-MCM-48 > H-MCM-48.

3.3.2. HPLC

3.3.2.1. H-MCM-48. The molar ratio of the different products was determined by dividing the molar mass of the compound by the total amounts of moles in cellulose converted into glucose. In the beginning of the reaction the main product formed over H-MCM-48 was xylose reaching a maximum after 60 min (Fig. 1). The amount of furfural started to increase rapidly when xylose reached its maximum and continued to increase as the formation of the pentose started to decrease. This indicates that furfural was formed through the intermediate xylose. Furfural itself is also an intermediate, which was further transformed into furfuryl alcohol. Glucose was also formed at an initial stage reaching its maximum concentration after 120 min and then declining. Shortly after the formation of glucose some amounts of 5HMF were detected indicating that the formation of 5HMF proceeds through the intermediate glucose as well known. The dimensions of glucose are about 6.1 Å by 6.8 Å [14], whereas the pore size of MCM-48 is about 28 Å [9]. The polymer chains are very long but not very wide, which theoretically could allow the ends of the polymer to enter the pore system of the catalyst. One could assume that most of the reactions take place on the external surface whereas some reactions also could take place inside the pores of the mesoporous material.

3.3.2.2. Pt-MCM-48. The products detected over Pt-MCM-48 were similar to those formed over H-MCM-48, i.e. xylose, glucose, 5HMF, furfural and furfuryl alcohol. However, in addition to the products detected over H-MCM-48, sugar alcohols were also formed over the metal modified mesoporous material (Fig. 2), as a result of xylose and glucose hydrogenation. Consecutive nature of the generation of the sugars and their subsequent hydrogenation is apparently clear from the kinetic curves. Thus, xylitol formation speeded up after xylose concentration reached its maximum and sorbitol was produced after the formation of glucose started. The formation of both sugar decreased as the concentration of the sugar alcohols increased, as expected. No leaching of Pt was detected by ICP.

3.3.2.3. Ruthenium on carbon. The formed products over ruthenium on carbon were xylose, glucose, 5HMF and xylitol (Fig. 3). The profiles of the curves of the formed products were very similar for metal modified carbon and the MCM-48 catalysts. Glucose and xylose were the main products in the beginning of the reaction and xylitol and 5HMF were the main products in the end of the experiment. The amounts of the products formed over the Ru/carbon catalyst were, however, about 10-fold lower than in case of the Pt-MCM-48 catalyst. This indicates that, although being suitable for hydrogenation reactions the Ru catalyst is not efficient in the hydrolysis of the pulp under the investigated conditions.

3.3.2.4. Non-catalytic transformations and transformation of glucose. Non-catalytic experiments with the pulp were also done to determine the background activity in the absence of catalyst. Detected products were similar to those in the catalytic experiments i.e. xylose, furfural, 5HMF and glucose. However, the amounts of the detected products were substantially lower than in the catalytic experiments. Furthermore the amount of formed xylose reached a maximum molar ratio of 0.05 after 120 min reaction time and the amount started to increase again towards the end of the experiment. This can be compared to the catalytic experiments with MCM-48 where the maximum molar ratio of xylose (~0.1) was achieved after 20 min and 60 min and thereafter steadily decreasing (Figs. 1 and 2). Catalytic transformations of glucose over Pt-modified MCM-48 and acidic zeolite were also performed. Over the metal modified catalyst products like sorbitol, 5HMF, furfural and furfuryl alcohol were detected, whereas the non-metal catalyst yielded similar products except for sorbitol and furfuryl alcohol. Formic acid and levulinic acid were also detected originating from 5HMF degeneration as reported recently [15,16]. The formation of acids explains the order of the pH measured of the solution

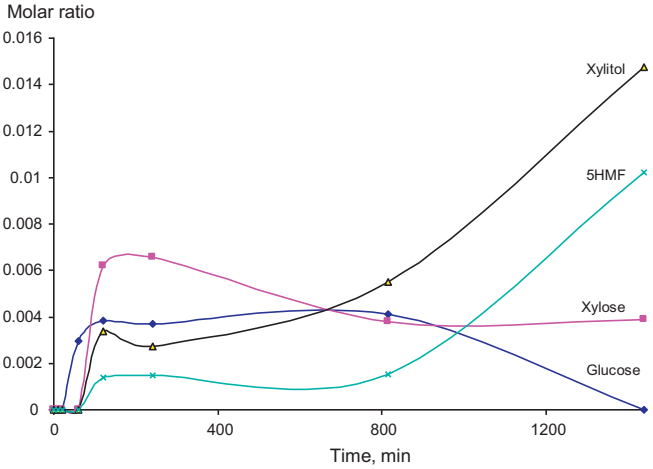
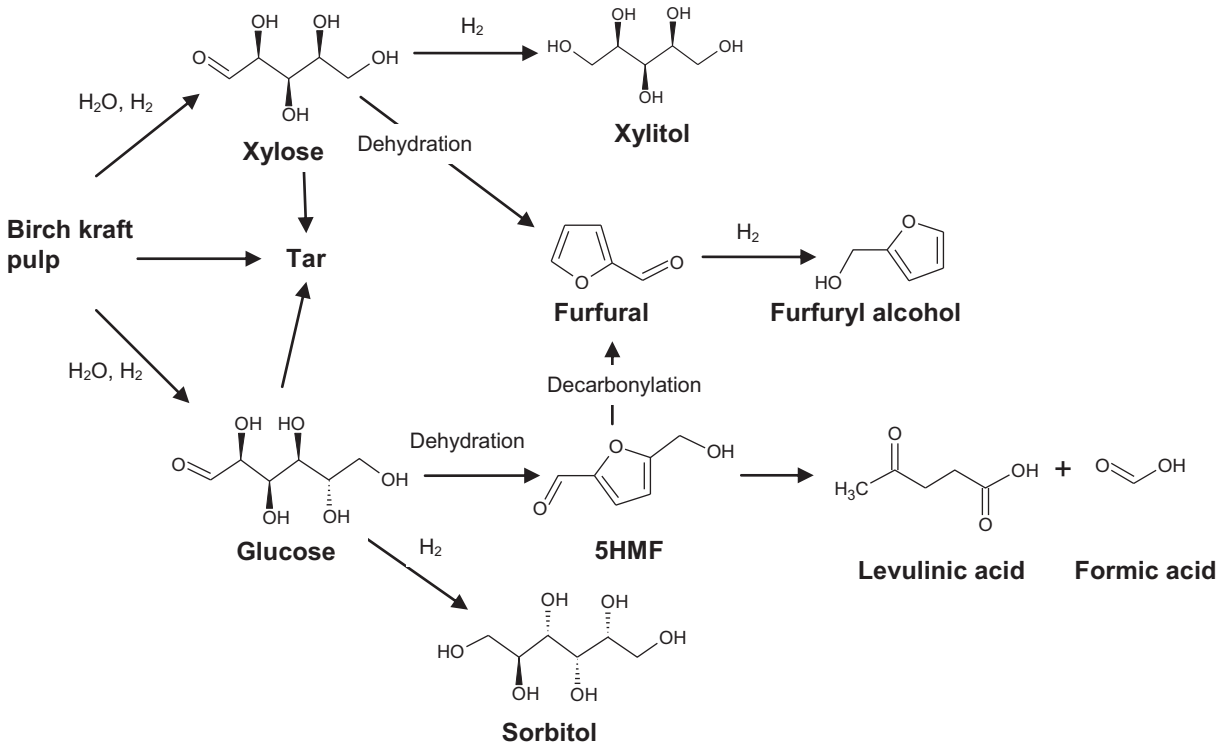


Fig. 3. Products formed over Ru/C catalyst.



Scheme 1. Reaction network in hydrolytic hydrogenation of bleached birch kraft pulp.

(Table 1). When metal is present the formed monosaccharides are hydrogenated into sugar alcohols instead of being dehydrated into 5HMF and decomposed further into acids. The formed acids could furthermore theoretically increase the rate of hydrolysis, since the high temperature makes the otherwise crystalline polymer more prone for modification.

3.4. Reaction network

The reaction pathways based on the experimental data are shown in Scheme 1. The hydrolytic degradation of the pulp mill cellulose pulp proceeds through two reaction pathways. One of them leads to the formation of xylose, while another generates glucose. The formation of xylose confirms the presence of hemicelluloses in the pulp since native birch wood (betula pendula) has been reported to contain 23% of xylose, bound in the form of the hemicellulose xylan [17]. Sundberg et al. investigated the amount of monosaccharides originating from hemicelluloses in four different bleached birch pulps from Finnish paper mills and found that the average amount of xylose in the pulps was 14.3 wt% (13.6–15.3%) [18]. This means that xylose originates from hemicelluloses but not from glucose, which in turn originates from the cellulose in the pulp. In the presence of Pt these monosaccharides are hydrogenated into xylitol and sorbitol. There are, however, also some competing pathways including dehydration resulting in furfural and 5HMF from xylose and glucose respectively. Furthermore formation of tar directly from cellulose and the five and six carbon sugars was detected. Furfural could also be produced via 5HMF decarbonylation and it was furthermore detected that furfural was hydrogenated into furfuryl alcohol.

4. Conclusions

Hydrolytic hydrogenation of bleached birch kraft pulp from a Finnish pulp mill was performed over proton and metal form of H-MCM-48 and Ru on carbon at 458 K and 20 bar of hydrogen. Xylose and glucose were the main products formed with some sugar alcohols produced through hydrogenation of the corresponding sugars along with different furfural derivatives. A reaction network was advanced.

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