LEVOGLUCOSAN TRANSFORMATION OVER ALUMINOSILICATES

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Catalytic transformation of levoglucosan (1-6-anhydro-β-D-glucopyranose) was carried out in the liquid phase in the batch mode, at 20 bar and 150 °C, and in the continuous mode, at 300 °C and at atmospheric pressure over aluminum silicates. Proton forms of Beta-25 zeolite and MCM-48 mesoporous material were tested as catalysts, while quartz sand was used as a reference material in non-catalytic transformation experiments. Levoglucosan conversion varied with residence time and catalyst. A variety of products was detected with HPLC, GC and GC-MS. The yields of the main products, *e.g.* different oxygenated species (glucose, glycolaldehyde, formaldehyde, acetaldehyde and acetic acid) varied, as a function of conversion, residence time and zeolite structure.

Keywords: levoglucosan, glucose, glycolaldehyde, Beta-25, MCM-48

INTRODUCTION

The catalytic conversion of lignocellulosic biomass is gaining more interest at a global scale, because of limited oil reserves, constraints in the use of fossil fuels and restrictions on carbon dioxide emissions causing global warming. Catalytic pyrolysis of different raw materials over zeolites and mesoporous materials has recently been investigated[1-4] by several research groups. The chemistry of the catalytic upgrading of woody biomass is, however, very complex, resulting in several hundreds of different compounds. For better understanding the complex reactions, the pyrolysis of model compounds derived from biomass should be studied. One of the main intermediates in cellulose and hemicellulose pyrolysis is levoglucosan (1,6-anhydro-β-D-glucopyranose), through which polysaccharides decompose, forming lower molecular weight products[5,6] (Fig. 1). Correspondingly, the secondary reaction of levoglucosan is expected to affect the subsequent pyrolysis and final product composition in the breakdown of cellulose. Under acidic conditions,[7] anhydro sugars, such as levoglucosan, formed during wood pyrolysis, can be further hydrolyzed into other sugars. Hosoya *et al*.[8] proposed a pyrolytic reaction pathway for levoglucosan in vapor and liquid/solid phases, with two competing pathways: volatilization and polymerization. Volatilization yields levoglucosan vapors, which degrade in non-condensable gases CO and CO_2. Polymerization gives rise to polysaccharides, which further react into low molecular weight products, such as furfurals, aldehydes and acids, or – through carbonization – form char. Furthermore, the low molecular products were suggested to act as H-donors, which could terminate the radical chain reactions taking place when the vapor form of levoglucosan degrades into gases. Cellulose is by far the most abundant compound found in biomass. For this reason, the production of chemicals derived from cellulose originating from different kinds of biomass is an important step towards a sustainable society. Aluminosilicates, *i.e.* zeolites, are important catalysts in the upgrading of fossil fuels catalyzing reactions such as bond breaking, cracking and alkylation; also, they might have applications in the upgrading of biomass and refinement processes of sugars. Through their shape selectivity, they can favor the reaction pathways, leading to the desired products.

Furthermore, as easy to reuse and recover heterogeneous catalysts, they support the principles of sustainability and green chemistry. The structure of the Beta zeolite is a 3-D pore system composed[9,10] of a polymorph A, with straight channels of 7.3 x 6.0 Å and tortous channels of 5.6 x 5.6 Å, and a polymorph B, with straight channels of 7.3 x 6.8 Å and tortous channels of 5.5 x 5.5 Å. MCM-48 has a large pore diameter (27.8 Å) and a three-dimensional system advantageous for molecular diffusion.[11] Levoglucosan, with a cross-section of about 4 Å, is thereby able to penetrate all pores of the tested catalysts.

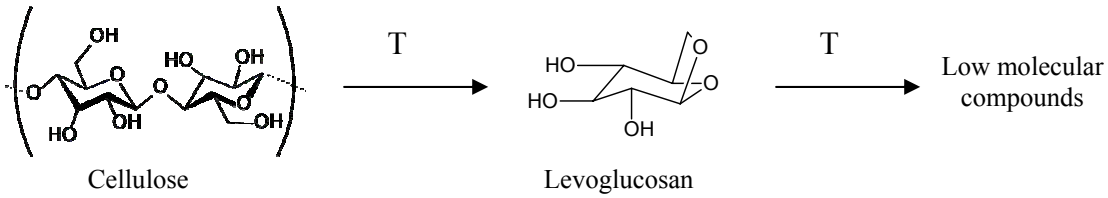

Figure 1: Levoglucosan as an intermediate in cellulose pyrolysis

In the present paper, the catalytic transformations of levoglucosan were studied over H-Beta-25 and mesoporous MCM-48, which could provide better accessibility of the reactants to the active sites.

EXPERIMENTAL

Catalyst synthesis and characterization

Synthesis of H-MCM-48

Synthesis of Al-MCM-48 was carried out by the method described by Pu *et al*.,[11] with some modifications. NaOH and cetyl trimethyl ammonium chloride (CTMACl) were added to distilled water. Aluminium isoporopoxide (AIP) was added to the solution and stirred for 15 min to allow AIP hydrolysis. 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, after which the synthesis was carried out at 100 °C for 75 h. Na-MCM-48 was ion-exchanged with an ammonium chloride solution for 48 h, washed with distilled water, dried and calcinated to obtain H-MCM-48.

Synthesis of H-Beta-25

The NH_4-Beta-25 zeolite was received from Zeolyst International Company. Number 25 indicates the Si/Al ratio, thus a low number corresponds to high acidity. H-Beta catalysts were obtained by drying and calcination of the NH_4 form of Beta zeolite in a muffle oven at 300 °C. The H-Beta was pelletized and crushed to obtain suitable particle size for catalyst testing.

Catalyst characterization

The specific surface areas of fresh, used and regenerated catalysts were measured by the nitrogen adsorption method (Sorptometer 1900, Carlo Erba Instruments). The catalysts were outgassed at 150 °C prior to the measurement. The BET equation was used for the mesoporous materials and the Dubinin equation for the Beta zeolite, to calculate the specific surface area. The used catalysts were regenerated at 450 °C for 2 h.

Acidity of the synthesized mesoporous materials was measured by infrared spectroscopy (ATI Mattson Infinity spectrometer), with pyridine (≥99.5%, a.r.) as a probe molecule for qualitative and quantitative determinations 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, radius – 0.65 cm). Pyridine was first adsorbed for 30 min at 100 °C, then desorbed by evacuation at different temperatures (250, 350 and 450 °C), to obtain the distribution of acid site strengths. All spectra were recorded at 100 °C 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 the corresponding spectral bands, with the molar extinction coefficients reported by Emeis.[12]

Catalytic experiments

Batch reactor

The catalytic experiments were performed in a 300 mL steel Parr autoclave connected to a prereactor with a volume of 200 mL (Fig. 2). The

autoclave was provided with a 5 µm filtered reactor sampling outlet, which prevented the catalyst particles from passing through it. Temperature was measured with a thermocouple and controlled automatically (Brooks Instrument). 0.2 g of levoglucosan (Aldrich, purity 99%) was dissolved in 100 mL of deionised water to make a 0.2% solution. 0.25 g of catalyst with the particle size between 150-250 µm was put in the reactor. To get a narrow particle size range for the zeolite catalyst, pellets of the zeolites powder were first pressed and thereafter crushed and sieved. The stirring rate was 1105 rpm, to eliminate external diffusion. The levoglucosan solution was poured into a preheater, at a 20 bar pressure applied with argon, and the solution was heated to 150 °C. When the two vessels reached their set temperatures (*i.e.* 150 °C), the valve between the two reactors was opened and the solution was flushed into the autoclave. Liquid samples were taken from the sampling valve within different time intervals, ranging from 5 min to 5 h, and analyzed with an HPLC equipped with an HPX-87C column.

Fixed bed reactor

The catalyst testing equipment consisted of a quartz mini-reactor, an oven, an evaporator and a condenser (Fig. 3). 1 g of levoglucosan was dissolved in 100 mL water, to get a 1% solution. The reactor made of quartz, with an inner diameter of 9 mm, was packed with quartz wool, catalyst and glass balls and put in an oven at 100 °C for drying. The reactor was then weighed for determining the dry weight. The particle size of the catalyst ranged between 150-250 µm, and the amount of catalyst used was of 0.125, 0.25 and 0.5 g. Nitrogen gas (58.1 mL/min) was applied as a carrier gas. The evaporator and the reactor operated at 300 °C. The temperature of the catalyst bed was measured using a thermocouple and the temperature of the reactor was monitored with a temperature controller. Feeding of the levoglucosan solution was set to 4 mL/h after temperature stabilization. The experiment lasted for 5 h, feeding a total volume of 20 mL of the levoglucosan solution, corresponding to 0.2 g of pure levoglucosan. The products were cooled down with a condenser containing a glycol solution at -5 °C and collected in a flask. After finishing the experiment, the flask was weighed and the liquid was analyzed. The quartz reactor was dried in a separate oven at 100 °C over night and weighed again, to determine the amount of tar and char formed on the walls of the quartz reactor.

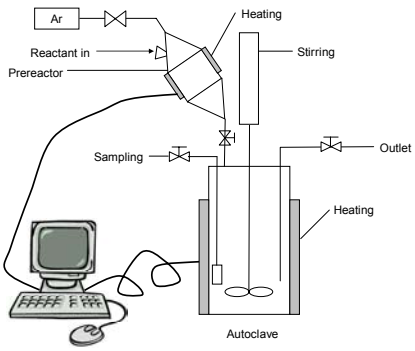

Figure 2: Set-up for catalytic transformation of levoglucosan in batch mode

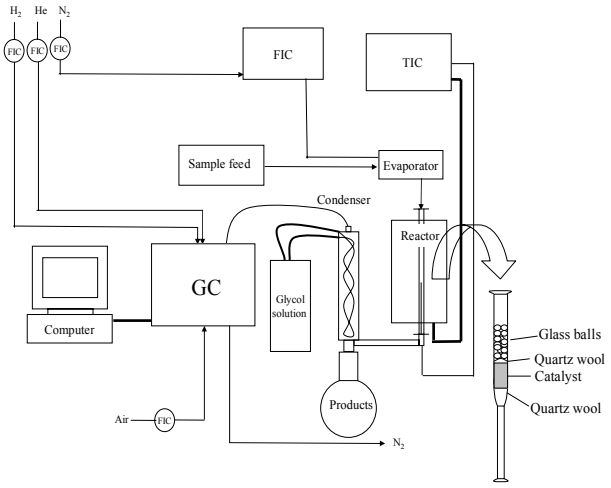

Figure 3: Set-up of catalytic testing equipment for levoglucosan transformation in gas phase

Product analysis

Silylation-GC-MS

500 µL of the liquid samples were transferred to a test tube and dried in a water bath operating at 40 °C 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, then transferred into small ampules and analyzed with GC-MS. The GC-MS was equipped with an HP-1 column (25 m x 0.2 mm x 0.11 µm) and the following temperature program was used: dwelling at 60 °C for 0.25 min and heating to 300 °C, at a heating rate of 6 °C/min).

GC/MS solid-phase micro-extraction

The volatile compounds were analyzed with GC/MS and headspace solid-phase micro-extraction (HS-SPME). HS-SPME combined with GC-MS has been reported as successful for the determination of furfurals.[13] 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 47 °C. 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 carboxen/polymethylsiloxane (CAR/PDMS) type, coated with a 2 cm 75 µm thick 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 270 °C, at which temperature the absorbed and adsorbed analytes were thermally desorbed into the hot injector of the gas chromatograph. The desorption time, of 10 min, 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 x 0.2 mm x 0.5 µm). The following temperature program was used: dwelling for 10 min at 40 °C, heating by 0.9 °C/min to 75 °C, followed by heating by 1.1 °C/min to 120 °C, heating by 10 °C/min to 200 °C and dwelling at 200 °C for 20 min.

HPLC

The products obtained and the conversion of levoglucosan were analyzed quantitatively with HPLC, with two different columns. The samples taken from the reaction in batch mode were analyzed with an Aminex HPX-87C column connected to a refractive index (RI) detector, in which a diluted calcium sulphate solution ($CaSO_4$, 1.2 mM) was used as a mobile phase. The flow was of 0.4 mL/min and the temperature was set to 80 °C. The samples from the reaction in the continuous mode were analyzed with an acid Aminex cation H+ column, where low-concentrated sulphuric acid (0.005 M) was used as a mobile phase. The flow was of 0.5 mL/min and the temperature was set to 65 °C. The samples were injected into the HPLCs immediately after the experiments, without any pretreatment other than filtering, to prevent solid particles from entering the columns. Several different concentrations of different standards were prepared and analyzed by the HPLC. The standards, purchased from Aldrich or Fluka, had a purity of ≥99%. The HPLC was calibrated by different standards, which made it possible to calculate the molar ratios of the achieved products. HPLC data were also used to calculate the conversion of levoglucosan.

RESULTS

Catalyst characterization results

Acidity

H-Beta-25 exibited the highest acidity (Table 1), being much more acidic than H-MCM-48. The Beta catalyst contained more Brønsted acid sites, while the mesoporous MCM-48 exibited a higher Lewis acidity.

Surface area

The results from the analysis of the surface area measurements of the catalyst particles are shown in Table 2. As expected, the surface area for the fresh microporous beta catalyst was lower than for the mesoporous H-MCM-48 catalyst. The used catalysts exhibited a considerably lower surface area compared to the fresh ones. In the case of H-Beta-25, it was however possible to regain the original surface area. The failure to regain the surface area of H-MCM-48 might indicate some structural changes.

Table 1
Brønsted and Lewis acid sites of fresh catalysts

	Brønsted acid sites (µmol/g)			Lewis acid sites (µmol/g)		
Catalyst	523 K	623 K	723 K	523 K	623 K	723 K
H-Beta-25	239	215	143	89	41	7
H-MCM-48	59	18	2	63	25	7

Table 2
Surface area of the different catalysts determined by nitrogen adsorption

Catalyst	Surface area (m^2/g), Dubinin		
	Fresh	Used	Regenerated
H-Beta-25 (liquid phase)	580	248	550
H-Beta-25 (gas phase, 0.25 g)		213	557
	Surface area (m^2/g), BET		
H-MCM-48	719	249	277

Catalytic data

Batch reactor

GC analysis revealed that the silylated samples contained mainly glucose and levoglucosan, with some small traces of other compounds, which could be attributed to sorbose and galactose.

According to HPLC analysis, glucose was the main compound formed in the batch reactor. The conversion of levoglucosan and the formation of glucose may occur even in the absence of a catalyst, leading, however, to a low conversion (Fig. 4). The consumption of levoglucosan was somewhat higher over the H-MCM-48 catalyst, although the formation of glucose was similar to the non-catalytic reaction.

H-Beta-25 exhibited a much higher activity than the H-MCM-48 mesoporous material (Fig. 5). The conversion over the microporous catalyst was almost complete, leading, besides glucose, to some amount of 5-hydroxymethyl furfural (5HMF), the formation of which is assumed to proceed through ring opening and dehydration of glucose, or by ring opening and dehydration of both levoglucosan and glucose.

Fixed bed reactor

The high temperature required to bring levoglucosan to the gas phase led to a high catalyst activity and complete conversion, independent of the amounts of H-Beta-25 catalyst. Moreover, the primary product – glucose, observed in the liquid phase reaction at a lower temperature, was not detected. Instead, the main products were aldehydes and acetic acid (Fig. 6), with glycolaldehyde as the main product, followed by formaldehyde. The formation of aldehydes was the highest at low residence times, *i.e.* small amounts of catalyst, decreasing with increasing residence time, thus favoring the formation of acetic acid. No liquid products were detected in the non-catalytic experiments performed with quartz sand.

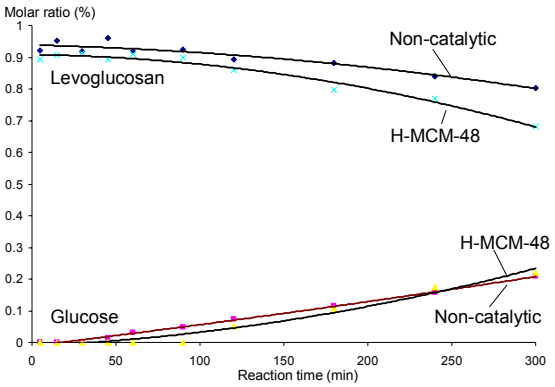

Figure 4: Non-catalytic and catalytic transformations of levoglucosan over H-MCM-48 in batch mode

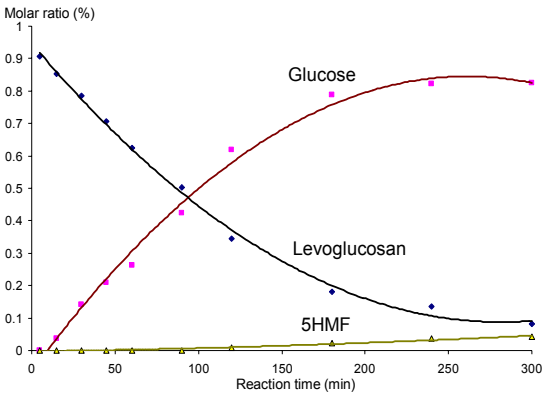

Figure 5: Levoglucosan transformation over H-Beta-25 catalyst in batch mode

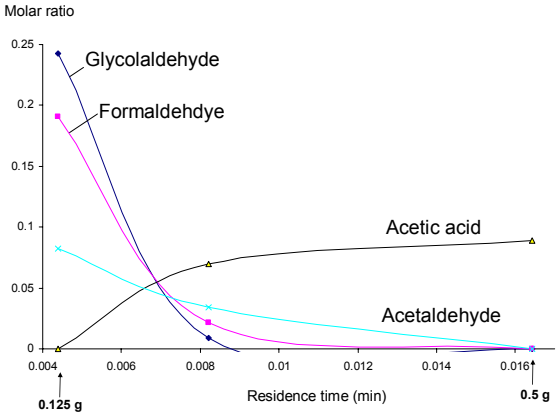

Figure 6: Liquid-phase products formed in gas-phase transformation of levoglucosan at different residence time values over H-Beta-25 catalyst