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Kinetic investigation of the catalytic conversion of cellobiose to sorbitol

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ABSTRACT

The reaction pathway and the kinetics of the conversion of cellobiose to sorbitol catalyzed by silicotungstic acids combined with ruthenium supported on activated carbon were studied. Two competing reaction pathways starting from cellobiose could be confirmed. The conversion of cellobiose either follows the hydrolysis to glucose or it passes through a hydrogenation of cellobiose to cellobitol (3-β-D-glucopyranosyl-D-glucitol). Cellobitol is subsequently hydrolyzed to sorbitol and glucose. At moderate temperatures of 393 K cellobitol becomes the main product with a maximum selectivity of 81%. Raising the reaction temperature to 443 K decreases the cellobitol selectivity to 1% while the maximum sorbitol selectivity increases to 75%. Kinetic modeling shows activation energies of 115 and 69 kJ mol^{-1} for the hydrolysis of cellobiose and subsequent hydrogenation of glucose. For cellobitol formation followed by hydrolysis 76 and 103 kJ mol^{-1} can be determined together with overall higher reaction rates at lower temperatures.

1. Introduction

In recent years concerns about depletion of fossil fuel reserves, increasing energy demand and global challenges have motivated our society to look for alternative sources of energy and feedstocks for chemical industry. Biomass is a highly promising alternative carbon source which is renewable and potentially sustainable [1–3]. Among all types of biomass cellulose is the most widespread non-edible polysaccharide and is considered to be one of the main feedstocks for sustainable fuel and chemical production. However, valorization of cellulose is still challenging due to its robust crystalline structure and insolubility in conventional solvents [4–9]. Most processes suffer from high energy consumption and low chemical selectivity. Therefore, designing more selective and efficient catalytic systems for the conversion of cellulose to platform chemicals is highly desirable. Especially combining molecular acids with supported metal catalysts provides a promising opportunity for the conversion of cellulose into value-added chemicals such as sorbitol [10]. Sorbitol is used as precursor in food and pharmaceutical industry and as platform chemical for the synthesis of chemical compounds such as isosorbide, sorbitan, glycerol, L-sorbose, etc [11]. Additionally, a further transformation of sorbitol into alkanes as well as efficient aqueous phase reforming for hydrogen generation have been demonstrated [12,13].

Recently several studies have reported the catalytic conversion of cellulose into sorbitol. A catalytic system containing molecular acids such as H_2SO_4, HCl or heteropoly acids combined with supported metal catalysts like Pt, Pd and Ru could efficiently catalyze the conversion of cellulose to sorbitol [10,14,15]. The highest yield of sugar alcohols (81%) could be achieved by the combination of heteropoly acids with supported ruthenium catalysts [14]. Previous studies focused on the design of efficient catalytic systems for the conversion of cellulose to sorbitol in order to maximize productivity. However, only a few mechanistic investigations are available [16] and a complete kinetic model describing the catalytic conversion of cellulose to sorbitol is still missing. Mechanistic studies and reaction kinetics can provide an insight into the reaction pathway and help to identify key intermediate compounds in the reaction network. Such studies allow a quantitative description of the effects of reaction conditions on reaction rates and the selectivity of the desired products. Therefore, a kinetic analysis may help to improve the catalytic performance and to rationalize process development.

The aim of this work is to gain insights into the reaction mechanism and kinetics of the catalytic conversion of cellobiose to sorbitol. Cellulose is a polymer with a very complex molecular structure driving a detailed kinetic study of its transformation difficult. Therefore, studying simple model molecules of cellulose such as cellobiose presents a promising possibility. Cellobiose represents

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Nomenclature

a	liquid-solid interface area ($m^2\ m^{-3}$)
C	concentration ($mol\ m^{-3}$)
$C^*_{H_2}$	solubility of hydrogen in the liquid ($mol\ m^{-3}$)
Ca	Carberry number
C_b	concentration in bulk liquid ($mol\ m^{-3}$)
d_p	catalyst particle diameter (m)
d_s	stirring diameter (m)
D	diffusion coefficient ($m^2\ s^{-1}$)
D_e	effective diffusion coefficient ($m^2\ s^{-1}$)
E_a	activation energy ($kJ\ mol^{-1}$)
$k_{i,0}$	pre-exponential constant (s^{-1})
K	adsorption constant ($m^3\ mol^{-1}\ kg_{cat}^{-1}$)
k_La	volumetric gas–liquid mass transfer coefficient (s^{-1})
k_{LS}	liquid–solid mass transfer coefficient ($m\ s^{-1}$)
k_i	reaction rate coefficient (s^{-1})
n	reaction order
N_s	stirring speed (s^{-1})
N_p	power number
P	pressure (Pa)
P_2	pressure after absorption state (Pa)
P_1	pressure before saturation state (Pa)
P_0	pressure at initial state before absorption (Pa)
r_{obs}	observed volumetric reaction rate ($mol\ (m^3\ s)^{-1}$)
R	ideal gas constant ($Pa\ m^3\ (mol\ K)^{-1}$)
t	time (s)
T	temperature (K)
S_p	catalyst particle external surface area (m^2)
V_L	volume of liquid (m^3)
V_p	catalyst particle volume (m^3)

Dimensionless numbers

Re	Reynolds number
Sc	Schmidt number
Sh	Sherwood number

Greek letters

η_i	internal catalyst effectiveness factor
η_e	external catalyst effectiveness factor
μ_L	dynamic viscosity of the liquid ($kg\ (m\ s)^{-1}$)
ρ_L	density of the liquid ($kg\ m^{-3}$)
ϕ	Thiele modulus
Φ	Weisz modulus

the basic repeating unit of cellulose and consists of two glucose monomers linked by a β(1–4) glycosidic bond (Fig. 1).

The presented study focusses on the kinetics of the hydrolytic hydrogenation of cellobiose to sorbitol with a catalytic system consisting of heteropoly acids and a supported ruthenium catalyst (5 wt.% Ru/C). Furthermore, possible reaction pathways and key intermediate compounds of this reaction are discussed. In the kinetic study the effects of mass transfer on the hydrogenation reaction are evaluated and kinetic models covering different reaction temperatures are developed.

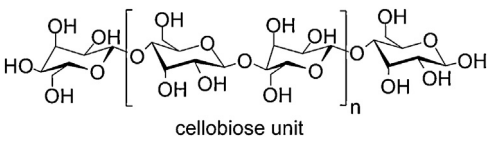

Fig. 1. Structure of cellulose and cellobiose.

2. Materials and methods

The experiments were carried out in a 50 ml stainless steel batch autoclave equipped with a sampling valve. The autoclave was loaded with 1.17 mmol cellobiose, 0.175 g heteropoly acid (silicotungstic acid), 0.1 g Ru/C (5 wt.%) and 20 ml of water. The reactor was then purged and vented with N_2 and H_2 at room temperature. The pressure was immediately adjusted to the experimental conditions. The reactor was then preheated under hydrogen pressure to the desired temperature and operated at a pressure range of 3.5–5 MPa and at 393–463 K for 3 h. At various time intervals liquid samples were taken and analyzed off-line using an HPLC (Shimadzu LC-10A) with a RI-detector. Separation of the components was achieved by an organic acid resin column (CS-Chromatographie, Germany, 300 mm × 8.0 mm and 100 mm × 8.0 mm) operated at 313 K. The eluent (154 μl of CF_3COOH in 1 l of water) was supplied at the 1 ml min^{-1} flow rate. Chemicals such as cellobiose, sorbitol, heteropoly acid (HPA, silicotungstic acid) and 5 wt.% Ru/C were purchased from Sigma-Aldrich. Cellobitol (3-β-D-glucopyranosyl-D-glucitol) was self-synthesized and characterized by ^{13}C NMR spectroscopy.

3. Results and discussion

3.1. Mechanistic study of hydrolytic hydrogenation of cellobiose

Numerous studies have reported the hydrolytic hydrogenation of cellulose or cellobiose to sorbitol to follow a cleavage of the glycosidic (C–O–C) bonds via hydrolysis and consecutive hydrogenation of glucose to sorbitol [17–19]. However, our experimental results of the cellobiose conversion to sorbitol indicate an additional reaction pathway to occur. We were able to emphasize that in the presence of a molecular acid and a supported metal catalyst cellobiose either undergoes hydrolysis to glucose or as an alternative pathway proceeds through a hydrogenation of the C–O bond on one of the glucose rings leading to cellobitol (3-β-D-glucopyranosyl-D-glucitol). In a subsequent reaction cellobitol can undergo hydrolysis to sorbitol and glucose. The proposed reaction pathways of the conversion of cellobiose are illustrated in Scheme 1.

Only few studies discuss the formation of cellobitol during the transformation of cellobiose. Therein, Kuo et al. reported the formation of cellobitol under neutral and basic conditions applying ruthenium nanoclusters in the ionic liquid 1-butyl-3-methylimidazolium chloride [20]. However, they concluded that the formation of cellobitol was not related to sorbitol formation. Instead, sorbitol was formed via direct hydrogenolysis of the β(1,4)-glycosidic bond of cellobiose under such conditions delivering sorbitol and dideoxyhexitol. A first study discussing cellobitol as intermediate in the transformation of cellobiose to sorbitol has been presented by Wang et al. [16]. They observed cellobitol in the conversion of cellobiose over carbon nanotube-supported Ru catalysts in neutral aqueous solutions and concluded that the formation of cellobitol followed by hydrolysis is the main pathway for sorbitol formation. Recently, Makkee et al. investigated the reaction mechanism of the transformation of cellobiose into sorbitol in aqueous $ZnCl_2$ with Ru/C as hydrogenation catalyst [21]. Their experimental data pointed towards a competition of two reaction pathways, (1) via cellobitol formation followed by hydrolysis and (2) via hydrolysis of cellobiose and subsequent hydrogenation. Under the presented reaction conditions path (1) was kinetically most important. Nevertheless, they suggested that various parameters such as reaction temperature, catalyst loading as well as the